

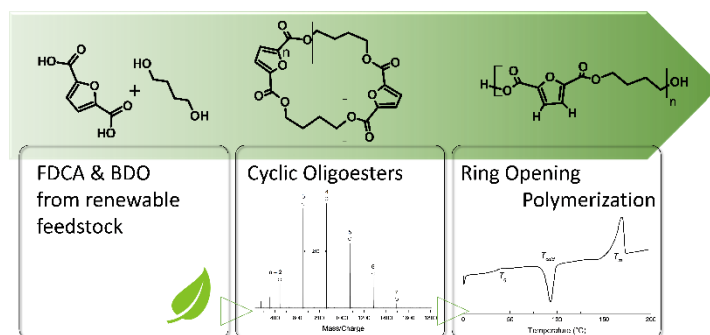
Full Paper

Synthesis & Ring-Opening Polymerization of Cyclic Butylene 2,5-furandicarboxylate

David Pfister, Giuseppe Storti, Francesca Tancini, Liborio I. Costa, Massimo Morbidelli*

D. Pfister, Prof. G. Storti, Prof. M. Morbidelli
Institute for Chemical and Bioengineering
Department of Chemistry and Applied Biosciences
ETH Zurich
8093 Zurich, Switzerland
E-mail: massimo.morbidelli@chem.ethz.ch
Dr. F. Tancini, L. I. Costa
Polymer Application and Test Center
Sulzer Chemtech Ltd
8404 Winterthur, Switzerland

A new synthetic pathway for the polymerization of furan based polyesters is reported in this work. Firstly, poly(butylene 2,5-furandicarboxylate) cyclic oligoesters (COEs) are chemically synthesized by semi-batch esterification. The structure of the COEs is confirmed by FT-IR, ^1H and ^{13}C -NMR, while the COEs molecular weight distribution is determined by MALDI-ToF mass spectroscopy. The cyclic oligoesters are then successfully polymerized via ring-opening polymerization using tetrakis(2-ethylhexyl)-titanate as catalyst. DSC and ^1H -NMR analysis unambiguously proves the formation of polymeric species. Both end-group analysis from ^1H -NMR spectrum and calculation through Flory-Fox equation give comparable estimates of the number average molecular weight: $5.8 \cdot 10^3$ g/mol and $7.8 \cdot 10^3$ g/mol, respectively (DP~30).



1. Introduction

Furanic polyesters derived from 2,5-furandicarboxylic acid (FDCA) are highly attractive polymers, due to their low permeability, good technical properties^[1-3] and their compatibility with the existing processing and recycling technologies.^[4] Additionally, the possibility to be produced from renewable feedstock^[1, 5-7] makes them potential sustainable substitutes of some performance-related fossil-based commodities, like polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). To date, furanic polyesters have been produced exclusively by polycondensation or polytransesterification.^[1, 2, 5, 8-21] The need for by-product removal, long reaction times and modest polymer molecular weights are the major limitations of this approach. A still unexplored alternative route to produce this class of macromolecules consists in performing a ring opening polymerization (ROP), exploiting the benefits of a living polymerization mechanism to overcome the typical polycondensation limits. In addition, the ROP method would enable a more precise control of the molecular weight and structure of the synthesized polymer and therefore of the material properties.^[22, 23] A ROP strategy is applied for the very first time to the polymerization of furan based polymers. To pursue this strategy, a viable synthesis of the cyclic precursors must be envisioned and developed, and the ring opening polymerization of these latter has to be proved. In short, the aim of this work is to explore the possibility to apply to furan-based polyesters a synthetic pathway similar to the one successfully developed for the production of polylactic acid, which is actually well-established also at industrial scale.^[24, 25]

Accordingly, herein we present for the first time the chemical synthesis of cyclic oligomers of butylene-2,5-furandicarboxylate and their successful polymerization into polybutylene 2,5-furanoate (PBF) by ROP. The proposed synthetic pathway could be generalized in the future to other furan-based copolymers, such as the market-strategic target polyethylene 2,5-furanoate (PEF), thus broadening the horizons for furanic polyester production.

2. Experimental Section

2.1. Materials

2,5-furandicarboxylic acid, 98% (FDCA) was purchased from ABCR-Chemicals and used as received. Thionyl chloride 99.5%, and 1,4-butanediol (BDO) 99% were purchased from Acros and used as received. 1,4-diazabicyclo[2.2.2]octane \geq 99% (DABCO) from Sigma-Aldrich was further purified by sublimation at 60°C and 25 mbar just before use. Tetrahydrofuran (THF), and dichloromethane (DCM) were dried over molecular sieves. 2,5-Furandicarbonyl dichloride (FDCC) was prepared according to literature procedure.^[13]

2.2. Characterization Methods

2.2.1. Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) was performed on a Agilent 1100 Series system equipped with Variable Wavelength UV Detector, Refractive Index detector, a 5 μ m PLgel guard column, followed by Agilent Oligopore (300 \times 7.5 mm) and PLgel 5 μ m MIXED-C (300 \times 7.5 mm) columns in series working at 25°C. THF was used as eluent at a flow rate of 0.5 mL/min.

2.2.2. MALDI-ToF

Matrix-assisted laser desorption/ionization Time of Flight (MALDI-ToF) mass spectroscopy was performed on a Bruker Daltonics Ultraflex II Mass Spectrometer. The matrix (trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene] malononitrile, DCTB), cationisation agent (CF₃COONa) and analytes were dissolved in dichloromethane and mixed in ratio 1:10:1.

Proton nuclear magnetic resonance spectroscopy (¹H-NMR) measurements were made on a Bruker AV 300 spectrometer (300 MHz) and on a Bruker AV 400 spectrometer (400 MHz). Carbon nuclear magnetic resonance spectroscopy measurements (¹³C-NMR) were made on a

Varian Mercury 300 spectrometer (75 MHz). The residual peaks of the deuterated solvents were used as reference.

2.2.3. FT-IR

FT-IR measurements were performed on neat samples with a Nicolet Nexus 870 ESP spectrophotometer using a single bounce of ZnSe for horizontal attenuated total reflectance. For each spectrum, 100 scans were recorded in the transmission mode at room temperature between 600 cm^{-1} and 4000 cm^{-1} .

2.2.4. Thermal Properties

Differential scanning calorimetry (DSC) analyses were performed on a Mettler-Toledo DSC 823e Module, using standard $40\text{ }\mu\text{L}$ Al-crucibles. The samples were heated from 0°C to 200°C at $10^\circ\text{C}/\text{min}$, quenched in liquid nitrogen, and heated again from 0°C to 200°C at $10^\circ\text{C}/\text{min}$. The thermograms shown correspond to the second heating scan. Glass transition and cold crystallization were recorded during the second scan.

Melting point was measured using a Büchi B-450 melting point apparatus in open capillaries.

2.3. Synthesis of cyclic (butylene-2,5-furandicarboxylate) oligomers

A solution of FDCC (510 mg, 2.65 mmol) in THF (5 mL) and a solution of butylene glycol (225 mg, 2.5 mmol) in THF (5 mL) were added to a solution of 1,4-diazabicyclo[2.2.2]octane (DABCO) (700 mg, 6.2 mmol) and Et_3N (40 μL) in CH_2Cl_2 (12.5 mL) at 0°C , over a period of 60 minutes, maintaining constant the 1.05:1 stoichiometry. The mixture was kept under nitrogen atmosphere and stirring was continued at 0°C for 10 minutes. An additional portion of furan-2,5-dicarbonyl dichloride (50 mg, 0.25 mmol) was finally added over 15 minutes. The reaction was quenched by addition of 1:1 $\text{H}_2\text{O}/\text{NaOH}$ mixture (200 μL). Linear oligomeric chains were partially removed by filtration. The organic phase was washed with 1M HCl and H_2O , filtered through PTFE membrane and concentrated to dryness. The

obtained product was further purified either by dissolution in THF and filtration or by flash chromatography (SiO₂; CH₂Cl₂/Et₂O 9:1) giving a mixture of cyclic PBF.

¹H-NMR (300 MHz, CDCl₃, 25°C): δ= 1.95 (4 H; H_b), 4.41 (4 H, H_a), 7.22 (2 H, H_c) (Figure S1 for assignment); ¹³C-NMR (75 MHz, CDCl₃, 25 °C): 25.5 (C_b), 64.8 (C_a), 118.6 (C_e), 146.4 (C_d), 157.7 (C_c) (Figure S2 for assignment); MALDI-ToF-MS: m/z: 442.92 ([M₂+Na]⁺, calc. for C₂₀H₂₀O₁₀Na⁺: 443.36), 653.05 ([M₃+Na]⁺, calc. for C₃₀H₃₀O₁₅Na⁺: 653.15), 863.13 ([M₄+Na]⁺, calc. for C₄₀H₄₀O₂₀Na⁺: 863.20), 1073.19 ([M₅+Na]⁺, calc. for C₅₀H₅₀O₂₅Na⁺: 1073.25), 1283.25 ([M₆+Na]⁺, calc. for C₆₀H₆₀O₃₀Na⁺: 1283.31), 1493.29 ([M₇+Na]⁺, calc. for C₇₀H₇₀O₃₅Na⁺: 1493.36), 1703.33 ([M₈+Na]⁺, calc. for C₈₀H₈₀O₄₀Na⁺: 1703.41); FT-IR (neat): $\tilde{\nu}$ =2960-2919 (w), 1716 (s), 1285 (s), 764 cm⁻¹ (m).

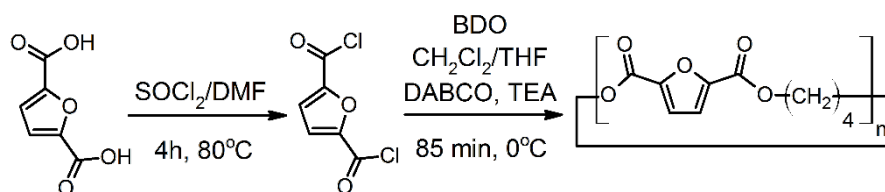
2.4. Synthesis of poly(butylene-2,5-furandicarboxylate)

A 0.01 M solution of tetrakis(2-ethylhexyl)-titanate (TOT) was prepared in *o*-dichlorobenzene. 20 mg of cyclic PBF were dissolved in THF. Catalyst was added to COEs solution in 0.5 mol% ratio with respect to the repeating unit (FDCA+BDO). The solvent was slowly evaporated in a vacuum oven at 60°C overnight. The catalyst impregnated COEs were then placed into 160 μL aluminum crucibles and sealed in a glove box under nitrogen atmosphere to avoid parallel degradation reactions with oxygen. The pans were then placed in a Mettler Toledo DSC823^e Module Calorimeter, rapidly heated from 30°C to 270°C within a minute, and kept at 270°C for 15 minutes. After the reaction, the polymer was taken out from the crucible, solubilized in TFA, precipitated in an excess of THF, and recovered by filtration. Solubilization/precipitation/filtration cycles were repeated until no residual cyclic oligoesters were detected by GPC in the liquid phase. The polymer was then dried under vacuum at 60°C for 4 hours.

¹H-NMR (400 MHz, *d*-TFA, 25°C): δ=1.46 (H_b''), 2.19 (H_b+H_b'), 4.08 (H_a''), 4.72 (H_a+H_a'), 7.54 (H_c+H_c'), 7.62 (H_c'') (cf. Figure 2 for assignment).

3. Results and Discussion

Cyclic (butylene 2,5-furandicarboxylate) oligomers were prepared following a two-step synthesis (Scheme 1). FDCA was firstly chlorinated to form the more reactive acyl dichloride derivative (FDCC), which was purified by sublimation (cf. FT-IR in Table S1). Secondly, FDCC was reacted with butanediol (BDO), in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) and triethylamine (TEA) to give cyclic furanic oligoesters. The cyclization reaction was performed under starved conditions by slow addition of the reactants, namely FDCC and BDO, according to the Ziegler-Ruggli dilution principle. This strategy allows maintaining a very low concentration of the reactants, thus promoting the formation of cyclic over linear oligomers. The cyclization was performed under inert atmosphere and in dry solvents to prevent FDCC hydrolysis. TEA was added to neutralize the HCl formed during the reaction, while an excess of the unhindered DABCO was introduced to activate the acyl chloride towards cycle formation.^[26-29]



Scheme 1: Synthesis of cyclic poly(butylene-2,5-furandicarboxylate).

Almost no cycles were produced when reacting FDCC and BDO under strictly stoichiometric conditions. This finding can be explained taking into account that FDCC undergoes side-reactions with TEA, DABCO or the solvent,^[26] thus reducing the number of active COCl functionalities available to react with the hydroxyl-groups of the glycol and leading predominantly to linear oligoesters terminated with hydroxyl groups at both ends. In agreement with this view, the yield in cycles was greatly improved when using a slight excess of FDCC over BDO. More specifically, a yield ranging between 18 and 21% was achieved for the cyclization step. Isolation and purification of the obtained COEs were performed exploiting the different solubility of cyclic and linear species. A first filtration of the crude led to the removal

of the insoluble fraction consisting mainly in long linear oligoesters chains and FDCC-DABCO-TEA adducts which exhibit a limited solubility in THF/CH₂Cl₂. MALDI-ToF spectrum recorded for the recovered filtrate highlights the presence of a mixture of linear hydroxyl-terminated (L_n) and cyclic (COE_n) species (Figure 1a). The two populations are easily identified, being their peak-patterns separated by a 90 g/mol gap, corresponding to a unit of butanediol. Filtration did not allow for the complete removal of the linear by-products, so the purification of the COEs was finalized by flash chromatography. Alternatively the filtrate was washed with acidic water, concentrated to dryness, re-dissolved in THF to precipitate the remaining linear compounds, which were finally removed by filtration. MALDI-ToF spectrum of the so obtained COEs mixture is shown in Figure 1b.

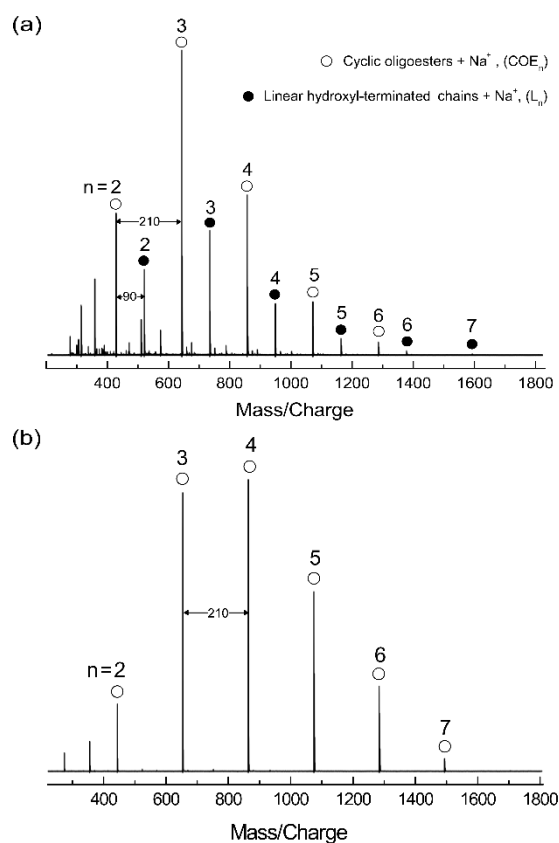


Figure 1: MALDI-ToF-MS spectrum of the oligoesters (a) after a first purification step, and (b) after complete purification. Integration led to the following mass distribution for the fully purified cyclic oligoesters: COE_2 (5%), COE_3 (31%), COE_4 (30%), COE_5 (21%), COE_6 (11%) and COE_7 (2%).

The structure of the purified COEs was proved by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ (Figures S1 and S2). The $^1\text{H-NMR}$ spectrum gave resonance peaks at 7.2 ppm, 4.4 ppm and 1.9 ppm with integration ratios (1:2:2), which were respectively attributed to the two aromatic furan protons and the eight aliphatic protons of the BDO. No traces of hydroxyl protons were found, thus confirming the cyclic structure. In addition, $^{13}\text{C-NMR}$ spectrum showed the expected peaks at 25.5 ppm and 64.5 ppm for the BDO, 157.7 ppm (carbonyl moieties) and 146.3 ppm (substituted carbons) as well as at 118.6 ppm (unsubstituted carbons) for the furanic ring. The DSC and FT-IR analysis were also performed to complete the COEs characterization (Figures S3 to S5 and Table S1). In particular, the DSC trace shows a flat profile till 200°C. COEs completely melt between 248 and 266°C, as determined by visual observation.

After being purified, the COEs were polymerized in small aluminum crucibles, inside a DSC module, as previously done by Nagahata^[30] for the ROP of cyclic dimers of PET. Tetrakis(2-ethylhexyl)-titanate (TOT) was selected as catalyst because of its well-known effectiveness to initiate ROP of cyclic oligoesters.^[29] In order to uniformly mix the monomer and the catalyst, a catalyst solution in *o*-dichlorobenzene was mixed with the COEs dissolved in THF and the so obtained solution was dried under vacuum. The final powder was finely grinded, further mixed and finally reacted in the DSC crucible. ROP reactions were carried out with 0.5 mol% catalyst (vs. repeating units) at 270°C for 15 minutes. Due to the high temperature used to melt the COEs, the polymerization reaction rate was observed to be extremely fast. The reaction crude was solubilized in trifluoroacetic acid (TFA); the polymer was precipitated by addition of THF and recovered by filtration. At the end of the polymerization the yield was estimated to be 85%. ROP is acknowledged to be an equilibrium process between the cyclic precursors and the growing chains. In this particular case, the equilibrium is expected to be strongly displaced towards the formation of linear chains due to the high temperature and high concentration. This observation is consistent with previous studies on the ROP of terephthalic acid-based cyclic precursors.^[26-29] Typically, for this kind of polymerization, residual amounts of cycles between

1 to 3% are reported, as discussed by Brunelle.^[26] The relatively large amount of residual COEs is certainly due to the ring-chain equilibrium, but not only: as a matter of fact, the purity of the COEs, the mixing of the catalyst with the monomers, and the polymerization rate (which should be high enough to allow reaction completion before the polymer crystallization occurs) have already been shown to have pernicious consequences on the conversion.^[26] In our case, almost no traces of cyclic oligoesters were detected, thus confirming their reactivity, except for the dimeric species which were observed to be more stable and almost not consumed during the polymerization. Reactions performed for longer times, up to 60 minutes, did not provide significant differences in yield. The formation of PBF chains was proved by DSC (Figure 2a). The DSC thermogram of the purified ROP product is substantially different from that of the cyclic species, and features a glass transition at $T_g=35^\circ\text{C}$, a cold crystallization transition at $T_{cold}=89^\circ\text{C}$ and a melting transition at $T_m=169^\circ\text{C}$, thus unambiguously fingerprinting a polymer. Additionally, the measured transition temperatures are perfectly in line with literature data for PBF produced by conventional polycondensation and polytransesterification methods.^[2, 15, 27, 28]

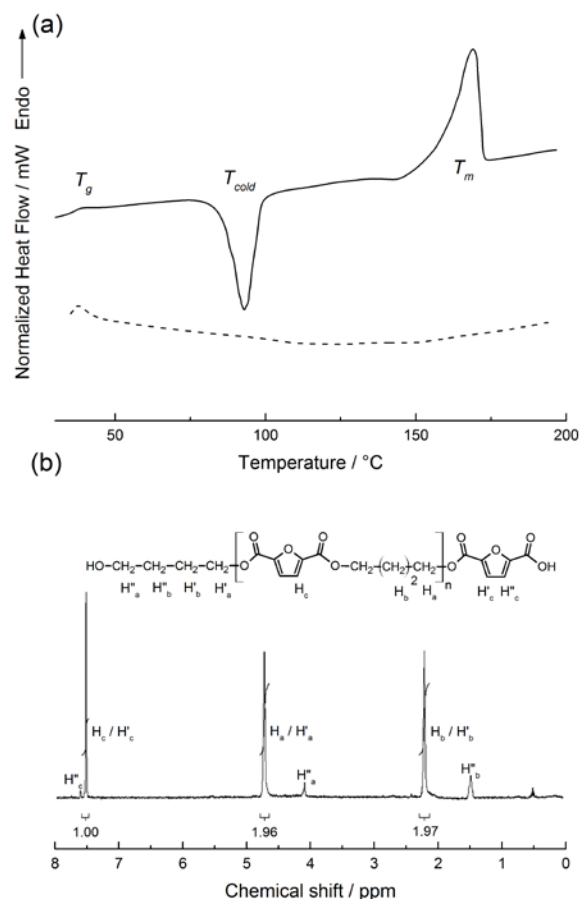


Figure 2: (a) Second heating DSC trace for COEs (dashed line) and PBF (solid line, vertically shifted for better clarity); (b) ^1H -NMR spectrum of PBF in *d*-TFA.

The FT-IR spectrum of PBF (see Table S1 and Figure S5) is quite similar to the one obtained for the COEs. No evidences for *OH* or *COOH* bands were found in the regions between 3300 and 3600 cm^{-1} and between 2500 and 3300 cm^{-1} , respectively, thus suggesting that the obtained molecular weight is high enough to neglect the end groups FT-IR signal. In addition, the ^1H -NMR spectrum features all the signals expected for linear PBF.^[2] Aromatic furanic protons resonate at 7.54 ppm, while the protons corresponding to the internal *CH*₂ of the butylene chain are found at 4.72 and 2.19 ppm. Additional signals were observed at 7.62 ppm, 4.08 ppm and 1.46 ppm and identified as the end group protons.

Applying the method used by Ma et al.,^[2] based on the analysis of end-groups by NMR, the average degree of polymerization was estimated to be 26, corresponding to a number average molecular weight, M_n of $5.8 \cdot 10^3 \text{ g mol}^{-1}$.

Alternatively, the molecular weight was estimated from the measured T_g value using the Flory-Fox equation:

$$T_g = T_{g,\infty} - \frac{K}{M_n} \quad (1)$$

where $T_{g,\infty}$ and K are the glass transition temperature at infinite molecular weight and the Flory-Fox parameter, respectively. Starting from literature data^[15] a fitted correlation is proposed with $T_{g,\infty}=42^\circ\text{C}$ and $K=54,500 \text{ K g mol}^{-1}$ (Figure S6). Using these values, the number average molecular weight for the produced PBF was estimated to be $7.8 \cdot 10^3 \text{ g mol}^{-1}$, which is consistent with the data obtained by end-group analysis through NMR.

4. Conclusions

Poly(butylene-2,5-furandicarboxylate) macrocyclic precursors were successfully synthesized by semi-batch esterification in the presence of DABCO to favor the formation of cycles. The molecular weight distribution of the COEs was determined by GPC and MALDI-ToF mass spectroscopy while the structure was confirmed by ^1H and ^{13}C -NMR, and FT-IR. The analyses also revealed the high purity of the obtained cyclic species.

The cyclic oligoesters were then successfully polymerized via ROP with TOT catalyst. The presence of polymer chains was confirmed by DSC analysis whose pattern, showing clear glass transition, cold crystallization and melting peaks, is characteristic of semi-crystalline polymers. The structure of the obtained polymer was also confirmed by ^1H -NMR and FT-IR. Because of the low solubility of PBF, GPC could not be used to estimate the polymer average molecular weight. Instead, alternative methods were applied. Both end-group analysis by NMR and estimation through Flory-Fox equation gave comparable results: $5.8 \cdot 10^3 \text{ g/mol}$ and $7.8 \cdot 10^3 \text{ g/mol}$, respectively. The preliminary results presented in this work are encouraging and confirm the possibility of using ROP to overcome the typical limitations of polycondensation processes for the production of renewable furan-based polyesters.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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