

Exploring the Potential of High Molar Mass Poly(hydroxymethylfuroate): Synthesis, Properties, and Recyclability Studies

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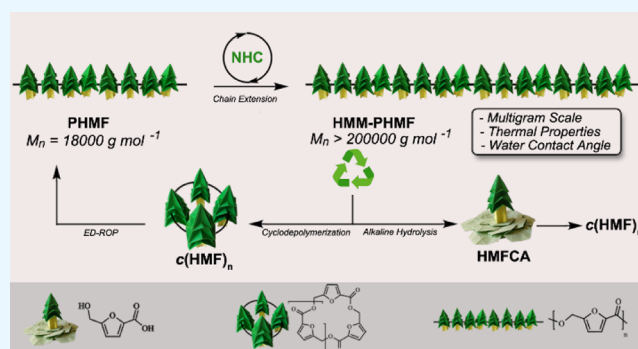
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Supporting Information

ABSTRACT: The synthesis of the fully furan-based high-molar-mass poly(hydroxymethylfuroate) (HMM-PHMF) is herein presented along with the investigation of thermal properties, filmability, water contact angle (WCA), and recyclability. The polymer ($M_n > 200000 \text{ g mol}^{-1}$) has been produced on a multigram scale by N-heterocyclic carbene (NHC)-promoted chain extension of PHMF ($M_n = 18000 \text{ g mol}^{-1}$) (1 h, $190 \text{ }^\circ\text{C}$), which can be directly synthesized from 5-(hydroxymethyl)furfural (HMF) or 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA). The polyester is thermally highly stable up to $280 \text{ }^\circ\text{C}$, showing a semicrystalline behavior with $T_m \sim 194 \text{ }^\circ\text{C}$ when processed from solvent and an amorphous character with $T_g \sim 90 \text{ }^\circ\text{C}$ when processed from the melt. HMM-PHMF has been efficiently filmed by compression molding and submitted to WCA analyses ($86 \pm 2^\circ$), behaving as a potential biobased food packaging material. Finally, recyclability has been assessed through alkaline hydrolysis producing HMFCFA and cyclodepolymerization affording the starting hydroxymethylfuroate macrocyclic oligoesters $c(\text{HMF})_n$, which can be converted again through entropically driven ring-opening polymerization (ED-ROP), in a closed-loop cycle.

KEYWORDS: biobased, 5-HMF, furanic polymers, polyesters, polymer recycling, N-heterocyclic carbene



INTRODUCTION

The fast and progressive depletion of crude oil resources and growing environmental concerns represent the main issues faced by the scientific community nowadays. The development and implementation of innovative technologies for substituting fossil resources with renewable raw materials can provide a practical answer to these problems, and researchers in various fields of chemistry and materials are carrying out research programs in this direction. In this context, biobased plastics represent a greener alternative to fossil-based ones reducing dependency on fossil fuels.^{1,2} Within the plethora of different potential renewable sources, plant biomass has proved its central position as a viable platform for the production of biobased materials, with furanic compounds generated directly from natural polysaccharides being the most promising.^{3–5}

5-(Hydroxymethyl)furfural (HMF), defined as the “sleeping giant” of sustainable chemistry,^{6,7} together with its valuable derivatives 2,5-furandicarboxylic acid (FDCA)⁸ and 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA)⁹ represents pivotal furanic compounds, which have been efficiently employed as renewable monomers in the production of new promising biobased polymers such as polyesters,^{10,11} polyamides,¹²

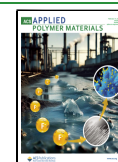
polyesteramides,¹³ and polyurethanes.¹⁴ Among biobased polyesters, polyfuranates¹⁰ represent effective sustainable alternatives to industrial fossil-based polyesters derived from terephthalic acid, such as poly(ethylene terephthalate) (PET). In this regard, the furan-based poly(ethylene 2,5-furandicarboxylate) (PEF)¹⁵ has emerged as the future substitute of PET,¹⁶ finding applications in the manufacturing of bottles and a variety of food packaging materials thanks to favorable mechanical properties, even outperforming PET in terms of barrier properties, thanks to the higher rigidity of the furan ring. In addition, recyclability and potential integration within the context of a circular economy¹⁷ represent other attractive advantages that have been fostering the rapid intensification of research activities devoted to the study of PEF¹⁸ and other different furan-based polyesters.

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The urgent need for fossil-based material replacement is closely related to the strong demand for greener polymerization strategies and sustainable alternatives to traditional, long-time established synthetic routes. In this respect, organocatalysis^{19–24} and biocatalysis^{25–27} can play a prominent role in green polymer chemistry, improving the sustainability of consolidated protocols and paving the way for unexplored synthetic scenarios.

As part of our research activities in the field of unconventional catalytic approaches to furanic polymers,^{28,29} in 2022 we described for the first time the fully organocatalytic synthesis of poly(hydroxymethylfuroate) (PHMF) starting from 5-hydroxymethyl furfural (HMF) or 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA).³⁰ The synthetic strategy involved the formation of hydroxymethylfuroate macrocyclic oligoesters $c(\text{HMF})_n$ under high dilution conditions (HDC), followed by entropy-driven ring-opening polymerization (ED-ROP) of the macrocycles (Figure 1). Optimization of the reaction

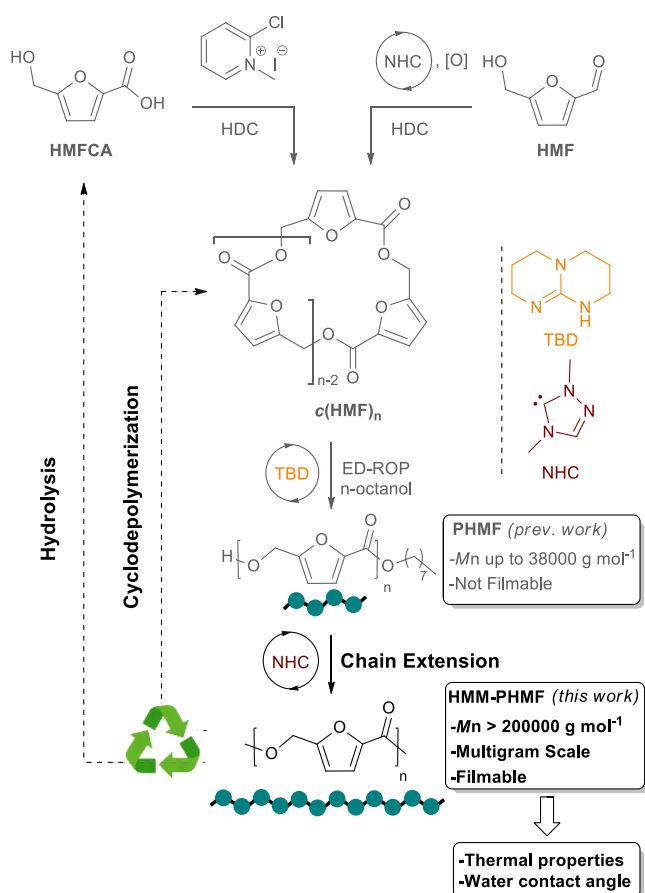


Figure 1. Fully organocatalytic synthesis of PHMF (previous work,³⁰ gray) and subsequent chain extension to HMM-PHMF, physicochemical properties and recyclability studies (this work).

conditions allowed the production of a colorless PHMF with almost quantitative yield and M_n up to 38000 g mol⁻¹. The furan-based polyester displayed a semicrystalline structure with a melting temperature above 160 °C and remarkable thermal stability up to 310 °C. It is noteworthy to remind that the unique synthesis of this fully furan-based polyester was previously attempted with little success by high-temperature transesterification polymerization of the methyl ester of HMFCFA, catalyzed by a mixture of calcium acetate and

antimony oxide.³¹ These promising results prompted us to investigate the main properties of the material, envisaging potential fields of application. In this regard, polymer film production was attempted by solvent casting or melt casting techniques, but unfortunately, both procedures failed. This behavior could be ascribed to an intrinsic fragility of the furanic polymeric material or to a polymer molar mass not high enough to guarantee reliable and efficient film production. To overcome this issue, in this publication, we report the development of an organocatalyzed chain extension process for the production of high molar mass poly(hydroxymethylfuroate) (HMM-PHMF) with $M_n > 200000$ g mol⁻¹. The resulting polymer was analyzed from the thermal point of view (thermogravimetric analysis, TGA and differential scanning calorimetry, DSC) and efficiently processed by melt casting. The resulting film has been employed in water contact angle (WCA) measurements and compared with other furan- and fossil-based polyesters. Finally, the chemical recyclability of the biobased material has been assessed through alkaline hydrolysis leading to HMFCFA and cyclodepolymerization under high dilution conditions, affording the starting macrocycles $c(\text{HMF})_n$, which can be in turn converted to the polymeric material in a closed-loop cycle.

RESULTS AND DISCUSSION

Our research commenced with the synthesis of PHMF, according to our reported procedure.³⁰ To provide a suitable amount of polymer, the process was scaled up to multigram scale (see Experimental Section for details), affording PHMF with 85% yield and $M_n = 18000$ g mol⁻¹ (¹H NMR spectrum in Figure 2a). With the polyester in our hands, the chain extension study was approached (Table 1). According to literature reports,^{32,33} we decided to perform the reaction in the melt phase, under vacuum, removing octanol (the initiator) from the reaction mixture, shifting the equilibria toward the product. For this reason, the reaction was conducted at 190 °C (PHMF starts to melt at ~160 °C) under vacuum, testing two different transesterification agents.

First, 1,5,7-triaza-bicyclo-[4.4.0]dec-5-ene (TBD) was chosen due to its widely reported activity as a transesterification agent.^{34–37} 5 mol % TBD loading led after 1 h to a slight molar mass increase without any yellowing or color change (entry 1). Extension of the reaction time to 2 h resulted in polymer elongation ($M_n = 35000$ g mol⁻¹, entry 2), while further time prolongation (4 h, entry 3) led to marked darkening and molar mass decrease due to the competitive depolymerization process. Inspired by our previous contributions in the field of organocatalytic polymer synthesis,^{28,29,38,39} *N*-heterocyclic carbenes (NHCs) were evaluated as effective transesterification agents.^{32,33,40–42} For this purpose, inexpensive triazolium salt A and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were selected as a precatalyst/base couple, employing a 5% mol loading. This catalytic system showed to be suitable for the chain extension process, leading to remarkable chain growth after 30 min ($M_n = 65000$ g mol⁻¹, entry 4) and 2 h ($M_n = 200000$ g mol⁻¹, entry 5, see Figure S2). Despite the satisfactory result, marked polymer darkening was observed after 2 h. To our delight, reduction of reaction time to 1 h allowed the production of HMM-PHMF with an improved molar mass ($M_n > 200000$ g mol⁻¹, end group undetectable by ¹H NMR, Figure 2b) and only modest yellowing (entry 6). The disclosed protocol was efficiently applied also on a multigram scale (entry 7). Finally, a control experiment was

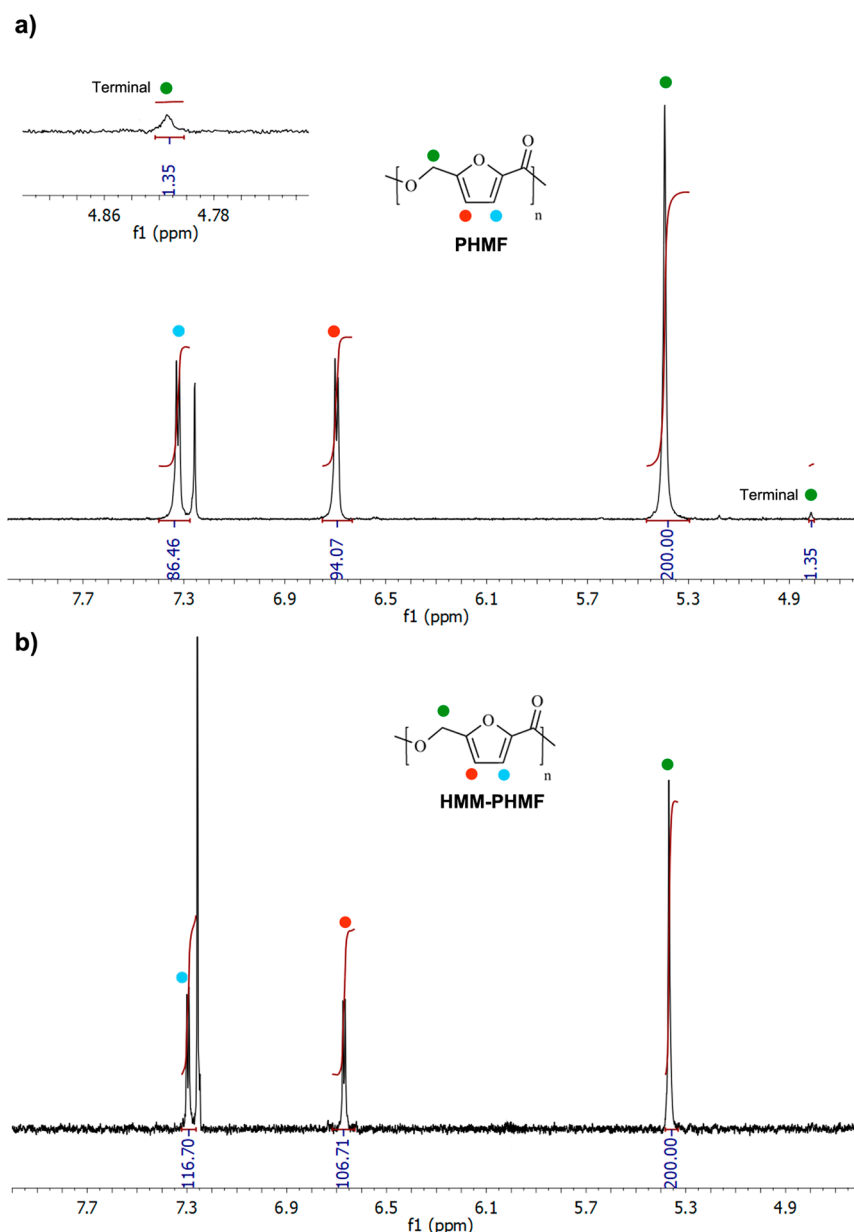


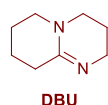
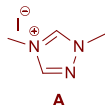
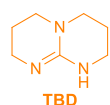
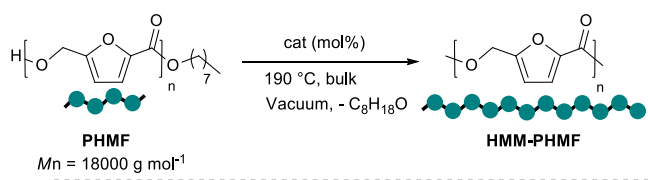
Figure 2. (a) ¹H NMR spectrum of PHMF (400 MHz, CDCl₃: TFA = 1:1). (b) ¹H NMR spectrum of HMM-PHMF (Table 1, entry 6) (400 MHz, CDCl₃: TFA = 1:1).

performed, to evaluate the role of the sole DBU as the transesterification agent under the optimized reaction conditions (entry 8); as expected, only a slight molar mass increase was observed, confirming the key role of the *in situ*-generated NHC in the chain extension process.

At this stage of the study, the thermal properties of the furanic polyester were then investigated by differential scanning calorimetry (DSC). HMM-PHMF exhibited a melting peak at 193.9 °C during the first heating cycle in standard DSC analysis (Figure 3), indicating its ability to crystallize. This value aligns with previous observations for PHMF. Further similarities were noted in the subsequent cooling and heating cycles between PHMF and HMM-PHMF, as both polymers did not crystallize when cooled from the melt or during the subsequent heating at 10 °C/min.³⁰ The amorphous polymers displayed comparable glass transition temperatures, with HMM-PHMF showing a slightly higher

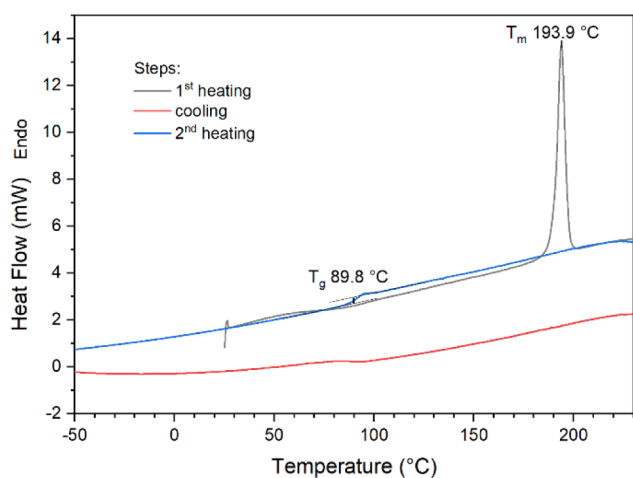
temperature of 89.8 °C compared to 86 °C for PHMF. This difference suggests a greater degree of entanglement in HMM-PHMF, which has a molar mass ten times that of PHMF.³⁰

The thermogravimetric analysis (TGA) plot of HMM-PHMF recorded under a nitrogen atmosphere (Figure 4) revealed minimal weight loss (<1%) before 200 °C, whereas a 3.3% loss was observed for the lower molar mass analogue.³⁰ Interestingly, the two weight losses in this temperature range are proportional to the concentration of chain ends in the two polymers, suggesting that this step may be attributed to degradation reactions involving these chain segments. The main degradation process for HMM-PHMF occurs in a multistep manner, starting with a sharp weight loss that begins at 280.5 °C. This onset temperature is unexpectedly 30 °C lower than that observed for PHMF.³⁰ The relationship between the onset of thermal degradation and molar mass is influenced not only by the specific polymer but also by the

Table 1. Optimization Study for the Chain Extension of PHMF into HMM-PHMF^a

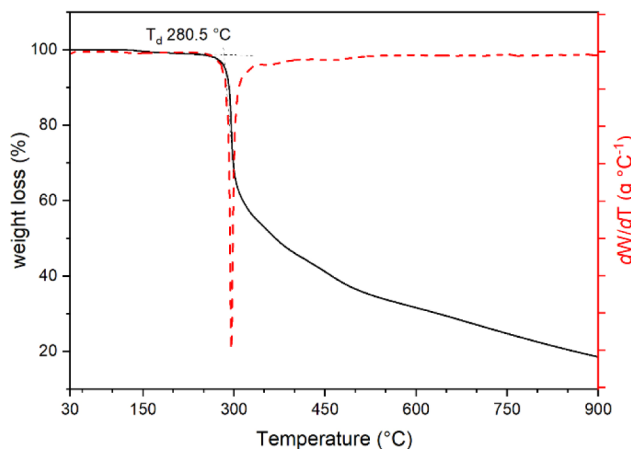
Entry	Catalyst (mol %)	Time (h)	Yield (%) ^b	M_n (g mol ⁻¹) ^c	Color
1	TBD (5)	1	95	22000	White
2	TBD (5)	2	95	35000	Ivory
3	TBD (5)	4	95	21000	Brown
4	A:DBU (5:5)	0.5	95	65000	Ivory
5	A:DBU (5:5)	2	95	200000	Brown
6	A:DBU(5:5)	1	95	>200000	Ivory
7 ^d	A:DBU (5:5)	1	95	>200000	Ivory
8	DBU (5)	1	95	20000	White

^aBased on polymer mass recovery after trituration. ^bDetermined by ¹HNMR (CDCl₃; TFA = 1:1). ^cPHMF (100 mg, 0.8 mmol of furanic units), $T = 190 \text{ }^\circ\text{C}$, vacuum. ^dPHMF (2 g, 16 mmol of furanic units).

**Figure 3. Differential scanning calorimetric analysis (DSC) of HMM-PHMF.**

synthetic method.⁴³ In the present case, it can be reasonably attributed to residual catalyst entrapped within the polymer, which could accelerate thermal degradation at elevated temperatures. Indeed, a larger catalyst amount (5 mol %) was used in the synthesis of HMM-PHMF compared to PHMF (0.6 mol %), resulting in an increased likelihood of higher catalyst residue inside the polymer, thereby accounting for its somewhat reduced thermal stability.

To predict the properties and explore the potential of HMM-PHMF, water contact angle (WCA) analyses were performed. PET and PEF were selected for comparison purposes; PET is the most widely used fossil-based polyester, while PEF is currently regarded as a valuable bioalternative to PET. Both polymers share interesting chemical similarities with HMM-PHMF: PEF, like HMM-PHMF, contains furan as its aromatic ring, whereas PET, similar to PEF, has a short

**Figure 4. Thermogravimetric analysis (TGA/DTGA) of HMM-PHMF.**

aliphatic chain with only 2 carbon atoms (Table 2). However, unlike the other two polymers, PET features a nonpolarized

Table 2. Chemical Structure, T_g , and WCA of Some Furan-Based Polymers^a

Polymer	HMM-PHMF	PEF	PET
Structure			
T_g (°C)	90	84	75
Linear length ^a (Å)	7.73	8.18	9.24
WCA (°)	86±2	95±2	78±2

^aLinear length of repeating units calculated by the software ChemScript/Python of PerkinElmer Informatics after the MM2Minimization.

aromatic ring. To perform our analyses, a commercial sample of PET (7001, Invista) was used, while PEF was synthesized by the authors following a previously published protocol.⁴⁴

The WCA for the films prepared by compression molding (see Experimental Section) from these three materials was determined and is reported in Table 2, alongside the glass transition temperature (T_g). Notably, HMM-PHMF is intrinsically the most rigid polymer, as indicated by the T_g trends. Unlike PET and PEF, HMM-PHMF has only one methylene group in its repeating unit and an asymmetric aromatic ring, which reduce its flexibility and limit chain mobility. PET is less rigid than PEF because its macromolecular chain allows for ring-flipping of the terephthalic ring, thanks to its symmetrical structure.⁴⁵

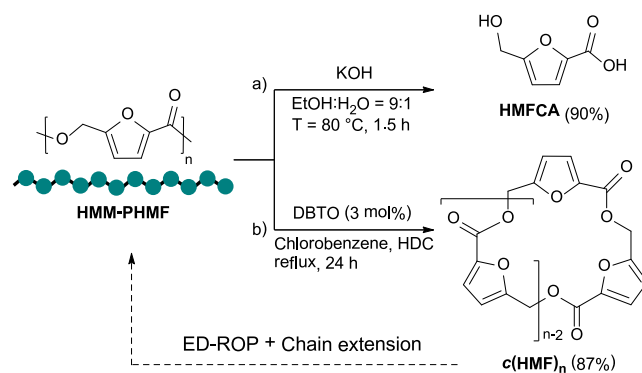
As shown in Table 2, the surfaces of HMM-PHMF and PET can be defined as hydrophilic, as they are characterized by a WCA of less than 90°. In contrast, PEF exhibits remarkable hydrophobic character. These results arise from the weak polar interactions that constrain the chains: PET, with its structure containing two carboxylic groups approximately every 9 Å, has a high number of polar groups available for interaction with water. PEF, despite having a similar structure and a higher frequency of polar groups (i.e., two COO functionalities every about 8 Å), contains a polarized aromatic ring, which means that some of its polar groups are involved in interactions with the ring, making them not accessible for interaction with water. HMM-PHMF, like PEF, has a polarized ring, but unlike PET and PEF, it has only one carboxylic group per repeating unit, resulting in a lower frequency of polar groups along the chain, even if it is characterized by the shortest repeating unit. This accounts for its intermediate WCA value, falling between those of PET and PEF. Finally, it is noteworthy that the WCA data do not align with the T_g data, as the two techniques reveal different characteristics of the materials. T_g reflects the intrinsic rigidity of the materials, determined by the chemical structure of the repeating unit along the macromolecular chain, while the WCA highlights the restrictions on chain movement imposed by weak polar interactions. The presence of polar bonds translates into high cohesive forces, which are typically associated with excellent barrier properties.^{46–48} This could be even more likely, as there is a general trend indicating that the higher the T_g , the better the barrier properties and permselectivity.⁴⁹ For these reasons, it can be speculated that HMM-PHMF could find a place in the food packaging sector currently dominated by PET, positioning itself as an additional bioalternative alongside PEF. To confirm this hypothesis, further studies will evaluate its barrier properties, mechanical performance, and processability.

The last part of our study concerned the investigation of potential recycling processes for our polymeric material. The tremendous increase of polymer production worldwide over the last few decades has been responsible for the rapid increase of plastic waste, and the development of a closed-loop life cycle for polymer materials is critically needed. In this regard, polyester chemical recycling is emerging as one of the most promising approaches.^{50–53} Indeed, the development of a solid chemical recycling protocol allows the direct conversion of polymer wastes under controlled conditions back to the starting feedstocks, which after purification can be in turn employed again as monomers for polymer production in a virtuous closed-loop cycle.^{54,55}

In this work, two main recycling strategies have been explored: alkaline hydrolysis producing HMFCA (Scheme 1a) and cyclodepolymerization under high dilution conditions, affording the much more valuable starting macrocycles $c(\text{HMF})_n$ (Scheme 1b).

Inspired by a recent report on PET depolymerization,⁵⁶ an alkaline hydrolysis in a high-concentration alcohol aqueous solution ($\text{H}_2\text{O}:\text{EtOH} = 10:90$) was performed. Stirring of the heterogeneous polymer suspension at 80 °C for 1.5 h led to the formation of a fully homogeneous solution. Acidification of the reaction mixture and solvent removal afforded the crude mixture, which was triturated with acetone and filtered (see Experimental Section for details). Concentration of the filtrate afforded quantitative formation of HMFCA, confirmed by ^1H and ^{13}C NMR (see Figure S4), a key-intermediate oxidation product of HMF,^{9,57–59} which represents one of the possible

Scheme 1. Chemical Recycling of HMM-PHMF^a



^a(a) Alkaline hydrolysis; (b) cyclodepolymerization under high dilution conditions.

starting materials of our multistep protocol for the synthesis of HMM-PHMF (Figure 1).

An intriguing alternative strategy consisted, as anticipated, of cyclodepolymerization under high dilution conditions. This approach was widely employed for different kinds of polymers, allowing complete controlled depolymerization into macrocycles, which can be in turn converted into the pristine polymers in a closed-loop system.^{60–65} For this purpose, we adapted previously reported cyclodepolymerization protocols for poly(ethylene naphthalene-2,6-dicarboxylate)⁶³ and poly(propylene terephthalate)⁶¹ to our furanic polyester, with slight modifications. It is important to point out that this process was performed in chlorobenzene as a solvent under high dilution conditions for analogy with those already reported.^{61–63} The cyclodepolymerization was performed on a small laboratory scale (200 mg of polymer) to assess the potential conversion of the polymer into the starting macrocyclic oligoesters $c(\text{HMF})_n$; for future scale-up of the process, the screening of environmentally friendly, recyclable alternative solvents will be carried out in order to avoid the use of toxic and carcinogenic solvents and enhance process sustainability. HMM-PHMF was suspended and refluxed in chlorobenzene under high dilution conditions (HDC) for 24 h in the presence of 3 mol % of di-*n*-butyltin oxide (DBTO) as a catalyst. Progressive consumption of the polymeric material was observed, obtaining after reaction workup and purification, a mixture of hydroxymethylfuroate macrocyclic oligoesters $c(\text{HMF})_n$ (87% isolated yield) with a cycles composition ($c(\text{HMF})_3 = 32\%$, $c(\text{HMF})_4 = 36\%$, $c(\text{HMF})_5 = 19\%$, $c(\text{HMF})_6 = 13\%$) determined by NMR according to our previous study,³⁰ almost comparable to that obtained in the direct synthesis from HMF or HMFCA³⁰ (see Experimental Section for details and Figure S5, for NMR analyses). The isolated cycle mixture could then be polymerized through the disclosed two-step protocol for the synthesis of HMM-PHMF (Scheme 1b).

CONCLUSIONS

In summary, we have described the unprecedented synthesis of the fully furan-based high molar mass poly(hydroxymethylfuroate) (HMM-PHMF) with a number-average molar mass greater than 200000 g mol⁻¹. The polymer was produced by organocatalyzed (NHCs) chain extension of PHMF ($M_n = 18000$ g mol⁻¹), which was in turn obtained directly from HMF or HMFCA according to our previous

contribution.³⁰ HMM-PHMF is a semicrystalline polymer with a melting temperature of 193.9 °C when processed from solvent, showing an amorphous behavior with a glass transition temperature of 89.8 °C when processed from the melt. Its thermal stability is very good, with degradation at ~280 °C under N₂ atmosphere and can be efficiently filmed by compression molding. WCA analyses of the films clearly show an intermediate behavior between PET and PEF, which can be directly correlated with the respective chemical structures, confirming the high potential of the polyester as a potential candidate in the food packaging sector. Finally, two recycling strategies have been successfully explored for HMM-PHMF: alkaline hydrolysis producing HMFCFA and cyclo-depolymerization under high dilution conditions affording the starting macrocycles $c(\text{HMF})_n$, which can be in turn converted again to the polyester by ED-ROP followed by chain extension in a closed-loop cycle. Further investigations will be carried out in the future to evaluate the barrier properties, mechanical performance, and processability of the furan-based polyester, gaining new insights into potential applications.

EXPERIMENTAL SECTION

General Experimental Conditions. All moisture-sensitive reactions were performed using oven-dried glassware under an argon atmosphere. Anhydrous solvents were freshly distilled and dried over a standard drying agent prior to use. Reactions were monitored by TLC on silica gel 60 F₂₅₄ with detection using phosphomolybdic acid. Flash chromatography was performed on silica gel 60 (230–400 mesh). ¹H (300 MHz, 400 MHz, 500 MHz) and ¹³C (101 MHz, 126 MHz) NMR spectra were recorded in CDCl₃ or CDCl₂; TFA = 1:1 or acetone-*d*₆ at room temperature. The chemical shifts in ¹H and ¹³C NMR spectra were referenced to tetramethylsilane (TMS). Peak assignments were aided by ¹H–¹H COSY and gradient-HMQC experiments. For high-resolution mass spectrometry (HRMS), the compounds were analyzed using the LTQ-Orbitrap XL mass spectrometer (Thermo Scientific Inc.) equipped with an electrospray ion source set as follows: positive ion mode, spray voltage 5.5 kV, capillary temperature 275 °C, capillary voltage 16 V, tube lens offset 120 V. The MS analyzer was externally calibrated with the LTQ-ESI Positive Ion Calibration Solution to yield accuracy below 5 ppm. Accurate mass data were collected by directly infusing samples in 80/20 H₂O/ACN 0.1% formic acid into the system at a flow rate of 20 μL min⁻¹.

Differential scanning calorimetry (DSC) was performed with a PerkinElmer DSC 8000 equipped with an Intracooler II cooling device and software Pyris for data acquisition and analysis. Analyses were accomplished under a nitrogen atmosphere (30 mL/min) on 4–5 mg of sample in an open aluminum pan. The program temperature was heating from 25 to 235 °C (first heating), holding for 5 min, cooling back to –60 °C (cooling), holding for 10 min, and heating to 235 °C (second heating). Heating and cooling steps were performed at 10 °C/min as the scanning rate. The instrument was calibrated with indium and lead as standards.

Thermogravimetric analysis was performed with a PerkinElmer TGA4000 equipped with software Pyris for data acquisition and analysis. 6–7 mg of the sample in an alumina pan was analyzed in the 25–900 °C temperature range under a nitrogen atmosphere (50 mL/min) at 10 °C/min as the heating rate.

For the film preparation, 0.60 g of sample powder was weighed and scattered on a Teflon foil. The foils were placed between the plates of a Carver press and heated to 210 °C under a pressure of 5 bar over 2 min. Then, the film was quickly cooled to 75 °C (over 3 min), brought to room pressure, and finally separated from the Teflon foil, resulting in a thickness of 200 μm. The procedure was repeated twice to avoid defects in the film.

To determine the molar mass of the polymers in comparison with that of HMM-PHMF, size exclusion chromatography (SEC) was

performed. PEF was dissolved in a CHCl₃/HFIP mixture (90/10, v/v), while PET was dissolved in a CHCl₃/HFIP mixture (98/2, v/v). The dissolved samples were then filtered through Teflon syringe filters prior to analysis. SEC measurements were conducted at 30 °C using a Knauer Azura system equipped with a PLgel 5 μm MiniMixed-C column. The flow rate was set at 0.3 mL/min. For PEF analysis, a CHCl₃/HFIP mixture (95/5, v/v) was used as the eluent, and an ultraviolet (UV) detector was employed. On the other hand, PET analysis utilized CHCl₃ as the eluent and a refractive index (RI) detector. Calibration curves for both conditions were generated by using monodisperse polystyrene standards.

To determine the film surface hydrophobicity, water contact angle (WCA) measurements were performed using a drop shape analyzer (DSA30S- Kruss). The drop (4 μL) of distilled water was positioned on the surface of the film by an autosyringe. Images were captured 5 s after a drop of distilled water was deposited on the surface of the composite films. The reported contact angle values are the mean values of at least ten different measurements.

The structures of short portions of the macromolecular chain for all the polyesters indicated in Table 2 were simulated using the software ChemScript/Python (20.1.1.125 June 7, 2021) of PerkinElmer Informatics. After MM2Minimization, the length of each repeating unit was calculated.

Precatalyst A, 1,5,7-triaza-bicyclo-[4.4.0]dec-5-ene (TBD), and di-*n*-butyltin oxide (DBTO) were purchased from commercial sources and used as received. DBU was freshly distilled before utilization. Macrocylic oligoesters $c(\text{HMF})_n$ mixture (cycle composition ($c(\text{HMF})_3 = 42\%$, $c(\text{HMF})_4 = 35\%$, $c(\text{HMF})_5 = 14\%$, $c(\text{HMF})_6 = 9\%$) was obtained according to a literature procedure.³⁰ For polymer comparison, PET 7001 ($M_n = 27200 \text{ g mol}^{-1}$, $M_w = 44500 \text{ g mol}^{-1}$) was supplied by Invista, and PEF ($M_n = 24500 \text{ g mol}^{-1}$, $M_w = 44500 \text{ g mol}^{-1}$) was synthesized according to a literature procedure.⁴⁴

Procedure for the Synthesis of PHMF. $c(\text{HMF})_n$ (2 g, 16 mmol of furanic units) was transferred into a reaction flask and dissolved in EtOAc (20 mL). Then, a mixture containing TBD (13 mg, 0.09 mmol), *n*-octanol (15 μL, 0.09 mmol), Irganox 1010 (2 mg), and Irgafos 126 (6 mg) in EtOAc (5 mL) was added to the cycle solution and stirred for 30 min. After this period, the solvent was removed under reduced pressure, and the reaction flask was connected to a glass oven (Büchi GKR-50) and dried under vacuum for 30 min. The mixture was degassed under vacuum and saturated with argon (by using an Ar-filled balloon) three times to remove residual oxygen, then heated at $T = 160 \text{ °C}$ under mechanical rotation for the requested time at atmospheric pressure. After cooling, the resulting product was triturated with EtOAc (100 mL). The soluble fraction contained unreacted cycles, while the precipitate corresponded to PHMF, which was then analyzed by NMR. ¹H NMR (400 MHz, CDCl₃; TFA = 1:1) $\delta = 7.31$ (d, $J = 3.5 \text{ Hz}$, 1H, Ar (H-3)), 6.68 (d, $J = 3.5 \text{ Hz}$, 1H, Ar (H-4)), 5.38 (s, 2H, CH₂), 4.80 (s, 2H, terminal CH₂OH). ¹³C NMR (101 MHz, CDCl₃; TFA = 1:1) $\delta = 160.6$ (CO), 153.7 (C-5), 143.2 (C-2), 121.2 (CH-3), 113.6 (CH-4), 58.9 (CH₂O).

General Procedure for the Synthesis of HMM-PHMF (Table 1, Entries 1–6). PHMF (100 mg, 0.80 mmol of furanic units) was transferred to a reaction flask and suspended in EtOAc (10 mL). Then, a mixture containing TBD (6 mg, 0.04 mmol) or the couple precatalyst A (9 mg, 0.04 mmol)/DBU (6 μL, 0.04 mmol) in EtOAc (5 mL) was added to the suspended polymer and stirred for 30 min. After this period, the solvent was removed under reduced pressure, and the reaction flask was connected to a glass oven (Büchi GKR-50) and dried under vacuum for 30 min. The mixture was heated at $T = 190 \text{ °C}$ under mechanical rotation for the requested time under vacuum. After cooling, the resulting product was triturated with EtOAc (20 mL) to afford HMM-PHMF, which was then analyzed by NMR. ¹H NMR (300 MHz, CDCl₃; TFA = 1:1) $\delta = 7.31$ (d, $J = 3.5 \text{ Hz}$, 1H, Ar (H-3)), 6.68 (d, $J = 3.5 \text{ Hz}$, 1H, Ar (H-4)), 5.38 (s, 2H, CH₂), 4.80 (s, 2H, terminal CH₂OH, if detectable). ¹³C NMR (101 MHz, CDCl₃; TFA = 1:1) $\delta = 160.6$ (CO), 153.7 (C-5), 143.2 (C-2), 121.2 (CH-3), 113.6 (CH-4), 58.9 (CH₂O).

Multigram Scale Synthesis of HMM-PHMF (Table 1, Entry 7). PHMF (2 g, 16 mmol of furanic units) was transferred to a reaction flask and suspended in EtOAc (15 mL). Then, a mixture containing TBD (120 mg, 0.8 mmol) or the couple precatalyst A (180 mg, 0.8 mmol)/DBU (120 μ L, 0.8 mmol) in EtOAc (10 mL) was added to the suspended polymer and stirred for 30 min. After this period, the solvent was removed under reduced pressure, and the reaction flask was connected to a glass oven (Büchi GKR-50) and dried under vacuum for 30 min. The mixture was heated at $T = 190$ °C under mechanical rotation for 1 h under vacuum. After cooling, the resulting product was triturated with EtOAc (100 mL), affording HMM-PHMF as an ivory powder (1.9 g, 95%).

Procedure for the Recycling of HMM-PHMF through Alkaline Hydrolysis. HMM-PHMF (200 mg, 1.6 mmol of furanic units) was transferred into a reaction flask and suspended in a KOH alcoholic aqueous solution (1.8 M, H₂O: EtOH = 10:90, 10 mL). The mixture was vigorously stirred at 80 °C for 1.5 h, resulting in a fully homogeneous solution. Acidification with HCl (2 N) and solvent removal afforded the crude reaction mixture, which was triturated with acetone (2 mL) and filtered. Concentration of the filtrate afforded quantitative formation of HMFCa as a white amorphous solid (180 mg, 90%). ¹H NMR (400 MHz, acetone-*d*₆) $\delta = 7.14$ (d, $J = 3.4$ Hz, 1H, Ar (H-3)), 6.46 (d, $J = 3.4$ Hz, 1H, Ar (H-4)), 4.58 (s, 2H, CH₂), 5.27 (bs, 2H, OH, COOH); ¹³C NMR (101 MHz, acetone-*d*₆) $\delta = 160.0$ (CO), 158.6 (C-5), 144.0 (C-2), 118.6 (CH-3), 108.7 (CH-4), 56.4 (CH₂O). HRMS (ESI/Q-TOF) calcd for C₆H₇O₄ ([M + H]⁺) 143.0339, found: 143.0336.

Procedure for the Recycling of HMM-PHMF through Cyclodepolymerization. HMM-PHMF (200 mg, 1.6 mmol of furanic units) was transferred into a reaction flask, suspended in chlorobenzene (12 mL) in the presence of di-*n*-butyltin oxide (DBTO) (12 mg, 0.05 mmol), and refluxed for 24 h. The resulting mixture was diluted with dichloromethane (10 mL), concentrated, and eluted from a column of silica gel with heptane/EtOAc = 1:2 to afford a mixture of *c*(HMF)_{*n*} as a white amorphous solid (170 mg, 85%). Cycle composition was determined by NMR, according to our previous study.³⁰ *c*(HMF)₃ (32 mol %); ¹H NMR (300 MHz, CDCl₃) $\delta = 7.25$ (d, $J = 3.5$ Hz, 3H, Ar (H-3)), 6.50 (d, $J = 3.5$ Hz, 3H, Ar (H-4)), 5.34 (s, 6H, CH₂). *c*(HMF)₄ (36 mol %); ¹H NMR (300 MHz, CDCl₃) $\delta = 7.22$ (d, $J = 3.5$ Hz, 4H, Ar (H-3)), 6.62 (d, $J = 3.5$ Hz, 4H, Ar (H-4)), 5.27 (s, 8H, CH₂). *c*(HMF)₅ (19 mol %); ¹H NMR (300 MHz, CDCl₃) $\delta = 7.18$ (d, $J = 3.5$ Hz, 5H, Ar (H-3)), 6.58 (d, $J = 3.5$ Hz, 5H, Ar (H-4)), 5.30 (s, 10H, CH₂). *c*(HMF)₆ (13 mol %); ¹H NMR (300 MHz, CDCl₃) $\delta = 7.16$ (d, $J = 3.5$ Hz, 6H, Ar (H-3)), 6.60 (d, $J = 3.5$ Hz, 6H, Ar (H-4)), 5.26 (s, 12H, CH₂).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscapm.4c03808>.

NMR spectra of PHMF, HMM-PHMF (Table 1, entries 5–6), HMFCa, and *c*(HMF)_{*n*}; SEC chromatograms of PET 7001 and PEF (PDF)

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Author Contributions

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Notes

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