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Approach to Circular Chemistry Preparing New Polyesters from Olive Oil

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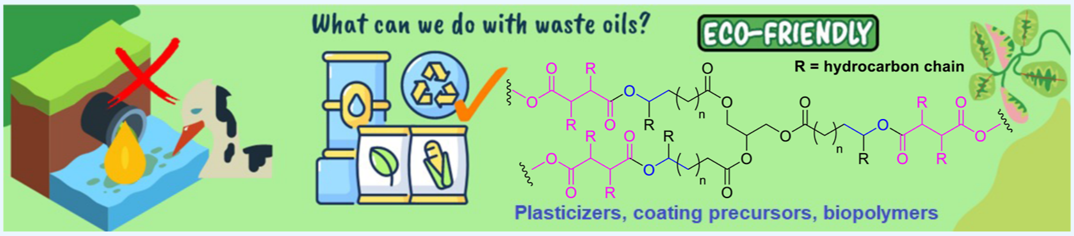

ABSTRACT: The transformation of cooking oils and their waste into polyesters is a challenge for circular chemistry. Herein, we have used epoxidized olive oil (EOO), obtained from cooking olive oil (COO), and various cyclic anhydrides (such as phthalic anhydride PA, maleic anhydride MA, and succinic anhydride SA) as raw materials for the preparation of new bio-based polyesters. For the synthesis of these materials, we have used the bis(guanidine) organocatalyst **1** and tetrabutylammonium iodide (Bu_4NI) as cocatalyst. The optimal reaction conditions for the preparation of poly(EOO-*co*-PA) and poly(EOO-*co*-MA) were 80 °C for 5 h using toluene as solvent; however, the synthesis of poly(EOO-*co*-SA) required more extreme reaction conditions. Furthermore, we have exclusively succeeded in obtaining the trans isomer for MA-polyester. The obtained biopolyesters were characterized by NMR, Fourier transform infrared, thermogravimetric analysis, and scanning electron microscopy analyses. Since there are few examples of functionalized and defined compounds based on olive oil, it is innovative and challenging to transform these natural-based compounds into products with high added value.

INTRODUCTION

During the 21st century, sustainability has played an important role in the global economy, society, and environmental resources. Sustainable development must be the central focus of all future research, which is why it is crucial to develop new synthetic routes and design novel chemicals that make our planet more sustainable in accordance with the "Twelve Principles of Green Chemistry".[1] Renewable raw materials have become very popular around the world and their demand in the polymer industry is expected to increase in the near future.[2,3]

In the last forty years, the amount of food waste has increased enormously, which has had a negative impact on the environment. In fact, Europe, Australia, the US, and Canada lead the per capita average in the generation of food waste in kg/person/year.[4,5] Food waste is mainly composed of residues based on cooking oils, peels, different vegetable leftovers, and others.[4] That is why the scientific community has recently studied the recovery of food waste through its transformation into a wide variety of materials and fine chemical products.[6] Among the different food wastes, used cooking oils (UCO), which are produced mainly in homes, hotels, and restaurants, are the most abundant food waste, since the estimated global amount of UCO generated annually is between 41 and 67 million tons.[5,7] UCOs are normally disposed of in rivers or oceans, causing considerable environmental problems. For these reasons, the development of UCO recycling has been a priority for many countries to reduce the negative effects caused by this type of waste in ecosystems and it is necessary to implement new UCO recycling methodologies to avoid environmental problems, maximizing its recycling and reuse. It should be noted that UCO can be used as a raw material for the preparation of biodiesel, soap, and polymers.[8−13] Chemical modifications can be made in vegetable oils by introducing reactive groups and, thus, producing raw materials for the synthesis of high added value products.[8−13] In addition, recycling of waste polymers is emerging as a highly promising strategy to mitigate plastic pollution. It is interesting to note, that the preparation of polymeric materials and biofuels is done using fresh edible oils as feedstock instead of UCO, so used vegetable oils can get a "second chance", initially for food

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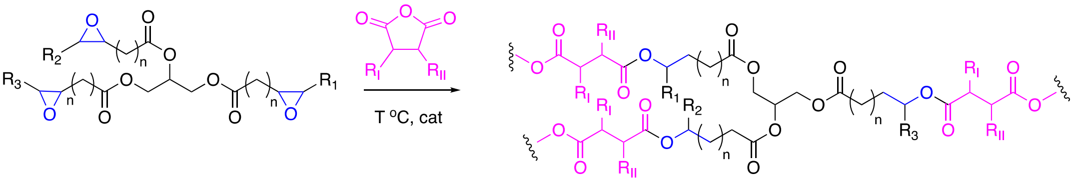
Scheme 1. Synthesis of Bio-Based Polyester by ROCOP Reaction between Epoxidized Vegetable Oils and Cyclic Anhydrides



purposes and then for disposal. UCOs can be used as chemical raw materials for the formation of bioproducts following a circular economy model that contributes to reduce the social and environmental effects associated with both the oleochemical industries and edible oil.[5,14−16]

The epoxidation of double bonds of the triglyceride units of vegetable oils is an interesting reaction with high potential for different applications since epoxides are known to have high reactivity.[17,18] Epoxidized vegetable oils have received much attention as they are used as bioprecursors for the synthesis of poly(vinyl chloride) polymers,[19−21] non-isocyanate polyurethanes (NIPU),[22−29] and polyhydroxyalkanoates.[30−32] In addition, UCO-derived bio-based epoxides can be used as an interesting feedstock for the synthesis of bio-based polyesters by their reaction with cyclic anhydrides via a ring-opening copolymerization (ROCOP) reaction (Scheme 1). It is important to highlight that this novel synthetic route has not been previously reported to date using olive-based epoxidized vegetable oils as precursors.[29,33] The first synthetic approach has been recently published by Kleij et al., where the preparation of attractive functional bio-polyesters has been achieved from the reaction between fatty acid epoxides and cyclic anhydrides.[34] This ROCOP reaction has been extensively investigated with commercially available cyclic epoxides and anhydrides, although it requires the presence of a metal catalyst[35−41] or an organocatalyst.[42−45] In recent years, organocatalysts have become more popular than metal catalysts, since metal-free catalysts offer several advantages, such as higher catalyst availability at lower costs, lower sensitivity to oxygen or water,[46] and they are more ecological and less toxic than metal-containing catalysts.[43]

Recently, our research group has focused its efforts on the design of new organocatalysts that have been used in the synthesis of cyclic carbonates from the reaction between epoxides and carbon dioxide.[47,48] In this contribution, we decided to explore the catalytic application of the bis(guanidine) organocatalyst **1**[47] (Figure 1) in the ROCOP reaction between epoxidized olive vegetable oil and different cyclic anhydrides.

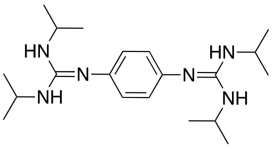


Figure 1. Bis(guanidine) organocatalyst **1**.

This new catalytic ROCOP reaction provides the opportunity to obtain new bio-based polyesters from epoxidized vegetable oils under mild reaction conditions. This process is challenging because it allows the reuse and revaluation of cooking oils through the formation of high value-added products.

■ RESULTS AND DISCUSSION

Cooking olive oil, COO, was used as a renewable raw material for the synthesis of its corresponding epoxidized olive oil, EOO. This transformation was carried out as previously reported[18,49] (see Scheme 2, Experimental Section and Supporting Information).

The fatty acid composition of this oil was determined by GC-FID (see Figure S1 and Table S1). This analysis showed that COO had 2.92 double bonds per gram of triglyceride unit, and the main fatty acid found in this vegetable oil was oleic acid (see Figure S1 and Table S1). The chemical composition of UCOO was also analyzed by ^{1}H NMR, and after five cooking cycles, its structure was not altered (see Figure S2). Given the exceptional catalytic activity and the wide range of substrates used for the preparation of cyclic carbonates from the reaction between CO_2 and terminal and internal epoxides, bis(guanidine) **1** was chosen as the organocatalyst.[47] We studied the use of compound **1** as a catalyst for the formation of a set of bio-based polyesters from the ROCOP reaction of EOO and different cyclic anhydrides [phthalic anhydride (PA), maleic anhydride (MA), and succinic anhydride (SA)] as starting materials.

The initial trials were carried out at 80 °C for 1 and 24 h, respectively (Table 1, entries 1 and 2), and the results revealed that moderate conversion was obtained at 1 h, however, quantitative conversion was achieved after 24 h. The influence of the temperature was also tested.

As can be derived from Table 1, at 50 °C, unfortunately, a poor conversion result was observed (Table 1, entry 3), which revealed the importance of the temperature in the ROCOP process. After that, the reaction time was optimized to 5 h in which an excellent polyester conversion was reached (Table 1, entry 4). Next, the diminution of catalyst and cocatalyst load to 1 mol % was investigated, noticing a notable decrease in the catalytic activity (Table 1, entry 5). Therefore, the selected reaction conditions for the preparation of polyester poly(EOO-*co*-PA) were 80 °C for 5 h employing 5 mol % of catalyst system (**1**/Bu_4NI) in toluene as a solvent. Finally, control tests were performed to determine that neither catalyst **1** nor cocatalyst Bu_4NI alone or the absence of the catalyst system exhibited considerable catalytic activity by themselves (Table 1, entries 6−8).

The preparation of poly(EOO-*co*-PA) was verified by spectroscopic techniques, revealing that the ROCOP of cyclic anhydrides and epoxides is performed in a controlled manner since no ether bonds were detected (see Supporting Information). The ^{1}H NMR spectra of polyester poly(EOO-*co*-PA), EOO, and COO are shown in Figure 2. Olefinic groups present in COO (5.28−5.43 ppm, Figure 2a) were transformed into the corresponding epoxides in which the CH protons at the α position of the epoxy functional group were shifted to high field (2.81−3.14 ppm, Figure 2b). Fourier transform infrared (FT-IR) spectroscopy is also an effective tool to investigate the formation of different compounds. The

Scheme 2. Preparation of Epoxide Olive Oil, EOO, from COO

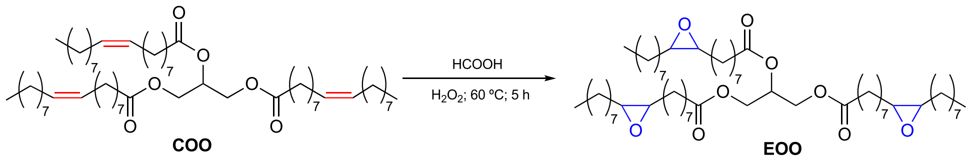
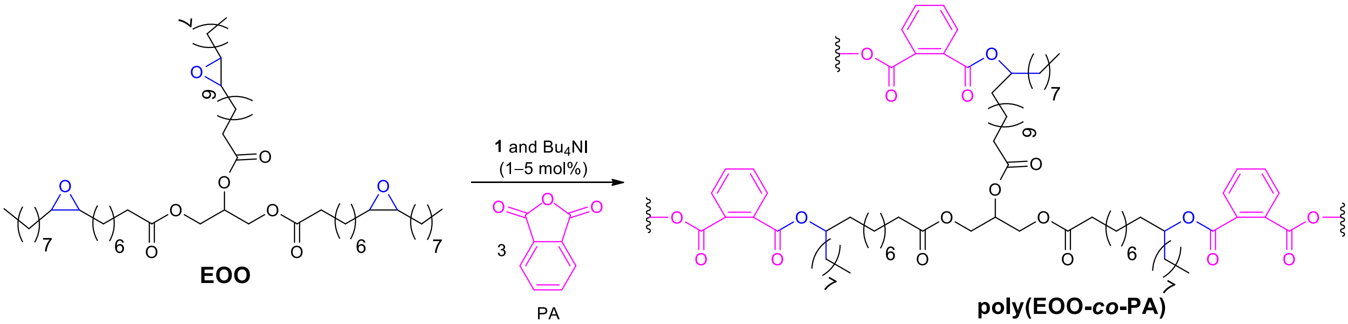


Table 1. ROCOP of PA and EOO Catalyzed by Bis(guanidine) 1 and Bu_4NI[a]



entry	temperature (°C)	time (h)	conversion[b] (%)
1	80	1	49
2	80	24	>99
3	50	24	32
4	80	5	>99
5	80	5	46[c]
6[d]	80	5	traces
7[e]	80	5	traces
8[f]	80	5	46

[a] Reactions were carried out at 50 or 80 °C in toluene for 1−24 h using 5 mol % of bis(guanidine) **1** and Bu_4NI. [b] Conversion was determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] 1 mol % of **1** and Bu_4NI were used. [d] No catalyst system was added. [e] No Bu_4NI was added. [f] No **1** was added.

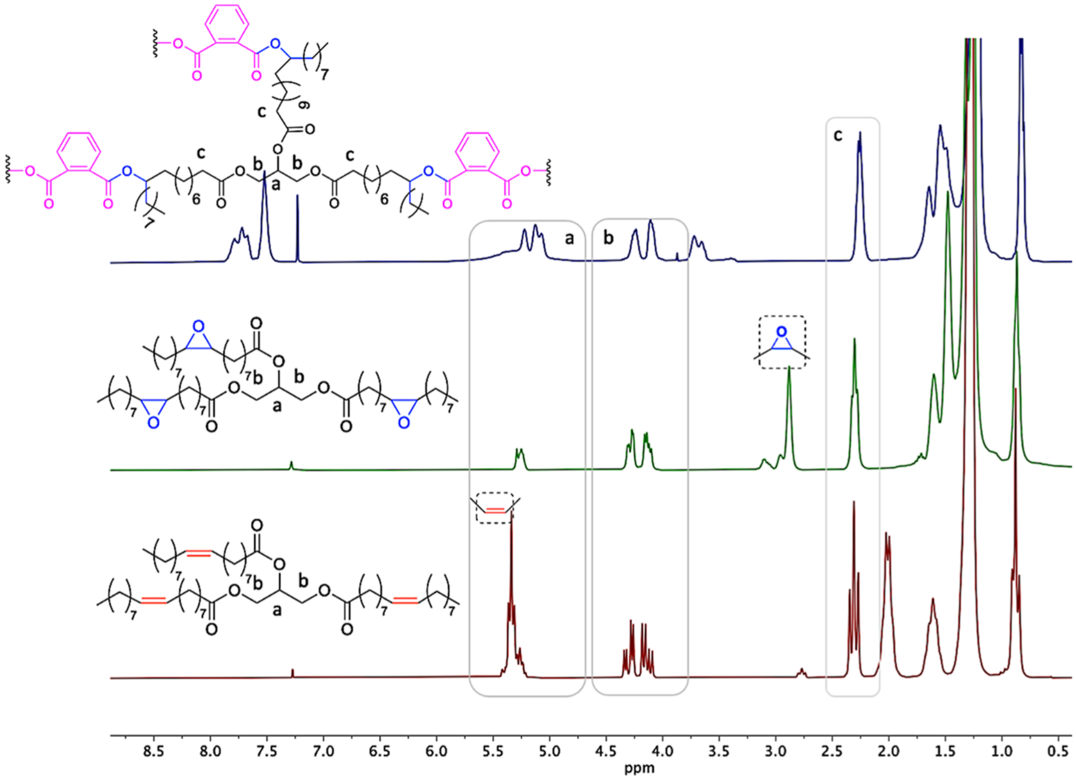


Figure 2. ^1H NMR spectra ($CDCl_3$) of COO (a), EOO (b), and poly(EOO-*co*-PA) (c).

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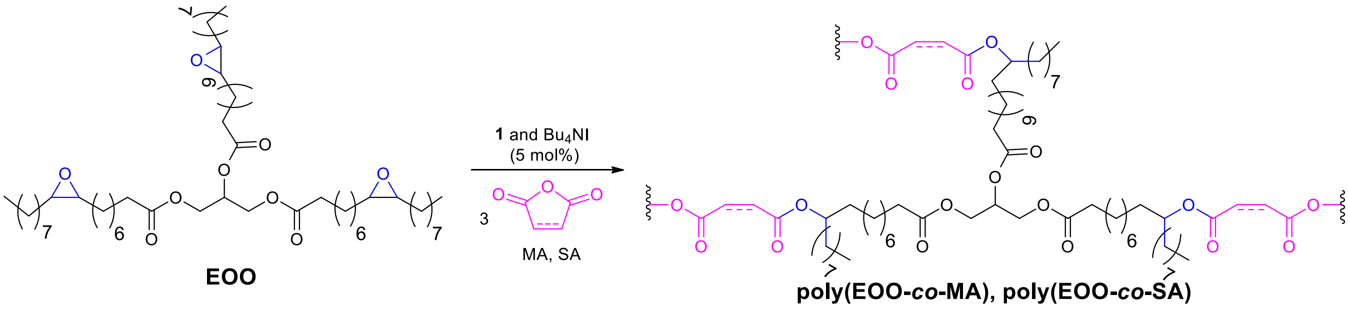
Table 2. . ROCOP of MA or SA and EOO Catalyzed by Bis(guanidine) 1 and Bu_4NI[a]



entry	monomers	temperature (°C)	time (h)	conversion[b] (%)	% cis/trans[c]
1	EOO/MA	80	1	64	95/5
2	EOO/MA	80	5	>99	89/11
3	EOO/MA	80	24	>99	79/21
4	EOO/MA	110	24	>99	0/100
5	EOO/SA	80	24	traces	
6	EOO/SA	110	72	42	

[a] Reactions were carried out at 80 or 110 °C in toluene for 24 or 72 h using 5 mol% of bis(guanidine) **1** and Bu_4NI. [b] Conversion was determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] *cis*−*trans* ratio of poly(EOO-*co*-MA) was determined by ^1H NMR spectroscopy of the crude reaction mixture.

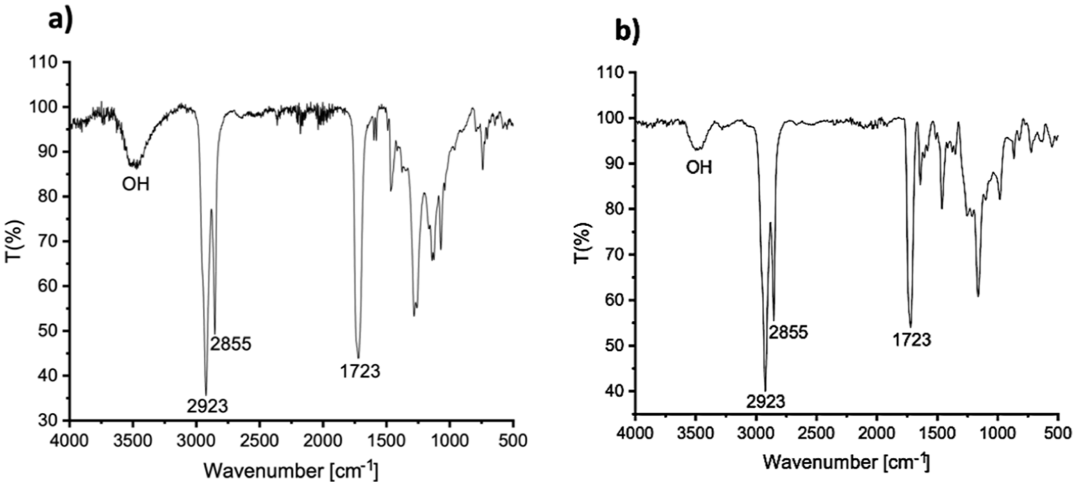


Figure 3. FT-IR spectra of poly(EOO-*co*-PA) (a) and poly(EOO-*co*-MA) (b).

preparation of EOO was confirmed by the disappearance of the alkene group signal at 3004 cm^{-1} (see the Supporting Information). The formation of poly(EOO-*co*-PA) was confirmed by the disappearance of the epoxy groups' signals. New signals that belong to the polyester groups were observed around 3.58−3.78 and 5.03−5.17 ppm (Figure 2c).

Additionally, two new resonance peaks corresponding to the PA fragment of the polyester appear around 7.52 and 7.72 ppm, respectively. Given the challenge of preparing new bio-based materials, other cyclic anhydrides, such as MA and SA, were used as starting materials together with EOO to obtain the corresponding poly(EOO-*co*-MA) and poly(EOO-*co*-SA) polyesters, respectively (Table 2). It is reported that in some cases for both MA and SA, there are more difficulties in the formation of polyesters by the ROCOP process.[34,50] However, under relatively moderate reaction conditions, MA and SA anhydrides have also been used as substrates for the creation of various polyesters, which is directly related to the activity of the applied catalytic systems.[38,41] Additionally, Thumrongpatanaraks et al. observed a notable difference in the reactivity between MA and SA with propylene oxide (PO) when using the same bis(amidinate)tin(II) catalyst where the poly(PO-*co*-MA) polyester was afforded at 80% conversion in only 1 h, whereas SA required 8 h to form poly(PO-*co*-SA) with a similar conversion.[37] In our case, the successful preparation of poly(EOO-*co*-MA) was performed under the same reaction conditions as poly(EOO-*co*-PA), although the synthesis of poly(EOO-*co*-SA) required more extreme reaction conditions (reflux in toluene for 72 h), as can be seen in Table 2.

It is possible that the unsaturations in the cyclic anhydrides (PA and MA) can facilitate their opening through the interaction with the EOO due to the formation of a conjugated system between the double bond and the ester group, which could explain why poly(EOO-*co*-PA) and poly(EOO-*co*-MA) polyesters are easier to synthesize than poly(EOO-*co*-MA) (EOO-*co*-SA). MA is an interesting monomer, which can form a set of unsaturated biodegradable polyesters. In general, when MA is used as a substrate, the *cis* isomer of the corresponding polyester is obtained, which could be later transformed into the *trans* form by an isomerization.[51,52] Interestingly, poly(EOO-

co-MA) was obtained as a *cis*—*trans* mixture using **1**/Bu_4NI catalytic system (see Supporting Information for more details), although this *cis*—*trans* ratio varied depending on the temperature and reaction time.

First, the *cis*—*trans* ratio of poly(EOO-*co*-MA) was analyzed at 80 °C and different reaction times (see Table 2, entries 1—3). As expected, for the reaction carried out during 1 h, we did not observe complete transformation of EOO/MA into the corresponding polyester (Table 2, entry 1). However, a quantitative conversion was obtained for those reactions carried out during longer reaction times (Table 2, entries 2 and 3). Under these reaction conditions, mainly the *cis* isomer was achieved. Further, we decided to investigate the influence of temperature on the *cis*—*trans* ratio for the obtained poly(EOO-*co*-MA), and the reaction was carried out under toluene reflux, achieving exclusively the *trans* poly(EOO-*co*-MA) isomer (see Table 2, entry 4, see Supporting Information for more details). To the best of our knowledge, this is the first time that the direct synthesis of a *trans*-MA-polyester occurs selectively and reveals the importance of reaction temperature in this process. Finally, formation of poly(EOO-*co*-SA) was performed at 42% of conversion under more extreme reaction conditions, toluene reflux for 72 h (see Table 2, entry 6).

The formation of poly(EOO-*co*-MA) and poly(EOO-*co*-SA) was corroborated by spectroscopic methods. The cis/trans poly(EOO-*co*-MA) isomers were identified by ^1H NMR. The olefinic protons for *cis* poly(EOO-*co*-MA) isomer appear around 6.33 ppm while the protons of the *trans* poly(EOO-*co*-MA) isomer (EOO-*co*-MA) can be found at 6.88 ppm in ^1H NMR spectra[49] (see Supporting Information). The formation of poly(EOO-*co*-SA) was confirmed by the appearance of a new signal around 2.65 ppm in the ^1H NMR spectrum that corresponds to the methylene groups of SA (see Supporting Information).

Polyesters, poly(EOO-*co*-PA), poly(EOO-*co*-MA), and poly(EOO-*co*-SA) were also characterized by FT-IR (see Figure 3). The characteristic signal around 1720 cm^{-1} in the FT-IR spectra belong to the C=O stretching frequencies of the ester groups. Additionally, the other two intense bands appear in the range of 2930—2850 cm^{-1} and correspond to the numerous $C(sp^3)$—H stretching vibrations present in polyesters. However, the most significant band was observed over 3500 cm^{-1}, confirming the presence of terminal OH groups in the synthesized polymers.

It is important to note that the presence of OH groups in the polyesters was also confirmed by ^1H NMR. Figure 4 shows the ^1H NMR of *trans*-poly(EOO-*co*-MA) (Table 2, entry 4). As can be seen, the signal around 6.1 ppm, belonging to hydroxy groups (Figure 4a), disappear after the addition of D_2O (Figure 4b) due to the exchange between the deuterated solvent and the hydrogen of OH groups of the poly(EOO-*co*-MA).

The molecular weights revealed by bio-based polyesters were quite low, as shown in Table 3, which allowed to conclude that poly(EOO-*co*-PA) and poly(EOO-*co*-MA) were produced as oligomers. This fact is reasonable since the EOO used as starting material is composed of different chains of fatty acids. Furthermore, these materials were obtained with narrow polydispersities. It is interesting to note that synthetic polyesters can be employed as plasticizers to create new polymeric materials as well as coating precursors because of their low molecular weight.[53−56]

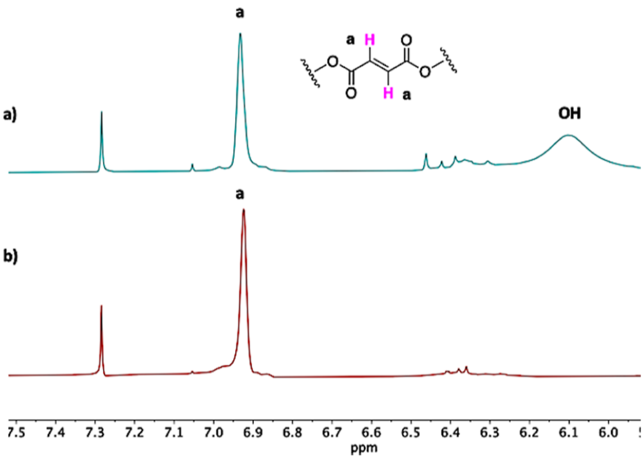


Figure 4. ^1H NMR spectra of *trans*-poly(EOO-*co*-MA) (a) and *trans*-poly(EOO-*co*-MA) (b) after D_2O addition.

Table 3. Molecular Weights and PDI Obtained from the Synthesized Bio-Based Polyesters

entry	polyester	$M_{n(exp)}$ (Da)[c]	PDI[c]
1	poly(EOO-*co*-PA)[a]	1044	1.08
2	poly(EOO-*co*-MA)[b]	1464	1.20

[a]Polyester used (Table 1, entry 4). [b]Polyester used (Table 2, entry 2). [c]Determined by GPC relative to PMMA standards in chloroform.

The thermal properties of the synthesized polyesters, poly(EOO-*co*-PA), poly (EOO-*co*-MA), and poly(EOO-*co*-SA), were determined by thermogravimetric analysis (TGA). This technique revealed that all polymers are stable in the interval of temperatures from 10 to 300 °C (see Supporting Information). The TGA analysis of the mixture of *cis*—*trans* poly(EOO-*co*-MA) showed that the thermal decomposition of both isomers occurred differently (see Figure S17). Surface morphology (SEM) analysis (Figure 5) shows the SEM micrograph of the surface for poly(EOO-*co*-PA). On a nanometer scale, a uniform surface morphology and the formation of a homogeneous polymer film is observed.

■ CONCLUSIONS

In this work, we have developed an efficient catalytic methodology for the preparation of a set of new bio-based polyesters by ROCOP of EOO and cyclic anhydrides. The obtained biopolymers were characterized by NMR, FT-IR, and TGA analysis. Additionally, the existence of hydroxy groups at the end of the polyester chain was confirmed by spectroscopic techniques. The catalytic system formed by bis(guanidine) **1** and Bu_4NI was able to form poly(EOO-*co*-PA) and poly(EOO-*co*-MA) with 100% conversion, while poly(EOO-*co*-SA) was obtained with 42% conversion. It is important to mention that, in this work, the direct synthesis of the *trans*-MA-polyester was achieved without requiring an additional isomerization reaction. Multiple types of UCO can be used as potential feedstocks for the formation of a wide variety of bio-based polyesters, expanding the opportunities for these macromolecules in several areas of polymer science. Our future objectives will focus on the design of new polymeric materials based on UCOs. It is exciting to think of these synthetic polyesters as plasticizers and coating precursors to create new polymeric materials. It has been more appealing to employ these synthetic plasticizers in place of traditional ones because

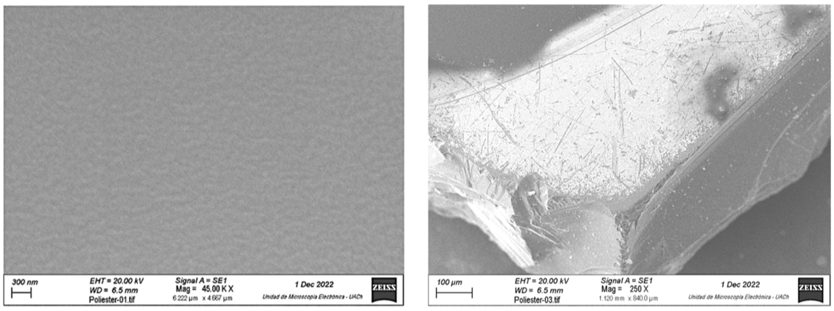


Figure 5. SEM micrograph of poly(EOO-*co*-PA).

of their low toxicity and strong compatibility with a variety of polymers.

EXPERIMENTAL SECTION

General Procedures and Techniques. All NMR spectra, ^{1}H and ^{13}C{^{1}H}, were recorded in a Bruker AVANCE III HD (300 MHz). Chemical shifts are given in parts per million relative to TMS [^{1}H and ^{13}C, $\delta(\mathrm{SiMe_4}) = 0$]. All coupling constants (J) are represented in Hz. Multiplicities are shown by brs (broad singlet), s (singlet), d (doublet), t (triplet), dd (double doublet), and m (multiplet). Thermogravimetric analyses were done in a Perkin Elmer TGA-4000. The heating rate for the sample was 10 °C/min, and the nitrogen flow rate was 20 mL/min. Finally, Infrared spectra were measured using a Jasco FT/IR-4200 equipped with a Jasco ATR model PRO450-S.

Materials and Reagents. The preparation of bis(guanidine) organocatalyst (**1**) was achieved using a previously reported procedure.[57] All reagents and solvents were purchased from common commercial sources and used as received.

Preparation of EOO. COO and formic acid (1:4 molar ratio) were placed into a 100 mL round bottom flask at 60 °C under powerful stirring. Then, H_2O_2 30% w/w (4:1 molar ratio of H_2O_2 per double bond in triglyceride unit) was slowly added over a period of 3 h (the addition of H_2O_2 should be done carefully and slowly to avoid any safety problem) (Scheme 2), and the reaction was stirred at 60 °C for 3 h. Then, diethyl ether was added (100 mL) and the resulting solution was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 100 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated to give the EOO as a white solid. EOO was then purified by column chromatography using a solvent system *n*-hexane/EtOAc (1:1). ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 5.33−5.21 (m, 1H, CH), 4.29 (dd, $^3J_{HH}$ = 11.7, 3.8 Hz, 2H, CH_2), 4.13 (dd, $^3J_{HH}$ = 11.7, 5.8 Hz, 2H, CH_2), 3.15−2.81 (m, 5H, CH), 2.37−2.27 (m, 6H, CH_2), 1.68−1.14 (m, 62H, CH_2), and 0.93−0.80 ppm (m, 9H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 297 K): δ 173.2, 173.1, 172.7, 68.9, 62.0, 57.1, 57.1, 34.1−22.6 (multiple CH_2 aliphatic signals), 14.1 ppm. IR (FT-IR): 2919, 2855, and 1740 cm^{-1}.

Representative Copolymerization Procedure. EOO (0.60 mmol), cyclic anhydride (1.80 mmol), organocatalyst **1** (0.03−0.006 mmol), and Bu_4NI (0.03−0.006 mmol) were dissolved in 10 mL of toluene in a round bottom flask equipped with a magnetic stirring bar. The reaction mixture was placed in a preheated oil bath at the desired temperature (50−110 °C) and stirred for the desired reaction time (1−72 h). After the appropriate time, the reaction was cooled to room temperature and toluene was removed under reduced pressure from the reaction mixture. NMR analysis was used to determine the monomer conversion from the crude. To eliminate the catalyst system, diethyl ether was added (20 mL) to the reaction mixture and the solution was filtered. After that, polyesters were washed with hexane (20 mL) for 30 min and were dried overnight in a vacuum oven. Polymers were collected as viscous solids.

Poly(EOO-*co*-PA) was prepared according to the general polyester preparation procedure, ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 7.87−7.65 (m, 6H, H−Ar), 7.58 (s, 6H, H−Ar), 5.28 (s, 1H, CH), 5.21−5.02 (br s, 3H, OH), 4.29 (s, 2H, CH_2), 4.17 (s, 2H, CH_2), 3.80−3.63 (br s, 4H, CH), 2.28 (s, 6H, CH_2), 1.83−1.15 (m, 86H, CH_2), and 0.85 ppm (s, 9H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 297 K): δ 173.4, 172.9, 167.8, 131.3, 131.0−128.8 (multiple CH aromatic signals), 68.9, 62.1, 34.0−22.7 (multiple CH_2 aliphatic signals), 14.1 ppm. IR (FTIR): 3644−3235, 2923, 2855, and 1723 cm^{-1}.

Poly(EOO-*co*-MA) was prepared according to the general polyester preparation procedure, ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 6.92 (s, 3H, *trans* CH═CH), 5.27 (s, 1H, CH), 4.96 (s, 3H, terminal OH), 4.30 (d, *J* = 11.6, 7.5 Hz, 2H, CH_2), 4.17 (dd, *J* = 12.2, 5.8 Hz, 2H, CH_2), 3.68 (s, 2H, CH), 2.32 (t, *J* = 7.5 Hz, 6H, CH_2), 1.77−1.10 (m, 77H, CH_2), 0.88 ppm (s, 9H, CH_3).^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 297 K): symbol = 173.5, 173.0, 167.4, 164.9, 134.5, 133.8, 72.5, 69.0, 62.2, 34.1−22.7 ppm (multiple CH_2 aliphatic signals) 14.1, 13.6 ppm. IR (FTIR): 3591−3341, 2923, 2855, and 1723 cm^{-1}.

Poly(EOO-*co*-SA) was prepared according to the general polyester preparation procedure, ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 5.27 (s, 1H, CH), 5.08−4.81 (br s, 3H, terminal OH), 4.31 (dd, *J* = 11.9, 4.3 Hz, 2H, CH_2), 4.15 (dd, *J* = 11.9, 5.9 Hz, 2H, CH_2), 2.66 (s, 6H, CH_2), 2.32 (t, *J* = 7.8 Hz, 6H, CH_2), 1.71−1.15 (m, 102H, CH_2), and 0.89 ppm (t, *J* = 6.0 Hz, 12H, CH_3).

Representative GPC Measurements. Molecular weight estimations of synthesized poly(EOO-*co*-PA), poly(EOO-*co*-MA), and poly(EOO-*co*-SA) were assessed by gel permeation chromatography (GPC, Jasco, Japan) equipped with a refractive index detector (RI-4030, Jasco) and a divinylbenzene-based column (DVB column, Jordi Labs) enclosed in a column oven at 40 °C (CO-4060, Jasco). 10 mg of polymeric sample were dissolved in 1.0 mL of chloroform and stirred overnight up to total dissolution of polymer into the solvent. Samples were measured in GPC running with chloroform as mobile phase at 1.0 mL/min. Molecular weight calculations (M_w, M_n, and polydispersity index) were done using ChromNAV-GPC software (Jasco), a molecular weight calibration curve made using different narrow polymethylmethacrylate standards (ReadyCal Kit, Polymer Standard Service GmbH).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c00623.

^{1}H and ^{13}C spectral copies for all new compounds and comparison of spectroscopic data, GPC, TGA, and FT-IR data (PDF)

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Notes

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