Research Article

Fully Biobased Aliphatic Anionic Oligoesters: Synthesis and Properties

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Biobased aliphatic sulfonated oligoesters with 10 to 30% of sulfonated units were synthesized by melt polycondensation of biobased monomers such as diethyl succinate, z-octadec-9-enedioic acid, dimer fatty acid, sodium (sulfonated dimethyl succinate), and various diols like 1,4-butane diol and isosorbide. Structural characterization of the resulting oligoesters was determined by 1H NMR spectroscopy and MALDI-TOF MS technique. Showing a regular structure, the nature of the different expected species present in the macromolecular structure allowed the detection of etherification and cyclisation side reactions. The study of the thermal properties indicates that the resulting oligoesters are amorphous or semicrystalline that essentially depend on the nature of monomers. Films of oligoesters treated in acidic, basic, and natural media at 37°C indicate that the remaining weight depends essentially on the composition of oligoesters. Finally, sulfonated oligoester was used to prepare a biobased poly(ester-urethane) thermoset, a material having tunable properties.

1. Introduction

The sulfonated polyesters constitute the most studied ionic polymer family. Indeed, the incorporation of sulfonated groups into the structure of aromatic polyesters, mainly PET and PBT, has been the subject of many researches for nearly three decades [1–3]. PET containing small amounts of sulfonated units has been known for a long time. They have been exploited by DuPont as textile fibers with improved dye ability to cationic dyes [4]. The pioneer works were interested in the preparation of sulfonated PET containing Na+, K+, and Cs+ counterions [5–10]. In particular, they were interested in the evolution of the thermal behavior and the crystallinity following the modification of the metallic counterion nature associated with the sulfonate group and the content of sulfonated units inside the copolyesters. The melt polycondensation of dimethyl terephthalate (DMT), dimethyl 5-sodosulfoisophthalate (Na-DMSI), and 1,2-ethanediol has been successfully realized by Fleury et al. [11] who show that the formation of diethylene glycol (DEG) and triethylene glycol (TEG) units by etherification reaction was inevitable but can be used to tune the thermal properties, stability, and mainly the hydrolytic degradation of these polymers. In addition to the etherification side reactions, Guo et al. [12] have mentioned that the molecular weight of copolyester ionomers depends on the sulfonate content. Therefore, the copolyesters that had the highest sulfonate content led to the lowest value of molecular weight. Sulfonated polyesters based on 1,4-butanediol (BD) and 1,6-hexanediol (HD) [13–16] were also prepared; these studies clearly show the major role of the sulfonated unit content on the copolymer chain mobility and as a consequence on Tg and hydrolytic degradation behavior. The replacement of petrochemical...
feedstocks by their biobased counterpart product from renewable resources in aromatic and aliphatic copolyesters has benefits relating to positive environmental impacts such as reduced carbon dioxide emissions. In this context, our team has been interested in the preparation of new biobased sulfonated copolyesters from furanic monomer derived from furfural, which can be easily obtained by chemical treatment of vegetal biomass. The original properties of these materials involving thermal stability, water sorption, and hydrolytic degradation help them to be good materials for a variety of demanding applications [17]. In the last few years, the synthesis of biobased aliphatic polyesters such as poly(butylene succinate) (PBS) and poly(butylene adipate) (PBA) received great interest from several research projects [18, 19] due to their excellent physical properties. They are among the most promising materials for biomedical applications and environmental protection. Particular interest has been given to aliphatic polyesters based on ionomers because of their potential biological properties, such as biocompatibility and biodegradability, and their relatively easy synthesis. Two main methods have been applied to prepare these materials: (i) by polycondensation of succinic acid or adipic acid and sodium (sulfonated dimethyl succinate) (Na-DMSS) obtained by sulfonation of dimethyl maleate (DMM) and various diols [20–25] and (ii) by postsulfonation of unsaturated polyesters. The second method was carried out to prepare surfactants by sulfonation of unsaturated poly(silicone-esters) [26, 27]. A more detailed study was realized to describe the sulfonation of unsaturated polyesters based on dimethyl maleate and 1,2-ethane diol (ED) by the addition of sodium bisulfitc in an aqueous-alcoholic medium [28]. Resulting materials are soluble in an aqueous-organic medium and exhibit micellar behavior in an aqueous medium which depends on the concentration of the sulfonated units. It is also noted that the presence of anionic aliphatic unit modifies the thermal and mechanical properties of the polyesters. Recently, a series of sulfonated poly(butylene succinate) (PBS) ionomers containing up to 14 mol% of sulfonated succinate units have been synthesized by Bautista et al. [29]. They report the synthesis, NMR characterization, and mechanical and thermal properties of PBS ionomers. The hydrolytic degradation of these ionomers was also performed in an aqueous medium at different pH to estimate their susceptibility to hydrolysis in different conditions.

This work is aimed at studying and characterizing fully biobased aliphatic sulfonated oligoesters based on diethyl succinate (DES), 1,18-octadec-9-enedioic acid with z configuration (C18), hydrogenated dimer fatty acid (DA), sodium (sulfonated dimethyl succinate) (Na-DMSS), and two biosourced diols: 1,4-butane (BD) diol and isosorbide (Is). The objective is to evaluate the effect of the nature of the aliphatic monomers on both thermal properties and hydrolytic degradation of these new oligoesters. Deep characterization by 1H NMR and MALDI-TOF analysis [30, 31] and hydrolytic stability of these materials both in aqueous and oxidative media were investigated [32]. Finally, in view of designing new ionic and biobased thermosets, we have tested one oligoester as macrodil in a polyurethane formulation and evaluated the thermal and hydrolysis properties of the corresponding cross-linked material.

2. Experimental

2.1. Materials. Diethyl succinate (DES) (98.00+ %); dimethyl maleate (DMM) (96.00+ %); 1,4-butane-diol (BD) (99.99+ %); isosorbide (Is) (98.00+ %); tetrabutoxysilane (Ti(OBu)4) (97.00+ %); zinc acetate (Zn(OAc)2) (99.99%); trimethylolpropane (TMP) (98+ %); and 4,4′-methylene bis-(cyclohexyl isocyanate) (HMDI) (90+ %) were all purchased from Sigma-Aldrich. 1,18-Octadec-9-enedioic acid with z configuration (C18) was kindly provided by the Institut Français du Pétrole (IFP, France) and was used without purification. Hydrogenated distilled dimer acid (HDA) Radiacid 0976 was supplied by OLEON. It presents an iodine value of 196 mg KOH/g.

2.2. Synthesis of Sodium (Sulfonated Dimethyl Succinate) (Na-DMSS). Sodium (sulfonated dimethyl succinate) (Na-DMSS) was prepared according to the procedure described elsewhere [33]. First, dimethyl maleate (DMM) (10 g) and NaHSO3 were dissolved in a mixed methanol/water (50/50 v/v) and were submitted to reflux at 80°C for 8 h. Then, the reaction mixture was filtered in order to remove traces of NaN3, and evaporate to dryness. The residue was dissolved in DMSO, the liquid phase was precipitated with a large amount of acetone, and the precipitate was collected by filtration and dried under vacuum at 80°C for 48 h.

2.3. Copolymerization

2.3.1. Synthesis of Poly(1,4-butylene succinate-co-1,4-butylene sodiosulfonate succinate) PBSuSx. PBSu70S30 was synthesized by the polycondensation of 5 g (29 mmol) of DES and 3.05 g (12.4 mmol) of Na-DMSS with 11.17 g (124 mmol) of BD. Transesterification reactions were carried out at 190°C under a nitrogen flow in the presence of 0.1 wt% of Ti(OrBu)4 for 6 h. Then, 0.1 wt% Ti(OrBu)4 was added to the resulting reaction medium and it was heated at a high temperature of 220°C during 3 h under vacuum to remove the remaining diol as efficiently as possible. The oligoesters PBSu100S0, PBSu60S40, and PBSu50S50 were obtained by perming the same protocol but by adjusting the ratio (DES)/(Na-DMSS): (100:0)/(80:20)/(60:40), respectively.

2.3.2. Synthesis of Poly(1,4-butylene isosorbide succinate-co-1,4-butylene isosorbide sodiosulfonate succinate) PBISuSx. PBISu70S30 was synthesized according the same procedure described above for PBSu70S30 but by substituting a part of BD (5.57 g; 61.9 mmol) by Is (9.03 g; 61.9 mmol). The oligoesters PBISu100S0, PBISu60S40, and PBISu50S50 were obtained by following a similar process but by adjusting the ratio (DES)/(Na-DMSS): (100:0)/(90:10)/(80:20), respectively.
2.3.3. Synthesis of Poly(1,4-butylene z-octadec-9-enedioate-co-1,4-butylene sodiosulfonate succinate) PBC18-Ss30. 
PBC18-Ss30 oligoester was prepared using 5 g (16 mmol) of C18, 1.7 g (6.8 mmol) of Na-DMSS, and 6.7 g (68 mmol) of BD. Transesterification reactions were carried out at 190 °C under a nitrogen flow in the presence of 0.1 wt% of Zn(OAc)2 for 6 h. Then, 0.1 wt% of Ti(OBu)4 was added to the resulting reaction medium and it was heated at 220 °C for 3 h. The oligoesters PBC18, PBC18-Ss10, and PBC18-Ss20 were obtained by following a similar process but by adjusting the ratio (C18)/(Na-DMSS): (100 : 0)/(90 : 10)/(80 : 20), respectively.

2.3.4. Synthesis of Poly(1,4-butylene dimer acid-co-1,4-butylene sodiosulfonate succinate) PBDA-Ss30. 
The previous procedure was used for the preparation of PBDA100-Ss0-30 but by introducing HDA instead of C18 at different ratios (HDA)/(Na-DMSS): (100 : 0)/(90 : 10)/(80 : 20). For PBDA70-Ss30, the raw materials are as follows: 5 g (0.886 mmol) of HDA, and 0.94 g (0.38 mmol) of Na-DMSS were reacted with 3.42 g of (38 mmol) of BD. The resulting copolymers were used for characterization without any purification.

2.3.5. Synthesis of Poly(ester-urethane) Network (Cross-Linked PBSu70-Ss30 or cPBSu70-Ss30). 
The poly(ester-urethane) network cPBSu70-Ss30 was synthesized in a way that the ratio of [OH]/[NCO] = 1.09. First, 0.495 g (0.258 mmol) of PBSu70-Ss30 oligoester with Mn = 1920 g/mol and 0.0346 g (0.25 mmol) of TMP has been dissolved in a limited quantity of DMF (80:20 wt%:wt%) at 120°C under a nitrogen flow.
atmosphere, while the mixture was stirred for a few minutes. Then, 0.338 g (0.517 mmol) of HDMI was added. After isocyanate addition, the mixture was stirred again for a few minutes and poured in a rectangular silicone mold and heated at 130 °C for 48 under vacuum in order to eliminate DMF and air bubbles.

In the extractible rate, the resulting cPBSu 70Ss30 was put in DMF for 24 h at ambient temperature. Then, the sample was filtered and dried under vacuum at 120 °C for 48 h in order to eliminate the traces of DMF. The extractible rate determined according to equation (1) was around 7.5%.

\[
\text{Extractible} = \frac{m_i - m_f}{m_f} \times 100, \quad (1)
\]

where \(m_i\) and \(m_f\) are the initial mass of matter and the final mass of dry matter, respectively.

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**Figure 1:** 1H NMR characterization of PBSu\textsubscript{70}Ss\textsubscript{30}. 1H NMR spectrum (400 MHz, DMSO-d6).
Table 2: Characterization of oligoesters: initial and final composition and molecular weight (Mn).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial (diacid)/(Ss)</th>
<th>NMR (diacid)/(Ss)$^a$</th>
<th>Mn (g·mol$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBSu$<em>{100}$Ss$</em>{50}$</td>
<td>100:0</td>
<td>100:0</td>
<td>6970</td>
</tr>
<tr>
<td>PBSu$<em>{80}$Ss$</em>{50}$</td>
<td>80:20</td>
<td>78:22</td>
<td>6789</td>
</tr>
<tr>
<td>PBSu$<em>{70}$Ss$</em>{50}$</td>
<td>70:30</td>
<td>71:29</td>
<td>9831</td>
</tr>
<tr>
<td>PBSu$<em>{60}$Ss$</em>{50}$</td>
<td>60:40</td>
<td>62:38</td>
<td>11459</td>
</tr>
<tr>
<td>PBC18$<em>{100}$Ss$</em>{50}$</td>
<td>100:0</td>
<td>100:0</td>
<td>d</td>
</tr>
<tr>
<td>PBC18$<em>{90}$Ss$</em>{50}$</td>
<td>90:10</td>
<td>88:12</td>
<td>7106</td>
</tr>
<tr>
<td>PBC18$<em>{80}$Ss$</em>{50}$</td>
<td>80:20</td>
<td>81:19</td>
<td>7652</td>
</tr>
<tr>
<td>PBC18$<em>{70}$Ss$</em>{50}$</td>
<td>70:30</td>
<td>72:28</td>
<td>8471</td>
</tr>
<tr>
<td>PBDA$<em>{100}$Ss$</em>{50}$</td>
<td>100:0</td>
<td>100:0</td>
<td>c</td>
</tr>
<tr>
<td>PBDA$<em>{90}$Ss$</em>{50}$</td>
<td>90:10</td>
<td>80:20</td>
<td>c</td>
</tr>
<tr>
<td>PBDA$<em>{80}$Ss$</em>{50}$</td>
<td>80:20</td>
<td>77:23</td>
<td>c</td>
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<tr>
<td>PBDA$<em>{70}$Ss$</em>{50}$</td>
<td>70:30</td>
<td>71:29</td>
<td>c</td>
</tr>
</tbody>
</table>

$^a$Diacid unit/sulfosuccinate unit molar ratio in oligoesters determined by $^1$H NMR. $^b$Molecular weight (Mn) determined by $^1$H NMR. $^c$End groups not detected by $^1$H NMR.

2.4. Solubility Tests. Qualitative solubility was determined by dissolving 100 mg of oligoesters in 900 mg of organic solvent under agitation at room temperature or upon heating.

2.5. Film Preparation. Films of oligoesters PBSu$_{80}$Ss$_{20}$, PBC18$_{80}$Ss$_{20}$, and PBDA$_{80}$Ss$_{20}$ were prepared by casting at room temperature from a 10% (w/v) solution in CHCl$_3$/MeOH (8/1 v/v) on silanized Petri dish. The films were cut and dried in vacuum at 50°C to constant weight.

2.6. Analytical Techniques. $^1$H NMR spectra were recorded on a Bruker Avance III 400 spectrometer. Samples were dissolved in DMSO-d$_6$ or CDCl$_3$ and analyzed at 80°C or at room temperature.

The MALDI-TOF MS spectra were recorded using 10 g/L solution of sample and in DMSO mixed with 2-(4-hydroxy-phenylazo)-benzoic acid of matrix solution (45/5 v/v) for PBSu$_{70}$Ss$_{30}$ and PBSu$_{70}$Ss$_{30}$. For PBDA$_{70}$Ss$_{30}$, the analysis was recorded using 10 g/L solution of sample in CHCl$_3$/THF (50/50 v/v) mixed with 2-(4-hydroxy-phenylazo)-benzoic acid of matrix solution (45/5 v/v).

Differential scanning calorimetry (DSC) experiments were performed with TA Instruments Q 22. The samples were cut and placed in a close hermetic aluminum capsule and were tested under the dry nitrogen condition, at a heating rate of 10°C/min. Tg was taken at the inflection point and Tm at the minimum of melting endotherms.

The hydrolytic degradation essays were performed with films of oligoesters and cPBSu$_{70}$Ss$_{30}$, after immersion in water (pH = 4.35, pH = 7.4, and pH = 11.5) at 37°C for one month, the samples were rinsed thoroughly in water and dried to constant weight. Sample weighting measurements were used to follow the rate of hydrolysis.

The oxidative degradation was carried out with films of oligoesters in a solution composed of 20 vol% H$_2$O$_2$ in combination with 0.1 M CoCl$_2$ for 15 days at 37°C [34]. Sample weighting was used to follow the rate of oxidative degradation.

3. Results and Discussion

3.1. Copolymerization. A set of novel biobased aliphatic oligoesters: series of sulfonated poly(butylene succinate) (PBSu$_{S_s}$), sulfonated poly(butylene z-octadec-9-enedioate) (PBC18$_{S_s}$), sulfonated poly(butylene dimer acid) (PBDA$_{S_s}$), and sulfonated poly(butylene-co-isosorbide succinate) (PBSu$_{S_s}$), containing various concentrations of sodiosulfosuccinate units were prepared according to a heating melt process with two successive steps: transesterification/esterification and polycondensation (Scheme 1). In the first one, the blend of monomers was mixed at a temperature raised to 190°C in a presence of catalyst: tetrabutoxytitanium (Ti(OBu)$_4$) or zinc acetate (Zn(OAc)$_2$) (Table 1). The temperature was maintained for 6 h to complete the transesterification reaction by evaporating by-products: methanol, ethanol, and water, coming from the reaction between diols and diesters (methyl and ethyl) and diacids. The second step was then performed at a higher temperature (220°C) under vacuum in order to release the excess of diol and thus displace the reaction equilibrium for getting higher molecular weight. This latter step was also catalyzed by an addition of Ti(OBu)$_4$. These conditions (limited temperature and titanium catalyst) were chosen not only for avoiding the degradation of the sulfosuccinate moieties by β-elimination and formation of the maleate or fumarate units [20] but also for facilitating the polycondensation of diacids and isosorbide which are less reactive than diester monomers and 1,4-butanediol [35, 36]. In particular, the introduction of isosorbide together with 1,4-butanediol has allowed the release of the excess of BD during the polycondensation step [1].

3.2. Characterization of Aliphatic Biobased Oligoesters. The chemical structure of oligoesters was investigated by $^1$H NMR and the MALDI-TOF MS method. As an example, the typical $^1$H NMR spectrum of PBSu$_{70}$Ss$_{30}$ is given Figure 1. It reveals the presence of the characteristic signals of the succinate proton H1 at 2.57 ppm and those of sulfonated units H4 (-CH2) and H5 (-CH-) at 2.79 and 3.70 ppm, respectively. This is different to what has been described by Ishida et al. [20, 25] who reported the presence of the -CH- signal at 6.77 ppm while the $^1$H NMR spectrum of Na-DMSS highlighted the presence of the -CH- signal at 3.70 ppm. The weak pic at 1.48 ppm is related to the 1,4-butanediol internal groups -CH2-CH2-CH2-CH2-OH. The singlets at 1.62 and 4.03 ppm are associated with H3 and H2 (-CH2-O-) protons of 1,4-butanediol internal groups -CH2-CH2-CH2-CH2-OH. The singlets at 1.62 and 4.03 ppm are associated with H3 and H2 (-CH2-O-) protons of 1,4-butanediol internal groups -CH2-CH2-CH2-CH2-OH. The singlets at 1.62 and 4.03 ppm are associated with H3 and H2 (-CH2-O-) protons of 1,4-butanediol internal groups -CH2-CH2-CH2-CH2-OH.
conformation at temperature above 160 °C did not occur in our conditions [29]. 1H NMR peak integrations allowed the quantization of succinate and sulfonated monomer units in oligoesters of the PBSu\textsubscript{x}Ss\textsubscript{y} series (equation (2)) confirming that the experimental molar fraction is close to the theoretical one (Table 2). The number average molecular weights (\(M_n\)) calculated by 1H NMR are ranged between 6970 and 11459 g mol\(^{-1}\). One can remark that the \(M_n\) slightly increases with the increase of the sulfonated unit content as already reported in the literature for poly(ethylene furoate-co-ethylene isophthalate sodiosulfonate) (PEFSI) copolyesters [17].

\[
F_{SS} = \frac{\nu_3(\nu_{5} + \nu_{4})}{\nu_3(\nu_{5} + \nu_{4}) + \nu_1/\nu_{1}} \times 100
\]

\[
F_{Su} = \frac{\nu_1(\nu_{5} + \nu_{4})}{\nu_1(\nu_{5} + \nu_{4}) + \nu_1/\nu_{1}}
\]

\[
\nu_{3}, \nu_{4}, \nu_{5}, \nu_{1}, \nu_{2}, \nu_{6}
\]
The MALDI-TOF MS spectrum of PBSu_{70}Ss_{30} oligoester is depicted in Figure 2. Five different peaks were detected and noted: \( L_{(x,y)} \), \( L'_{(x,y)} \), \( L''_{(x,y)} \), \( C_{(x)} \), and \( C''_{(x)} \) with \( L \) and \( C \) for linear and cyclic whereas \( x \) and \( y \) are succinate and sulfonated repeating units.

More precisely, \( L_{(x,y)} \) may correspond to linear oligomers containing hydroxyl end groups, as, for instance, the structure of \( L_{(3,1)} \) in Figure 3.

An increase of 172 uma corresponding to the molar mass of one butylene succinate unit leads to the \( L_{(4,1)} \) also detected in the spectrum as well as the \( L_{(5,1)} \). One can highlight that the \( L_{(5,0)} \) and the \( L_{(6,0)} \) were detected which means that a part of the oligoester chains was not sulfonated. Finally, even if the MALDI-TOF method is not quantitative, the peaks \( L_{(x,y)} \) having the highest intensity mean that their concentrations are logically higher than those of the other structures.
$L'(x, y)$ are oligoesters with $\alpha$ hydroxyl and $\omega$ (carboxylic acid) functionalized as $L'(3,1)$ in Figure 4.

As mentioned above, a gap of 172 uma is observed in Figure 2 stating the presence of $L'(4,1)$ oligoesters. However, one can assume that both oligoesters are in a less concentration than $L'(x, y)$ oligoesters because of the weak intensity of signals.

In the series of peaks, note $C_{x,y}$ was assigned to cyclic oligomers which were generated during the polycondensation reaction (Scheme 2) [37]. Finally, some other species: $L''_{(x,y)}$ and $C''_{(x,y)}$ resulting from side etherification reactions: etherification coupling between two 1,4-butandioi or one 1,4-butandioi and one hydroxyester end chain, already mentioned in the literature when 1,4-butandioi is used as comonomer [38] (Scheme 2), were highlighted in the MALDI-TOF MS spectrum. However, similar structures were not detected in the $^1$H NMR spectra probably suggesting that their concentrations are too low, below 1 mol %, to be detected.

**Figure 6:** $^1$H NMR characterization of PBDA$_{70}$SS$_{30}$ $^1$H NMR spectrum (400 MHz, CHCl$_3$-d6).
With respect to specific $^{1}$H NMR signals for the PBC1870Ss30 series (Figure 5), one can point out that the aliphatic proton H5 from the C18 units is visible at 1.29 ppm whereas those of protons in the $\alpha$ position of ethylenic proton H4 are located at 1.99 ppm, the ethylenic proton H1 being located at 5.33 ppm. The signals at 2.26 and 1.54 ppm were attributed, respectively, to H7 and H6 located in the $\alpha$ and $\beta$ position of the ester carbonyl groups integrated in fatty acid units. The difficulty to well esterify was stressed by the presence of the methoxy end.
groups (CH$_3$O-) at 3.60 ppm. However, such feature did not impact the good correspondence between the theoretical diacid C18/sulfosuccinate ratio and the experimental one (equation (3)). In addition, the level of molecular weight which ranged between 6740 and 8105 g·mol$^{-1}$ is similar to the previous series (Table 2). These oligoesters are no longer soluble in DMSO, probably because it has undergone a change over time, so the MALDI-TOF analysis was not possible.

\[ F_{\text{Ss}} = \frac{1/3(I_{\text{H}10} + I_{\text{H}9})}{1/3(I_{\text{H}10} + I_{\text{H}9}) + 1/4(I_{\text{H}7})} \times 100 \]

\[ F_{\text{Cl}8} = \frac{1/4(I_{\text{H}7})}{1/3(I_{\text{H}10} + I_{\text{H}9}) + 1/4(I_{\text{H}7})} \times 100. \]

The presence of the dimer acid units in PBDA$_{70}$Ss$_{30}$ oligoester (Figure 6) was set by the existence of characteristic $^1$H NMR peaks of the following cyclic protons: H7
(-CH-) and H6 (-CH2-) protons ascribed at 1.31 ppm and those of the methyl (-CH3) protons at 0.9 ppm. More importantly, signals at 2.31 and 1.64 ppm were attributed, respectively, to H1 and H4 protons located in the α and β position of the ester carbonyl groups confirming the integration of the dimer acid units inside the oligoester backbone. The experimental molar fractions of PBDAxSs y were determined from the following:

\[ F_{SS} = \frac{I_{H8} + I_{H9}}{I_{H8} + I_{H9} + 1/4(I_{H1})} \times 100, \]
\[ F_{DA} = \frac{1/4(I_{H1})}{I_{H8} + I_{H9} + 1/4(I_{H1})} \times 100. \]

The MALDI-TOF analysis (Figure 7) shows the presence of cyclic oligoesters C(x,y) in Figure 8.

Oligoesters with α hydroxyl and ω (ester) functionalized \( L'_{(x,y)} \) in Figure 10.

Finally, with the respect to oligoester PBISu70Ss30 (Figure 11), the isosorbide proton signals were clearly detected at 5.11 for H14 and at 5.02 for H13, H10, and H9 which were situated at 4.75 and 4.44 ppm; the signals from 3.71 to 3.83 ppm were attributed to H11 and H12 incorporated into the oligoester structures. The isosorbide end groups H11e and H12e were set at 3.30 and 3.38 ppm. H10e was situated at 4.15 ppm. The signal at 4.10 ppm was assigned for H9e protons. H14e and H13e were situated at 4.67 and 4.39 ppm, respectively. The final compositions ((diacid)/(Ss), (butandiol)/(Is)) and molar masses of oligoesters PBISu70Ss30 were not determined because of the complexity of the 1H NMR spectra. However, the MALDI-TOF spectra highlighted that all oligomers are dihydroxy functionalized and that the hydroxyl functions come in majority

\begin{align*}
L'_{(x,y)} & = \frac{I_{H8} + I_{H9}}{I_{H8} + I_{H9} + 1/4(I_{H1})} \times 100, \\
F_{DA} & = \frac{1/4(I_{H1})}{I_{H8} + I_{H9} + 1/4(I_{H1})} \times 100. 
\end{align*}

Oligoesters with α hydroxyl and ω (carboxylic acid) functionalized \( L_{(x,y)} \) in Figure 9.

\begin{align*}
L'_{(x,y)} & = \frac{I_{H8} + I_{H9}}{I_{H8} + I_{H9} + 1/4(I_{H1})} \times 100, \\
F_{DA} & = \frac{1/4(I_{H1})}{I_{H8} + I_{H9} + 1/4(I_{H1})} \times 100. 
\end{align*}

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\begin{align*}
L'_{(x,y)} & = \frac{I_{H8} + I_{H9}}{I_{H8} + I_{H9} + 1/4(I_{H1})} \times 100, \\
F_{DA} & = \frac{1/4(I_{H1})}{I_{H8} + I_{H9} + 1/4(I_{H1})} \times 100. 
\end{align*}
from the isosorbide moieties, those playing the role of end-cappers. More precisely, \( L_{(m,n,y,z)} \) are oligoesters with 1,4-butanediol end groups in Figure 13. \( L_{(m,n,y,z)} \) oligoesters with isosorbide end groups in Figure 14.

These results confirm the low reactivity of isosorbide due to the steric hindrance and the nature of hydroxyl function; here secondary alcohol knowing that the reactivity of hydroxyl functions on C2 and C5 is close even if not strictly equivalent [39].

### 3.3. Thermal Properties of Aliphatic Biobased Oligoesters

Each DSC measurement was performed with a heating rate of 10°C/min and a first heating cycle in order to reduce the presence of absorbed water molecules which could plasticized the polymer followed by a second one for evaluating the thermal characteristics. Thus, the data reported in Table 3 and Figure 15(a) shows that sulfonated poly(butylene succinate) (PBSu\(_{S_y}\)), having 0 to 20% of sulfonated units have a semicrystalline character and a glass transition temperatures increasing from –38 to –24°C with the increasing of sulfonated unit content. This is in good agreement with those ionomers containing up to 14 mol% of sulfonated units [29]. Moreover, the authors attributed the increasing of Tg to the intermolecular ionic interactions between the sulfonates units. This trend is also consistent with that of Bougarech et al. [17] who have reported on the role of sulfonated moieties which rigidify the oligoester backbone limiting the flexibility of the macromolecular chains and thus leading to higher Tg. For PBSu\(_{100S_y}\) oligoesters, DSC traces (Figure 15(b)) highlighted their semicrystalline character which clearly indicates that the aliphatic units promote the arrangement of macromolecular chains so the crystallization phenomenon occurs. The melting point decreased from 18 to 6°C with the increasing of the sulfonated content. On the other hand, both melting and recrystallization enthalpies appear to strongly depend on the ionic content (Table 3). It is noteworthy to indicate that the presence of the ionic groups reduces the regularity of macromolecular backbone giving birth to a decrease in melting temperature, and melting and recrystallization enthalpies as for the PBS ionomer [29]. Tg values of PBSu\(_{S_y}\) oligoesters were ranged from –68 to –63°C that is lower than their homologous PBSu\(_{S_y}\). Indeed, the length of the aliphatic units of the fatty acid helps the segmental rotation of macromolecular chains and thus leads to a decrease of Tg. Concerning the PBDA\(_{S_y}\), the bulky character of the cyclic units gave rise to amorphous structures (Figure 15(c)) with Tg ranging between –56 and –54°C, the effect of sulfonated units being quite limited. The incorporation of isosorbide in the oligoester structures also generated amorphous oligomers and led to the increasing of the glass transition temperatures with a value up to 12°C for the PBSu\(_{70S_y}\). This was expected because the two fused tetrahydrofuran rings tend to impart a stiffness in the macromolecular backbone as already reported with other copolysters [40].

Thermal decomposition of biobased sulfonated oligoesters was evaluated by TGA measurements under nitrogen atmosphere. Thermal gravimetrical traces from 30°C to 600°C are reported in Figure 16, and the temperatures for 5% weight loss (Td (5%)) are gathered in Table 3 to compare their thermal stabilities. First, it clearly appears that thermal stability of oligoesters decreased with the increasing of the sulfonated unit content probably because of a possible acidic character of these units. Then, the thermal degradation depends obviously on the overall composition. Thus, stability of PBSu\(_{S_y}\) oligoesters (between 268 and 260°C) was found lower compared to that of the PBC18\(_{S_y}\) and PBDA\(_{S_y}\) ones which showed stability up to 312°C and 353°C, respectively. As the trend for chain scission should be higher in polyesters having a higher number of methylene groups [41], one can suppose that the presence of double bond in C18 units and the cyclic character of HDA have limited the thermal degradation by favoring cross-linking reactions. This is not the case for PBSu\(_{S_y}\) containing isosorbide units in their macromolecular backbone which can undergo a hydration reaction at a high temperature, leading to 1,4-sorbitan formation. Thus, the thermal degradation was close to that of PBSu\(_{S_y}\) oligoesters [42].

The remaining weight of all oligoesters after the degradation at 500°C increased with the sulfonated content (Table 3). Indeed, PBSu\(_{70S_y}\), PBC18\(_{70S_y}\), PBDA\(_{70S_y}\) and PBSu\(_{70S_y}\) show a remaining weight value much greater than their homopolysters. The remaining weight of PBSu\(_{S_y}\) goes from 2.7% to 24%. Residual weight depends also on the chemical structure of oligoesters. In fact, oligoesters based on C18 and HAD presented a lower

### Table 3: Thermal properties of biobased oligoesters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Td_(5%) (°C)</th>
<th>RW (%)</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>ΔHm (Jg(^{-1}))</th>
<th>ΔHr (Jg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBSu(_{100S_y})</td>
<td>277</td>
<td>2.7</td>
<td>–38</td>
<td>114</td>
<td>111</td>
<td>68</td>
</tr>
<tr>
<td>PBSu(_{60S_y})</td>
<td>268</td>
<td>16.3</td>
<td>–33</td>
<td>99</td>
<td>45</td>
<td>–</td>
</tr>
<tr>
<td>PBSu(_{50S_y})</td>
<td>263</td>
<td>17.8</td>
<td>–29</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PBSu(_{40S_y})</td>
<td>260</td>
<td>24.2</td>
<td>–24</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PBSu(_{30S_y})</td>
<td>298</td>
<td>10.8</td>
<td>–64</td>
<td>8</td>
<td>15</td>
<td>22</td>
</tr>
<tr>
<td>PBSu(_{20S_y})</td>
<td>289</td>
<td>10</td>
<td>–63</td>
<td>6</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>PBSu(_{10S_y})</td>
<td>384</td>
<td>0.5</td>
<td>–56</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PBSu(_{10S_y})</td>
<td>353</td>
<td>2.1</td>
<td>–55</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PBSu(_{20S_y})</td>
<td>335</td>
<td>3.3</td>
<td>–54</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PBSu(_{30S_y})</td>
<td>288</td>
<td>6.9</td>
<td>–55</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PBSu(_{40S_y})</td>
<td>308</td>
<td>4</td>
<td>–7</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PBSu(_{50S_y})</td>
<td>286</td>
<td>13</td>
<td>–2</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PBSu(_{60S_y})</td>
<td>269</td>
<td>16</td>
<td>9</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PBSu(_{70S_y})</td>
<td>227</td>
<td>24</td>
<td>12</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

\(^{*}\)Degradation temperature at which a 5% weight loss was observed in TGA.
\(^{\text{b}}\)Remaining weight at 500°C. \(^{\text{c}}\)Glass transition temperature taken as the inflection point of the DSC traces. \(^{\text{d}}\)Melting temperatures were registered by DSC. \(^{\text{e}}\)Melting enthalpies were registered by DSC. \(^{\text{f}}\)Crystallization enthalpies were registered by DSC.
residue value than PBSuSs. For PBISuSs, the remaining weight slightly increased compared to their homologous PBSuSs.

3.4. Degradation in Aqueous Solutions of Aliphatic Biobased Oligoesters. The solubility of oligoesters was first tested at room temperature and/or upon heating in water and organic solvents having various polarities. Most of the sulfonated oligoesters were not soluble in water. Thus, in the PBSuSs series, only the PBSu60Ss40 with the highest content of sulfonate group was partially soluble in water and all oligoesters from the PBISuSs series were hydrophilic which confirms the hydrophilic character of the isosorbide units already highlighted in the literature. Indeed, isosorbide was used for preparing hydrotropes [43]. Moreover, these results confirm that the macromolecular design of water-soluble ionic polyesters or oligoesters needs at least two hydrophilic monomers [11].

To assess their sensitivity to hydrolysis in acidic, neutral, and alkaline media, films of PBSu60Ss20, PBC1880Ss20 and PBDA80Ss20 oligoesters were soaked in water. The temperature of bath was fixed at 37°C over a period of four weeks. The data presented in Figure 17 show that the remaining weight (RW%) of PBSu80Ss20 was decreased both in acid and basic media, 76 and 83, respectively. Contrarily, the degradation at pH 7.4 was minor with a RW% of 94. These values should be compared with those reported by Bautista et al. [29] in the case of high molecular weight polyester having a close chemical composition (PBSu85Ss15). Data are different within a particular higher degradation level at basic pH (RW% of 60 instead of 83) and at neutral pH (RW% of 85 instead of 94). This might be caused by difference in the

Figure 15: DSC curves of biobased oligoesters: (a) DSC curves of PBSuSs, (b) DSC curves of PBC18Ss, (c) DSC curves of PBDA Ss, and (d) DSC curves of PBISuSs.
hydrolysis protocol and/or by the molar mass effect. Nevertheless, our results are expected because ester bonds are generally more sensible to hydrolysis at extreme pH [44].

The hydrolytic degradation of oligoesters based on C18 was high in basic conditions. However, in neutral conditions, hydrolytic degradation stayed higher than in acidic media. The $^1$H NMR analysis of the degraded sample in acidic media logically revealed the presence of acid end groups at 12 ppm, proving the cleavage of the macromolecular backbone by hydrolysis of ester functions. In addition, a residual resonance with very low intensities was also detected at 5.31 ppm and attributed to ethylenic protons. Thus, the $^1$H NMR spectra suggested that in acid conditions, the ethylenic double bonds were affected by migration in order to form carbocation located at the 4- or 5-position on a fatty acid backbone. Probably, an intramolecular cyclization of a fatty acid carboxyl group with carbocations took place to form γ- and δ-stearolactone [45] because of the presence of novel peaks at 4.62 ppm (Figure 18). The mechanism of the formation of γ- and δ-stearolactone is detailed in Scheme 3 [46].

Finally, oligoester based on dimer acid HDA (PBDA$_{80}$S$_{20}$) remained as it is with nonvariation of RW% even after four weeks in water, whatever the pH. These data clearly illustrate the protective role of the dimer acid which hampers the ester accessibility by water molecules due to its hydrophobic character.

PB$_{Su}$$_{100}$S$_{y}$, PB$_{C}$18$_{x}$S$_{y}$, and PBDA$_{x}$S$_{y}$ films underwent an oxidative degradation for 15 days at 37°C in two solutions composed of (i) 30 vol% H$_2$O$_2$ and (ii) a combination of 20 vol% H$_2$O$_2$ and 0.1 M CoCl$_2$, respectively. The data presented in Table 4 show that practically, films of PBDA$_{80}$S$_{20}$ were very stable in both oxidative solutions which was expected because of the hydrophobic character of that oligoester. Contrarily, a fall in sample weight took place for PB$_{Su}$$_{80}$S$_{20}$ and PB$_{C}$18$_{80}$S$_{20}$ in a solution

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure16.png}
\caption{TGA curves of biobased oligoesters: (a) TGA curves of PB$_{Su}$$_{x}$S$_{y}$, (b) TGA curves of PB$_{C}$18$_{x}$S$_{y}$, (c) TGA curves PBDA$_{x}$S$_{y}$, and (d) TGA curves of PB$_{Su}$$_{x}$S$_{y}$.}
\end{figure}
composed of 30 vol% of H$_2$O$_2$, which resulted in reduction of 36% and 74% of the initial weight of the sample, respectively. In that case, one can assume that macromolecular chain’s scissions occurred concomitantly via hydrolysis and oxidative reactions. In H$_2$O$_2$/CoCl$_2$ solution, the remaining weight was close to 100 wt% (films PBSu$_{80}$S$_{20}$ and PBC18$_{80}$S$_{20}$ attained nearly 94% and 96%, respectively) suggesting that production of reactive hydroxyl radicals by the oxidation reaction may lead to cross-linking because in the same pH, one can observe a higher degradation [34].

3.5. Toward the Preparation of Poly(ester-urethane) Network. The preparation of sulfonated aliphatic oligoesters $\alpha$ and $\omega$ hydroxyl functionalized represents an opportunity to develop thermosets that are biosourced and have tunable properties [47]. Thus, a poly(ester-urethane) thermoset (cPBSu$_{70}$S$_{30}$) was performed by reacting together the oligoester PBSu$_{70}$S$_{30}$ and 4,4-methylenebis(cyclohexyl isocyanate) (HMDI) in a presence of trimethylolpropane chosen as the cross-linker. The quantity of reagent was calculated in order to have a stoichiometry OH/NCO close to one. After blending, the components were cured in a silicon mold at 130°C under vacuum for 48 h. Such conditions were chosen in order to facilitate the evaporation of the DMF previously added to ensure the miscibility between the reagents. The resulting material was insoluble in DMF, and the formation of network structures can be assumed because the extractible rate was 7.5 wt%. In addition, the glass transition temperature of the cPBSu$_{70}$S$_{30}$ was much higher compared to the PBSu$_{70}$S$_{30}$.
oligoester, 53°C and −29, respectively (Table 3). That increase of Tg is obviously due to the presence of the urethane linkage together with the tridimensional cross-linked structures which can increase the rigidity of the macro-molecule backbone [48, 49]. The hydrolytic degradability of that cross-linked material was also determined in water at various pH and at 37°C and were found in the same range as a non-cross-linking material. In this case, cPBSu70Ss30 is more degradable in acid and alkaline than neutral media because of the presence of ester bonds which are more sensible to hydrolysis in acid and alkaline conditions.

4. Conclusion

A series of biobased oligoesters containing up to 30% of sulfonated units, namely, sodium sulfonate succinate, were successfully prepared by melt polycondensation reaction using biobased monomers including isosorbide,
hydrogenated dimer acid, and C18 diacid (1,18-octadecanedi-9-enedioic acid). The structures of the resulting oligoesters were studied by 1H NMR and their regular structures were evidenced. Thus, the MALDI-TOF MS analysis showed the presence of expected linear species but also cyclic species resulting from cyclisation reactions commonly observed in polycondensation. It was also highlighted that end groups are in majority hydroxyl but that acid functions can also be detected. The study of the thermal properties clearly confirms the role of the oligoester compositions. Thus, a high content of sulfonate unit as well as bulky units such as isosorbide and hydrogenated dimer acid leads to amorphous polymers whereas oligoesters containing a low level of sulfonated units and long alkyl chains are semicrystalline. This study also clearly underlines that water solubility is only achieved with oligoesters having both sulfonated and isosorbide units or very high content of sulfonate moieties (>30 mol%). The degradation in aqueous solution films of oligoesters was also correlated with the composition, the most hydrophobic oligoester being more stable. Finally, a thermoset was prepared using sulfonated oligoesters, opening the way to prepare biobased poly(ester-urethane) materials having tunable properties.

**Data Availability**

The figures and schemes used to support the findings of this study are included within the article.

**Conflicts of Interest**

The authors confirm that this article content has no conflict of interest.
Acknowledgments
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Supplementary Materials
This is the 1H NMR spectrum of each series (SI.1-10) and the FT-IR spectra of prepared polyesters (SI.11).

( Supplementary Materials)

References


