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# Silylated and germylated lineal polyesters obtained from a fatty alcohol, Undec-10-en-1-ol

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## *ABSTRACT*

Novel metaled fatty polyesters were prepared using polytransesterification reactions between dimethyl terephthalate (DMT) and different fatty metaled (Si/Ge) alcohol obtained from the undec-10-en-1-ol. The corresponding yields were excellent and the structure of the polyesters were determined by spectroscopic methods. Considering one hour of polymerization, the polymers exhibited acceptable molecular weights. The thermogravimetric analysis showed that these polyesters were more stable than their corresponding monomers and presented thermal degradation above 400°C.

Keywords: *Polyesters, fatty alcohol, polytransesterification, thermal stability.*

## INTRODUCTION

The search of new materials, able to exhibit many different properties, is of a very attractive interest nowadays in different fields of applications such as electronic, energy, construction, medical and pharmaceutic devices [1-14]. As known, the use of polymers to prepare novel materials, is currently investigated, because the monomers involved in the polymer synthesis, are able to transfer their own properties to the polymeric structure [2,4,5,15-22].

Due to contamination problem in the world, the investigation in the search on new polymeric materials friendly with the environment is increasing drastically [1,2,4,6,7,12,13,18,23-27]. Among numerous solutions described by the researchers, the chemical transformation of compounds obtained from biomass [3,4,28-31] seems to represent a very attractive alternative in order to obtain monomer products able to form the most common industrial polymers, for example like polyesters, polyamides or polyurethanes REF. For the chemical industries, this strategy should also offer a very important solution in reducing or eliminating the use of petro-chemical derivatives, responsible of the major planet contamination [3,4,28-31].

Considering this context, fatty compounds [24,32-39] are considered as an important raw material. Because of its physical properties and the presence of functional organic groups, the fatty compounds can be transformed chemically and converted in many products, showing applications in different fields of the industry [24,32-39]. As known [31], the fatty compounds are present in natural oil, belonging to an important category of biomass.

Our group investigation was interested during many years in the use of 10-undeneate methyl to incorporate polymeric system [32,33,38,40-44]. This fatty ester, obtained from castor oil, present ethylenic terminal group and methyl ester function, could be transformed chemically in monomer monomers able to polymerize forming polyesters [32,33,38,40-44]. The main reactions used in our laboratory were hydrosilation and

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hydrogermylation, which allowed to link units of 10-undeneate methyl, through olefin functions [32, 33,38,40-44].

Once formed these monomers, the free methyl metalled esters present in the structure could be polymerized, through polytransesterification, with known diol monomers (polyethylenglicols PEGs and polytetramenthylenglicol PTMOs), leading to the formation of a new class of polyesters [32,33,38,40,41]. Thereby, in one hand, linear polyesters [32,38] were obtained with excellent yields and high molecular weight. In the other hand, these polymers showed very attractive properties as very high thermal stability and amphiphilic behaviour [32,38].

In this publication, we describe the synthesis and characterization of new polyesters using distinct monomers. From, a fatty alcohol, 10-unden-1-ol, it was reported reactions of hydrosililation and hydrogermylation, leading to the formation of fatty metalled diol [43,45]. Dimethyl terephthalate DMT is a very known monomer used in the industry for the preparation of polyester presenting elastomeric properties [46,47]. The polytransesterification between the fatty metalled diol mentioned previously and DMT leads to new polymeric structures and their characterizations are discussed in this paper.

## EXPERIMENTAL SECTION

### Materials

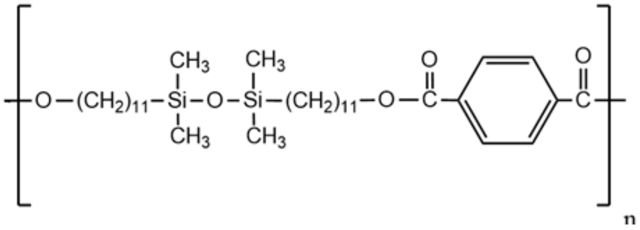
All experiments were carried out under a vacuum ramp and under an argon atmosphere using schlenck tubes. All reactants come from Aldrich and were used without additional purification. The germylated and sililated fatty alcohol were synthesized in the laboratory following the procedures described in the literature [43,45]. Catalysts are used at 1 mol% relative to the reactive.

### Characterization techniques

The fatty polyesters obtained in this investigation were characterized by FT-IR using on a NICOLET FT-IR spectrometer, model Magna 550, and analyzing in the mid-infrared range (4000 to 400 cm$^{-1}$). In addition, structural analyzes determined by nuclear magnetic resonance RMN were carried out in a Bruker ascend-400 MHz equipment, using deuterated chloroform. Thermogravimetry analyzes (TGA) were carried out with the aim to determine the decomposition temperature, and evaluate the thermal stability of the novel polyesters. The equipment used for such analysis is a TG 209 F1 thermobalance from the NETZSCH IRIS brand, and the analyzes were carried out in a nitrogen atmosphere with a temperature range from 25°C to 500°C, and an increment of 10°C/min.

The determination of the molecular weight Mw and Mn was established through a Perkin Elmer 200 series HPLC equipment, calibrated with standard samples and using tetrahydrofuran THF as effluent. An Ubbelohde viscometer was employed to measure the intrinsic viscosity [η] of the polyesters at 25°C.

**Figure 1.** Structure of the polyester **1**.



### Synthesis of the polyester 1

A mixture of 1,3-bis(11-hydroxyundecyl) tetramethyldisiloxane (0.50 g, 1.05 mmol, compound a) and dimethyl terephthalate ( 0.22g, 1.13 mmol, compound DMT) was warmed and stirred until 200°C in presence of the catalyst Ti(OBu)$_4$ (1 mol% relative to the reactive) and without any solvent. Once reached 200°C, the mixture was submitted to a low pressure (0.3 mmHg) during one hour at the same temperature. After cooling at room temperature, 0.53 g of yellow viscous liquid was obtained and identified to **1** (yield of 79%).

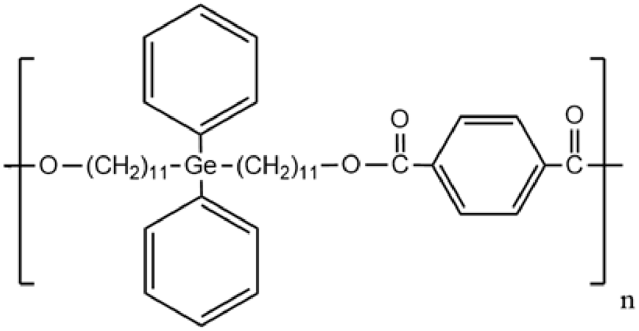
FT-IR (KBr) cm$^{-1}$: 1724 (C=O)

RMN 1H (CDCl3) (300.13 mHz): δ (ppm) = 0.06 (s. 12H, (CH$_3$-Si); 0.52 (t, $^3$JHH = 7.4 Hz, 4H, CH2-Si); 1.39 (s.I, 32H, (CH$_2$)$_7$); 1.78-1.83 (m, 4H, COOCH$_2$-CH$_2$); 4.36 (t, 3JHH= 6.7 Hz, 4H, COOCH$_2$); 8.12 (s, 4H, C$_6$H$_4$).

RMN 13C (CDCl3) (75.45 mHz): δ (ppm) = 0.42 (CH$_3$-Si); 18.44 (CH$_2$-Si); 23.32, 26.05, 28.70, 29.34, 29.43, 29.58, 29.62, 29.67 ((CH$_2$)$_8$); 33.42 (COOOCH$_2$-CH$_2$); 65.62 (COOCH$_2$); 129.50 (Co, Cm); 134.21 (Cipso), 165.93 (CO).

RMN $^{29}$Si (CDCl3) (79.49 mHz): δ (ppm) = 7.28.

**Figure 2.** Structure of the polyester **2**.



### Synthesis of the polyester 2

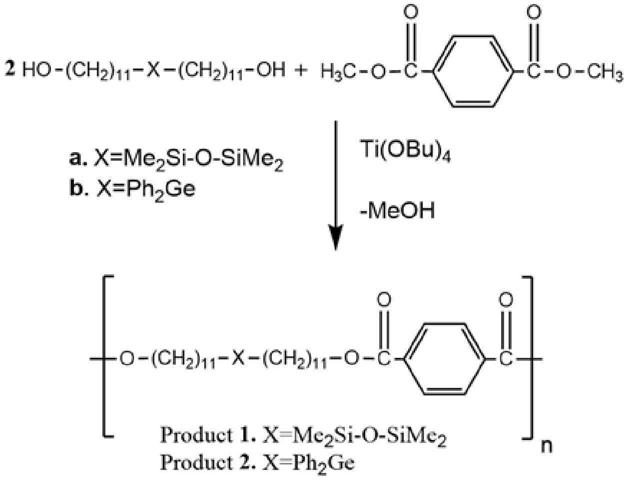
A same procedure, which was described previously, was applied to obtain the polyester **2**. The polytransterification between the bis(11-hydroxyundecyl)diphenylgermane (0.50 g, 0.88 mmol, compound, **b**) and dimethyl terephthalate (0.18g, 0.93 mmol, compound DMT) lead to 0.53 g of a transparent viscous liquid, identified to **2** (yield of 82%).

FT-IR (KBr) cm$^{-1}$: 1722 (C=O)

RMN $^1$H (CDCl3) (300.13 mHz): δ (ppm) = 1.15 (s.1, 32H, $(CH_2)_8$); 1.32-1.35 (m, 4H, CH2-Ge); 1.65-1.70 (m, 4H, $COOCH_2$-$CH_2$); 4.24 (t, $^3$JHH= 6.5 Hz, 4H, $COOCH_2$); 7.23-7.36 (m, 10H, $C_6H_5$); 8.01 (s, $_4$H, $C_6H_4$).

RMN $^{13}$C (CDCl3) (75.45 mHz): δ (ppm) = 13.35 ($CH_2$-Ge); 25.02, 26.08, 28.73, 29.22, 29.35, 29.58, 29.61, 29.63 ($(CH_2)_8$-$CH_2$); 33.51 (COOOCH$_2$-CH$_2$); 65.64 (COOCH2); 128.01 ($C_m$); 128.47 ($C_p$); 129.54 (Co, C, (C6H5)); 134.25 ($C_{ipso}$ ($C_6H_5$)), 134.49 ($C_0$); 138.93 ($C_{ipso}$); 165.93 (CO).

**Figure 3.** Chemical equation describing the preparation of the polyesters **1** and **2**.

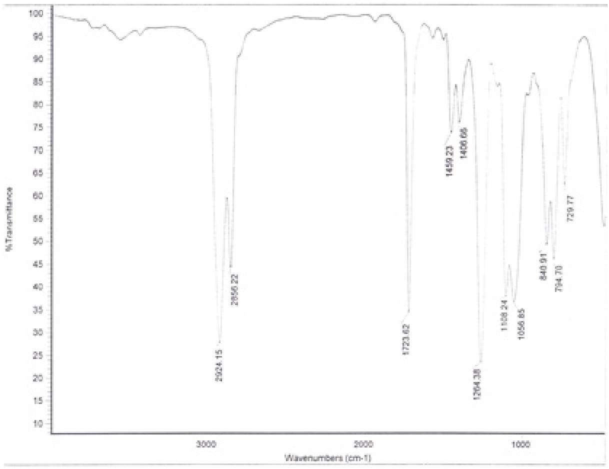


## RESULTS AND DISCUSSIONS

The synthesis of the novel linear polyesters was performed trough polytransesterification reaction as indicated in the Figure 1. The procedure employed in these preparations contemplates the same chemical steps and condition reactions described previously [32,38,40]. The polymerization was ended after one hour of reaction under vacuum (0.5 mmHg). The physical aspect of the polymer 1, obtained from the silylated fatty alcohol, was a yellow viscous liquid whereas, for the polymer 2, prepared from the germylated fatty alcohol, a transparent viscous liquid was obtained. The yields of both polyesters were excellent, above 80%, and this result was mostly explained by the non-use of solvent during the polymerization.

The characterization of the polyester **1** and **2**, by FT-IR spectroscopy, indicated mainly the presence of free carbonyl group around 1720 cm$^{-1}$, as seen in the Table 1. This analysis was very important to carry out, in order to dismiss any interaction between metal/carbonyl group and make sure that the polyesters exhibited linear structure. The FT-IR spectra of **1** is indicated in the figure 4, as an example.

**Figure 4.** FT-IR spectra of **1**.



In the $^1$H RMN spectra, we observed on the one hand, the disappearance of the signals characteristic of the terminal groups of different reagents, namely the CH2-OH signals of organometallic diols and the methoxyl group of DMT. On the other hand, we notet the appearance of a triplet for polyesters **1** and **2** around 4.24 and 4.36 ppm respectively. In the $^{13}$C RMN spectra, we were also able to verify the disappearance of the characteristic signals of the initial precursors: methoxy O-$CH_3$ and the CH2-OH group. The same analysis revealed the existence of a signal between 65.62 and 65.64 ppm for polyesters 1 and 2 corresponding to the COOCH2 group. This indicates that the condensation reactions have indeed taken place and are quantitative. In addition, we noticed that the characteristic signals of the organometallic fragments ($Me_2Si$ and $Ph_2Ge$) did not undergo any variation compared to the starting compounds, which means the absence of interaction between the ester groups and the metal in this type of polyesters as stated in FT-IR spectroscopy.

The carbonyl of the ester function of these polyesters In the $^1$H RMN spectra, we observed on the one hand, the disappearance of the signals characteristic of the terminal groups of different reagents, namely the CH2-OH signals of organometallic diols and the methoxyl group of DMT. On the other hand, we notet the appearance of a triplet for polyesters **1** and **2** around 4.24 and 4.36 ppm respectively. In the $^{13}$C RMN spectra, we were also able to verify the disappearance of the characteristic signals of the initial precursors: methoxy O-$CH_3$ and the CH2-OH group.

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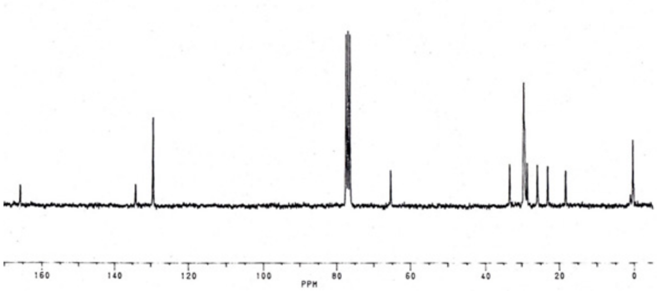
**Table 1.** RMN and FT-IR Spectroscopic data of the polyester **1** and **2**.

| | RMN $^1$H | RMN $^{13}$C | RMN $^{29}$Si | FT-IR | | | |
|---|---|---|---|---|---|---|---|
| Compounds | $CH_2$-E | $COOCH_2$ | $CH_2$-E | $COOCH_2$ | CO | δ (Si) | ν (CO) |
| 1 | 0.52 | 4.36 | 18.44 | 65.62 | 165.93 | 7.28 | 1724 |
| 2 | 1.33 | 4.24 | 13.35 | 65.64 | 165.93 | | 1722 |

The carbonyl of the ester function of these polyesters **1** and **2** was observed around 165 ppm. The $^{29}$Si NMR spectra of the silicon polyester **1** showed the presence of signal at 7.28 ppm which is very close to this recorded for the starting silicon fatty diol. This shows, once again, the absence of interaction between silicon and the oxygen of neighboring chains. The $^{13}$C RMN spectra of **1** was shown in the figure 5, as example.was observed around 165 ppm. The $^{29}$Si NMR spectra of the silicon polyester **1** showed the presence of signal at 7.28 ppm which is very close to this recorded for the starting silicon fatty diol. This shows, once again, the absence of interaction between silicon and the oxygen of neighboring chains. The $^{13}$C RMN spectra of 1 was shown in the Figure 5, as example.

**Figure 5.** $^{13}$C RMN spectra of **1**.



Molecular weights Mw and Mn of the polyesters **1** and **2** were estimated by gel permeation chromatography and shown in the Table 2. The germylated polyester **2** presented the highest molecular weight compared to its silicon analogue **1**. This can also be explained by the miscibility of the reagents. Indeed, Dimethyl terephthalate DMT, which displays a hydrophilic character, is in this case more miscible with the germylated diol with a more marked hydrophilic character than the silicon diol.

Furthermore, the presence of aromatic groups both in the germylated diol and in the dimethyl terephthalate can promote their miscibility by a "stacking" effect. Similar results were obtained previously [32], indicating that the increase of miscibility between monomers in polymerization free of solvents allows to enhance the molecular weights. Besides, for the polyesters **1** and **2**, we obtained viscosity values of 0.30 and 0.52 dl.g-1 respectively (Table 2), which are average values in agreement with the results given by chromatographic analysis (SEC).

Thermogravimetry analyzes (TGA) were carried out on the monomers **a**, **b**, DMT, polyesters **1** and **2**, in order to study and compare the thermal properties. Their respective thermal decomposition profiles are shown in the Figure 6. The monomers as well the corresponding polyesters, present a unique mass loss as observed in the figure 6. From these graphs, the thermogravimetric data T50, which corresponds to the temperature at which a polymer loses 50% of its molar mass, were determined and are reported in the table 3. High thermal stabilities, above 390°C, were observed for the polyesters, being the germylated polymer the most stable.

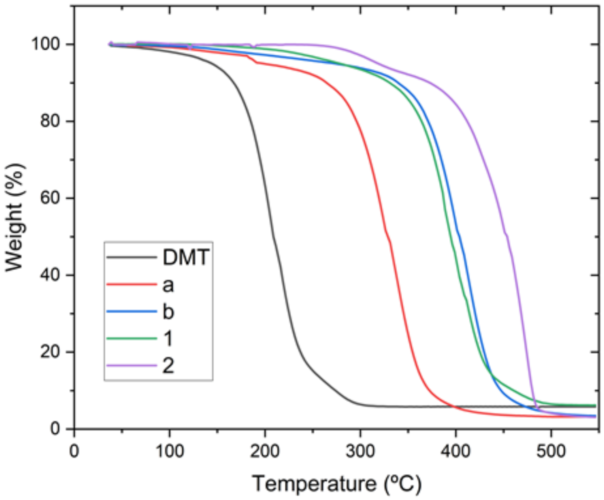
**Table 2.** Weight Average Molecular Weight (Mw), Number Average Molecular Weight (Mn), and Intrinsic Viscosity ([η]) for **1** and **2**.

| Polyesters | Mw (g/mol) | Mn (g/mol) | [η] (dL/g) |
|---|---|---|---|
| 1 | 10951 | 5467 | 0.30 |
| 2 | 25029 | 11116 | 0.52 |

**Table 3.** Weight Average Molecular Weight (Mw), Number Average Molecular Weight (Mn), and Intrinsic Viscosity ([η]) for **1** and **2**.

| | Compounds | T50 (°C) |
|---|---|---|
| monomer | DMT | 208 |
| | a | 325 |
| | b | 400 |
| Polyester | 1 | 393 |
| | 2 | 447 |

**Figure 6.** Thermogravimetric profiles of the monomers **a**, **b**, **DMT** and the polyesters **1** and **2**.



The higher molecular weight and the higher phenyl group ratio of 2 could be explained this result. Compared to their respective monomers, both polyesters showed thermal degradations at higher temperatures.

Once achieved the thermal degradation, residual mass is present for both polyesters. In the case of the silylated polymer 1, inorganic silica and silicon oxycarbides were formed after a complete thermal degradation of Si-C and C-C bonds [32,38,40] around 440°C. The germylated polymer 2 ended its thermal degradation around 490°C through a mineralization of germanium derivatives [32,33].

## CONCLUSION

The investigation described in this paper delivered very attractive results concerning the preparation of a novel molecular structure polyester, based on the use of fatty metaled alcohol. As indicated in this paper, the procedures of the synthesis are easy to carry out, with excellent yields, and are comparable to those used in the chemical industry. This parameter is very important to be considered, thinking in future applications. The spectroscopic characterization showed clearly that any side reactions occurred and only one polymer structure was obtained. The associations between the monomers was only done through a polytransesterification reaction between hydroxyl group of the fatty metaled alcohol and methyl ester group of dimethyl terephthalate.

The molecular weight obtained for these polyesters are not so high, however this is directly related with a low time polymerization applied in our experiments. Shortly, change in experimental conditions like time polymerization and temperature will be carried out, in order to improve the molecular weight. The thermal properties of these polymers are very remarkable, displaying a thermal stability above 400°C and surely can be improved once optimized the conditions reaction. This work concerning the change in experimental conditions is currently in progress. Finally, it is important to underline that, thanks to the characteristics mentioned previously, these new metaled fatty polyesters could potentially be used as biomaterials, and applied in wide areas, as for example electronic devices, thermoplastics and fibers.

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## CONFLICTS OF INTEREST

The authors declare no conflict of interest

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