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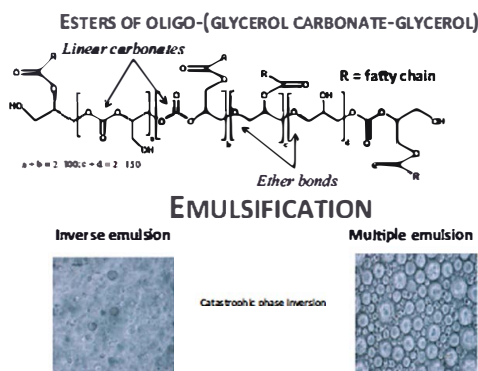
Esters of oligo-(glycerol carbonate-glycerol): New biobased oligomeric surfactants

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GRAPHICAL ABSTRACT



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ABSTRACT

Glycerol carbonate is one of the most potentially multifunction glycerol derived compounds. Glycerol is an important by product of the oleochemical industry. The oligomerization of glycerol carbonate, assisted by the glycerol, results in the production of polyhydroxylated oligomers rich in linear carbonate groups. The polar moieties of these oligomers ($M_w < 1000$ Da) were supplied by glycerol and glycerol carbonate rather than ethylene oxide as in most commercial surfactants. The insertion of linear carbonate groups into the glycerol based skeleton rendered the oligomers amphiphilic, resulting in a decrease in air/water surface tension to 57 mN/m. We improved the physical and chemical properties of the oligomers, by altering the type of acylation reaction and the nature of the acyl donor. The polar head is constituted of homo oligomers and hetero oligomers. Homo oligomers are oligoglycerol and/or oligocarbonate, hetero oligomers are oligo(glycerol glycerol carbonate). Coprah oligoesters had the best surfactant properties ($CMC < 1$ mg/mL, $\pi_{cmc} < 30$ mN/m), outperforming molecules of fossil origin, such as ethylene glycol monododecyl ether, glycol ethers and fatty acid esters of sorbitan polyethoxylates. The self assembling properties of oligocarbonate esters were highlighted by their ability to stabilize inverse and multiple emulsions. The oligo (glycerol carbonate glycerol ether) with relatively low molecular weights showed properties of relatively high molecular weight molecules, and constitute a viable "green" alternative to ethoxylated surfactants.

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1. Introduction

Plant oils are long chain fatty acid esters that can be obtained from agricultural crops. They may be saturated or unsaturated, and may bear functional groups, such as hydroxyl groups, epoxide groups or glycerol. They are used in many applications "as is", or as "supports" or additives in complex use formulations. However, technological developments have made it possible to transform plant oils directly into a multitude of "biological" industrial products, such as biosolvents, biodetergents, biolubricants, bioplastics, biomaterials, and biosurfactants [1].

Molecules synthesized chemically from plant oils, glycerol and fatty acids are considered to be biomolecules. We focus here on amphiphilic molecules with polar moieties based on glycerol and lipophilic moieties based on fatty acids. The market for non ionic amphiphilic molecules is dominated by polyethoxylated products with hydrophilic moieties composed of a polyethylene glycol chain generated by the polycondensation of ethylene oxide onto a hydroxyl or amine group. Molecules produced in this way are considered to be of fossil origin. The lipophilic moiety is introduced by the esterification of a renewable fatty acid with the OH group from the tip of a polyethylene oxide chain.

There is considerable interest in possible alternatives to ethoxylated surfactants, due to the widespread use of non ionic surfactants and their discharge into the environment [2]. Surfactant solutions containing short polyoxyethylene chains have been shown to be highly toxic, and may therefore have a major impact on aquatic life due to the discharge of detergents into the environment [3,4]. These data provide valuable information for the selection of surfactants for critical applications in industry and they also highlight the importance of removing detergent like substances from wastewater before its discharge into aquatic systems. The recent reinforcement of environmental legislation in Europe, particularly as concerns the protection of aquatic environments (Eco label, Blue Angel, Wasse Gefahrdung Klasse classification, etc.), air quality (Kyoto Protocol, etc.); and toxicological protection (Biocide guideline, European REACH project, etc.), has done much to refocus research on the goal of replacing raw materials extracted from fossil fuels with organic products from forestry and agriculture. These so called "agromolecules" are considered to be particularly advantageous, as they are natural, nontoxic, biodegradable and renewable, with a balanced carbon footprint. Considerable efforts are currently being made to promote the use of agromolecules in developed countries, in which there is a clear industrial market for alternatives to fossil fuels and their derivatives.

We decided to use glycerol for this work because it is an organic compound produced in large amounts during industrial scale transformations of oils and fats into soaps, fatty acids, fatty esters and, in particular, fatty acid methyl esters (used in the development of biofuels). Glycerol production levels are expected to reach 37 billion gallons by 2016, corresponding to about 4 billion gallons of crude glycerol [5]. Glycerol thus has the potential to become an available and sustainable raw material, due to its low cost and intrinsic properties (with high polarity and solvent properties: $\epsilon = 78.50$, $\mu = 1.67$ D, relative polarity = 0.812). The other major reason for choosing to use glycerol was that its reactivity can be increased by transformation into glycerol carbonate by heterocyclization [6]. The higher added value of glycerol carbonate, due to its remarkable properties as a solvent, has been highlighted in applications such as lithium batteries and NMR [7-9]. Glycerol carbonate has a high boiling point (351 °C), a low melting point (66.7 °C), and high dipolar moment ($\mu = 5.4$ D) and dielectric constant values ($\epsilon = 109.7$) relative to many other organic compounds. It is also nontoxic and can be used as a polymer stabilizer and as a synthetic intermediate in organic reactions [10-15], such as ester

ifications, transesterifications and carbamoylations. Glycerol carbonate can also be used as a formulation ingredient in many applications in the cosmetics, pharmaceutical and food industries. It can be transformed into oligomers and/or co oligomers. These polyhydroxylated compounds having many desirable physical and chemical properties, including multifunctionality, low ecotoxicity, high biodegradability, thermal stability, high levels of resistance to oxidation and hydrolysis [16], a high wetting power, rheological and hydrophilic properties, rendering these molecules water soluble. Stjernedahl and Holmberg [17] reported that carbonated surfactants are classified as biodegradable molecules, much like esters, for example.

The aim of this work is to study surfactants obtained from glycerol carbonate, and its esters. The physico chemical properties of partial and total esters of oligomers of glycerol carbonate were evaluated and compared with those of widely used surfactants, such as esters of ethoxylated sorbitans, polyethylene monoethers and polyglycerol esters. The ability of these molecules to stabilize different emulsified systems was evaluated.

2. Materials and methods

2.1. Materials

Glycerol (99.0% pure) and urea were obtained from Sigma Aldrich (Saint Quentin Fallavier, France), zinc sulfate monohydrate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) was obtained from Riedel de Haën and sodium methylate (NaOMe) was obtained from Fluka. Copra oil (Condat) and high oleic sunflower oil (HOSO, Arterris) are lipids of plant origin. The copra oil used contained 5% capric acid, 45% lauric acid, 20% myristic acid, 4% stearic acid, 8% oleic acid and 2% linoleic acid. The HOSO contained 4% palmitic acid, 3% stearic acid, 80% oleic acid and 10% linoleic acid. Copra oil is a source of lauric acid and HOSO is a source of oleic acid. The fatty acid composition of the oils was determined by gas chromatography [18].

The hydroxyl value was determined in accordance with the NFT 60 123 standard and is expressed as the number of available OH bonds.

High performance liquid chromatography (HPLC) analysis was carried out with a CarH column (30 cm long, i.d. 7.8 mm, Touzard and Matignon) fitted with a CarH jacket, at 35 °C [19]. Samples were eluted with deionized water acidified with 0.04 N sulfuric acid. The flow rate of the mobile phase was set to 0.8 mL/min, and the compounds at the outlet were detected by refractometry (I.C.S, Ri detector 8110). Pic 3 software was used for data acquisition.

Emulsions were prepared with a commercial rapeseed oil (Casino group) and ultrapure water obtained by the passage of deionized water through a Millipore filtration system.

2.2. Structural analysis

Electrospray ionization time of flight (ESI ToF) analysis was performed at the SCA CNRS Solaize central analysis service, with a Waters LC ToF mass spectrometer and an internal reference. Samples were diluted in a 50/50 (v/v) mixture of water and acetonitrile.

^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Advance[®] 300 MHz instrument with tetramethylsilane (TMS) as an internal standard. Samples were analyzed in D_2O .

Fourier transform infrared (FTIR) spectra were recorded by transmission on a Bruker Tensor 27 apparatus equipped with a DTGS detector, using a ZnSe flow cell. Samples were solubilized in propan 1 ol before analysis.

2.3. Physicochemical characterization

Kinematic viscosity: Viscosity, expressed in centistokes (cSt), was measured with a Canon Fenske viscosimeter, at 40 °C (NFT 60 100, NFT 60 136 and ASTM 445 96 standards).

A Nikon Eclipse E600 light microscope (Nikon Corporation, Japan) was used. Images were acquired with a high resolution, low noise Nikon DXM 1200 color CCD camera and analyzed with LUCIA G version 4.8 software.

Emulsions were prepared by premixing surfactant in plant oil and then adding water under high shear homogenization with an Ultra Turrax Model T25 basic high shear homogenizer (UT HSH) (IKA, Works Inc., Wilmington, NC, USA) for 5 min at 19,000 rpm. The water/oil ratio (WOR) was volumetric.

2.4. *In situ* oligomerization of glycerol carbonate by a one pot method [20,21]

Glycerol (120 g), urea (82 g) and monohydrated zinc sulfate (2.6 g) were introduced into a closed reactor to create the reaction medium. The reaction medium was heated, with stirring, for 3 h at 140 °C, maintaining a pressure of 4×10^3 Pa. The ammonia formed *in situ* was controlled by gas flow while maintaining the reduced pressure. Once ammonia release had ceased, the temperature of the reaction medium was increased to 160 °C for 150 min, at atmospheric pressure. The gaseous medium generated *in situ* consisted principally of nascent CO₂. Once no more gas was being given off, oligomerization was considered to be complete. The reactor was opened and the reaction medium was collected and analyzed.

2.5. Acylation of oligo (glycerol carbonate glycerol) [21]

Reactions were carried out in a 250 mL reactor equipped with a stirring device operating at 300 rpm, a Dean Stark system equipped with a vacuum pump to control internal pressure and means of heating the mixture and creating a controlled atmosphere by nitrogen flushing (10 L/h).

Partial acylation through transesterification reactions: Oligo (glycerol carbonate glycerol) (25.06 g, 351 mmol of OH groups), high oleic sunflower oil (103.5 g, 351 mol of acyl groups) or copra oil (79.5 g, 351 mmol of acyl groups) were introduced into the reactor with sodium methylate (1.26 g) and heated at 142 °C, with stirring under a pressure of 40 mbar for 8 h. Two phases were obtained on cooling. The lower phase contained residual non reacted oligomers, whereas the upper phase contained the desired esterified oligomers.

Total acylation by transesterification: Oligo (glycerol carbonate glycerol) (24.94 g representing 340 mmol OH groups), 107.79 g sunflower methyl ester (0.364 mol of acyl groups) and sodium methylate (1.41 g) were introduced into the reactor, stirred (300 rpm) and heated at 142 °C under a pressure 25 mbar for 8 h. The progress of the reaction was monitored by collecting samples and determining their kinematic viscosity and the hydroxyl values. The reaction was stopped after 8 h. Two phases were obtained on cooling. The materials recovered in the Dean Stark system were methanol (91%), water (7%) and traces of glycerol and glycerol carbonate.

3. Results and discussion

3.1. Oligo (glycerol carbonate glycerol)

Oligo (glycerol carbonate glycerol) were synthesized according the procedure described by Mouloungui et al. [20]. The reaction scheme (Fig. 1) takes place in two major steps, glycerol carbonate

synthesis and glycerol carbonate oligomerization, in one pot in the same reactor and with different reaction conditions for each step. For the first step, the catalytic process involves zinc sulfate nucleation. The glycerol carbonate was obtained after carbamoylation and carbonylation. Two molecules of gaseous ammonia were generated for each molecule of glycerol carbonate. Ammonia was flash removed from the reaction medium at 140 °C by stripping with nitrogen flow under reduced pressure (35 mbar). The step of oligomerization was carried up by increasing the reaction temperature (190–220 °C) and pressure (P_{atm}) and using a glycerol carbonate/glycerol initial molar ratio of 80/20. The final composition of the reaction medium for glycerol carbonate oligomerization was analyzed by HPLC (Fig. 2).

Peaks with retention times of 10.45 min and 14.85 min were obtained, corresponding to the unreacted monomers, glycerol and glycerol carbonate, respectively. Signals with retention times of 10.45 min or above correspond to products susceptible to alkaline hydrolysis with at least one cyclic or linear carbonate groups. Peaks with retention times between 5.50 and 10.45 min correspond to compounds that are not modified by alkaline hydrolysis, which do not, therefore, contain functional carbonate groups. These oligomeric compounds are completely decarbonated and are known as polyglycerols.

The composition of the medium was, therefore, as follows: 16% glycerol, 27% polyglycerols, 26% glycerol carbonate and 31% glycerol carbonate oligomers. ¹³C NMR spectroscopy analysis confirmed the presence of linear and cyclic carbonates through the presence of signals at 155.4 ppm for the linear carbonate group and at 154.5 ppm for the cyclic carbonate function. These findings were consistent with those of FTIR analysis, showing a vibrational stretch at 1790 cm⁻¹ characteristic of cyclic carbonate groups, and a vibrational stretch at 1738 cm⁻¹ for the linear carbonate group (See Supplementary material).

Through physicochemical analyses and mass spectroscopy (Supplementary material) [20], we elucidated the different oligomer structures (Fig. 1). Homo oligomers were present as either glycerol oligocarbonates consisting of repeated linear carbonate units bearing hanging hydroxyl groups, or as oligoglycerols consisting of repeated ether units bearing hanging hydroxyl groups. The hetero oligomers present consisted of repeated linear carbonate and ether units bearing hanging hydroxyl groups. The oligomers were capped with cyclic carbonate or hydroxyl end groups.

We monitored viscosity and hydroxyl values throughout the oligomerization reaction (Fig. 3). Kinematic viscosity increased with hydroxyl value. There was an induction period, corresponding to the first hour of the reaction, during which viscosity and hydroxyl value remained constant. These two parameters then increased, essentially in parallel, from 1.5 h into the reaction until the end of the reaction. This parallel increase may be due to the greater potential for hydrogen bonding in the presence of larger numbers of hydroxyl groups, rendering the medium more viscous. Indeed, at 40 °C, kinematic viscosity increased from 143 cSt one hour into the reaction to 2739 cSt after 4 h of reaction. During this period, the hydroxyl value increased by a factor of 1.4.

The chemical structure of these molecules resembles that of oligo (ethylene glycol)s and linear polyglycerols. Both these molecules are homopolymers. Glycerol oligocarbonates consist of repeated ethylene oxide monomers bearing only two functional hydroxyl groups, which limits their potential for functionalization. Oligoglycerols consist of repeated glycerol molecules rich in hydroxyl groups. Both are water soluble and amphiphilic only when functionalized with lipophilic moieties, such as fatty acids, to give amphiphilic esters, or fatty alcohols, to yield amphiphilic ethers [22]. By contrast, oligo (glycerol carbonate glycerol)s consist of repeated glycerol and glycerol carbonate units structured into homo oligomers and hetero oligomers (Fig. 1). These oligomers

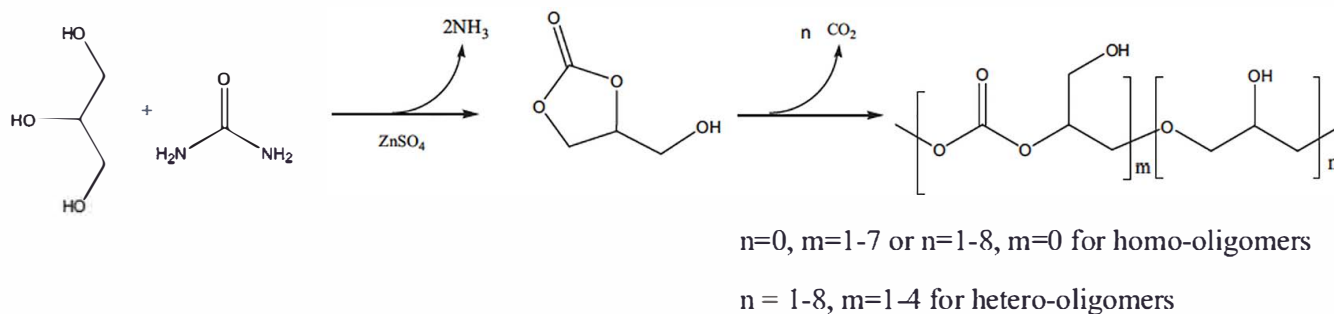


Fig. 1. Reaction scheme of synthesis of oligo-(glycerol carbonate-glycerol).

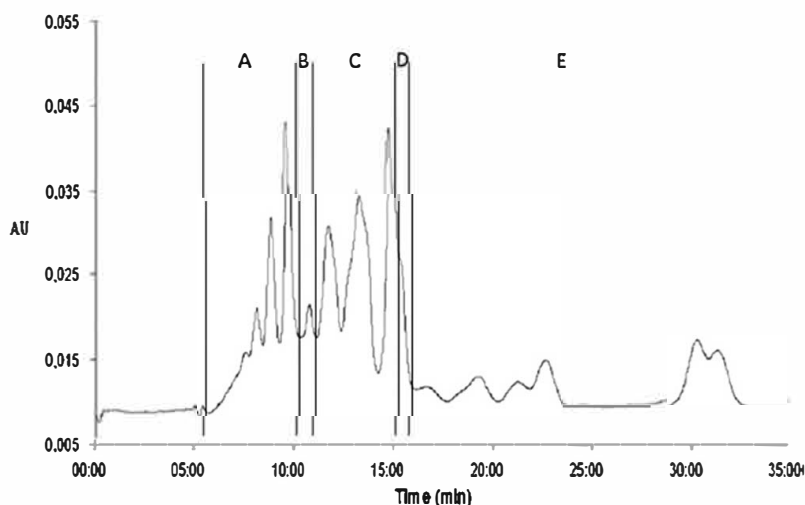


Fig. 2. Elution profile of oligo-(glycerol carbonate-glycerol). Zone A: the polyglycerol fraction. Zone B: glycerol. Zone C: oligomers of glycerol carbonate. Zone D: glycerol carbonate. Zone E: Oligomers of glycerol carbonate.

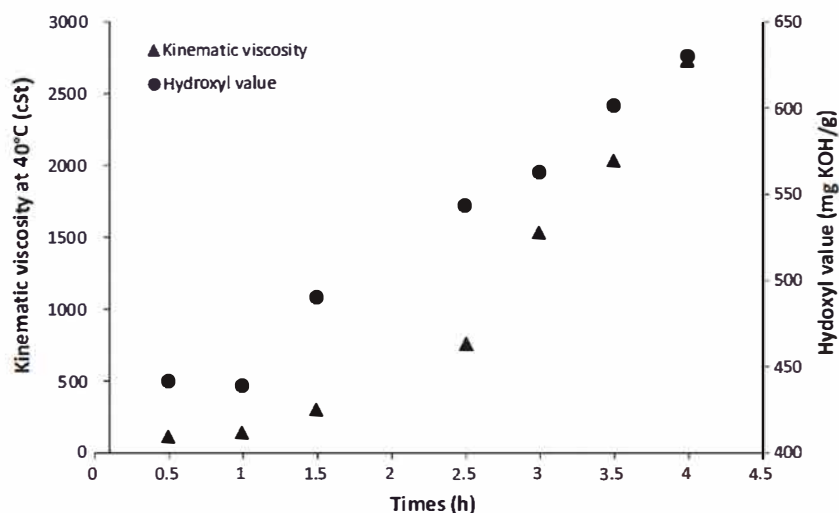


Fig. 3. Change in relative viscosity with reaction time for the oligomerization of glycerol carbonate.

are thus constructed by linking units with different polarities: hydroxy ethers and hydroxy carbonate moieties, conferring a certain amphiphilicity on the backbone oligomer. This amphiphilicity is highlighted by the ability of oligo (glycerol carbonate glycerol)s to decrease water surface tension to a plateau at 57 mN m^{-1} (Fig. 4). The shape of the plot of Fig. 4 is characteristic of the behavior of a surfactant and the value of 50 mg L^{-1} can be considered as

the critical micelle concentration. Above this value, the surface tension increases slightly, in particular at high concentration (467 mg/L) for which there probably occurs a phase segregation because this oligomeric medium is constituted of a mixture of molecules. The ether bond and the carbonate unit of the oligomeric skeleton provide a hydrophobic contribution that counterbalances the polarity of the hydroxyl groups. This observation is consistent with

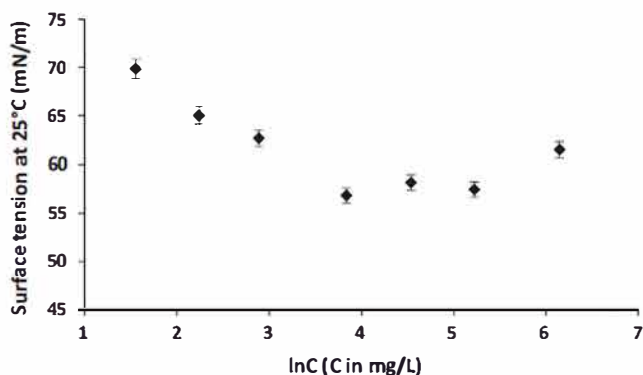


Fig. 4. Surface tension curve of oligo-(glycerol carbonate-glycerol).

the findings of a previous study [17] in which the carbonate linkage was found to be hydrophobic and the oxycarbonyl part of the carbonate group was found to be strictly equivalent to an extra methylene group in the alkyl chain of the surfactant.

3.2. Esters of oligo (glycerol carbonate glycerol)

Two kinds of partial esters of oligo (glycerol carbonate glycerol) were synthesized by inter esterification. Here, partial esters are defined as having a hydroxyl value in the range of 100–325 mg KOH g⁻¹. The first type of partial ester was generated by the reaction between oligomers of glycerol carbonate and high oleic sunflower oil to generate oleic esters of oligo (glycerol carbonate glycerol). The second type of partial ester was produced by the reaction of oligomers of glycerol carbonate with copra oil to generate lauric esters of oligo (glycerol carbonate glycerol). An increase in viscosity over time (Fig. 6) was observed for the reaction with high oleic sunflower oil. This increase in viscosity resulted from the increase in molecular mass and self emulsification of the reaction medium. The properties of the total and partial esters of oligo (glycerol carbonate glycerol) are presented in Table 1. The increase in viscosity of the final products was proportional to the increase in hydroxyl value. This implies that OH groups are available to form hydrogen bonds and to structure these reactive media, even in the lauric polyester of oligo (glycerol carbonate glycerol) or polyesters of oleic oligo (glycerol carbonate glycerol).

Oleic total esters of oligo (glycerol carbonate glycerol) were obtained by transesterification based on a hydroxyl value of 42 mg KOH g⁻¹ (for the purposes of this article, we will refer to these esters as “total esters”). The amount of methanol collected during the reaction indicated a yield of 83% relative to the available OH groups. Over the course of the reaction, kinematic viscosity increased steadily, in a linear fashion, whereas hydroxyl value followed a Bell curve distribution. These phenomena can be explained as follows. Firstly, the partially acylated glycerol carbonate units migrate into the oily (copra or sunflower oil) phase, in which the acylation rate is much higher. The hydroxyl value rises and then falls as hydroxyl units are converted into esters. Secondly, kinematic viscosity remains constant because the lower viscosity at

lower hydroxyl values (corresponding to lower levels of hydrogen bonding between oligomers) is offset by the increase in molecular weight due to acylation with lauric or oleic acid (see Fig. 5).

From the structural and physicochemical points of view, such molecules can be described as in Fig. 6. Oligocarbonate esters are multifunctional molecules with an “oligo gemini” structure comprising an oligomeric polar head containing different hydroxyl, carbonate and ethyleneoxy functions with different polarities. The rigidity of the polymeric polar head can be explained by its chemical nature: for example, linear carbonate and ethyleneoxy functions. The alternation on the oligomeric backbone of saturated lauric ester groups and monounsaturated oleic ester groups gives rise to a “rigid head” and “non rigid pendulous zones” that are modulated according to the nature of the fatty acid involved in the ester. Molecular mobility can be modified by altering the molecular order of the lipophilic fatty acid tail. Saturated fatty acids, such as lauric acid, produce more ordered esters of oligo (glycerol carbonate glycerol ether), than monounsaturated fatty acids, such as oleic acid, which is involved in esters of oligo (glycerol carbonate glycerol). Indeed, oleic acid contains a double bond in the *cis* configuration that increases the flexibility of the alkyl chain, whereas lauric acid is a straight saturated and inflexible fatty acid. Melting points are higher for saturated fatty acids (44 °C for lauric acid) than for monounsaturated fatty acids (16.3 °C for oleic acid) [23].

3.3. Surfactant properties

Zana [24] investigated the surfactant properties of gemini and oligomeric surfactants, by studying their behavior at the air/water interface. The surfactant activity of nonionic oligomeric surfactants was compared with that of trimeric nonylphenol polyoxyethylene surfactants and monomeric nonylphenol polyoxyethylene ether surfactants [25]. Differences in molecular organization, particularly in terms of the orientation of the molecules at the air/water interface, were observed. Mohamed et al. [26] studied trimeric nonionic surfactants based on tris(2-aminoethyl) amine with alkyl and poly(ethylene glycol) chains of various lengths. An increase in the number of hydrocarbon chains, from octyl to decyl to dodecyl, was associated with an increase in γ_{cmc} , whereas an increase in poly(ethylene glycol) chain length within the same group led to a decrease in γ_{cmc} [26].

We compared the behavior of total and partial ester oligomers at the water/air interface (Fig. 7). Acylation of the oligocarbonates improved their surfactant properties by causing a faster decrease in surface tension and critical micelle concentration (CMC). The degree of acylation, estimated by the hydroxyl value, proved to be the key parameter. Partial esters of oligocarbonates with hydroxyl values of 182, 223 and 325 had the strongest surfactant activity. Their CMC values were low, and surface tension at the CMC was also low. Greater acylation (hydroxyl value of 42) was associated with lower surface activity, with higher surface tension and CMC values. The effect of the fatty acid composition was very difficult to explain, because the degree of acylation was not identical for all samples. It was, therefore, difficult to draw any firm conclusions or to infer relationships between fatty acid composition and

Table 1
Main characteristics of partial and total esters of oligo-(glycerol carbonate-glycerol).

Properties	Lauric oligomers Copra oil			Oleic oligomers HOSO			
	201	336	267	194	257	46	229
Kinematic viscosity (cSt) at 40 °C							
Hydroxyl value NF 160-213	192	325	223	98	182	42	202
Fatty acid content	C12:0 (45%)	C12:0 (45%)	C12:0 (45%)	C18:1 (80%)	C18:1 (80%)	C18:1 (80%)	C18:1 (80%)

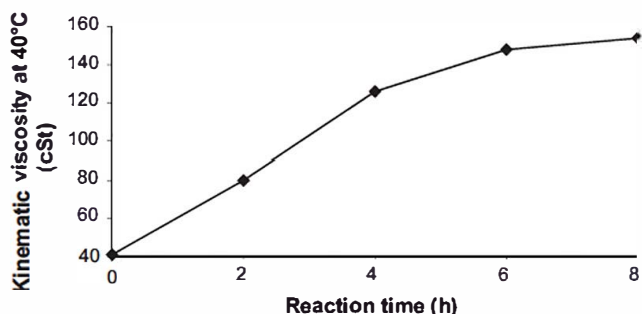


Fig. 5. Changes in kinematic viscosity with reaction time for the transesterification of oligo-(glycerol carbonate-glycerol). Acyl/OH ratio = 1.15, acyl donor: HOSO, catalyst: sodium methoxide (5%).

the effect of the degree of acylation on the surfactant properties of the oligomers. Data for all samples are summarized in Table 2.

The CMC values of the total and partial esters of oligocarboxates were particularly low, below those of ethoxylated surfactants containing oleic acid (i.e. Tween 80) or lauric acid (i.e. Tween 20, dodecyl polyethylene monoethers, polyglycerol monolaurates) as the lipophilic moiety. In case where surfactant were not pure, with different numbers of oxyethylene units clustered about some mean value (Table 2), their CMCs are slightly lower than those of single species materials containing the same hydrophobic group and with oxyethylene content corresponding to that mean value, probably because the components with low oxyethylene content in the commercial material reduce the CMC more than it is raised by those with high oxyethylene content [27,28]. It is notable to remark that partial esters of oligocarboxates are a mixture of amphiphilic molecules, rich in hydroxyl, carbonate and ether functions and able to create hydrogen bonds and promote interfacial activity leading to low CMCs.

Thus, the oligomeric polar head of oligocarboxate esters is a good alternative to ethoxylates, improving the surfactant properties of oligomeric surfactants. Whatever the number of ethylene oxide molecules (20 for Tween 20 and Tween 80, 4-8 for polyethylene monoether) or glycerol molecules (3-5 for polyglycerol monolaurates), the surface tension reached at the CMC was close to that for oligocarboxate esters, whereas CMC values were always higher than those for oligocarboxate esters. Thus, it should be possible to achieve the same decrease in surface tension with smaller amounts of oligocarboxate esters than of ethoxylated surfactants. Regard

less the number of ethylene oxide molecules (20 for Tween 20 and Tween 80, 4-8 for polyethylene monoether) or the number of glycerol molecules present in the surfactant, the CMC values obtained were slightly higher than those for oligocarboxate esters, for the same surface tension. We can therefore deduce that smaller amounts of oligocarboxate esters than of ethoxylated surfactants should be required to achieve a similar decrease in surface tension.

3.4. Stabilization of double W/O/W emulsions

Emulsions are dispersions of one liquid in another liquid, the two liquids being immiscible, like water and oil. They can be classified into two types, oil in water (O/W) and water in oil (W/O) emulsions. Multiple emulsions are complex and heterogeneous systems in which the two types of emulsion (O/W and W/O) coexist simultaneously. These systems can be called "emulsions of emulsions" [33], because the internal phase itself contains dispersed globules that are miscible with the continuous phase. Multiple emulsions have demonstrated potential applications in pharmaceutical and cosmetic formulations, due to their ability to entrap materials. They, therefore, constitute potential sustained slow release systems and have found many applications as cosmetic and pharmaceutical vehicles. Despite the potential usefulness of multiple emulsions, their use has been limited by their intrinsic instability and complex structures.

According to Bancroft, a normal emulsion is obtained if the phase in which the surfactant is predominantly solubilized is the continuous phase of the emulsion. This is a formulation variable. A W/O emulsion should form in systems in which the surfactant is oil soluble. According to the Ostwald packing concept [34], the dispersed phase volume fraction of an emulsion cannot exceed 0.74 (relative volume occupied in a closely packed sphere configuration). This is a composition variable known as the water/oil ratio (WOR) [35]. Bancroft reported the formation of an O/W emulsion when lauric esters of oligocarboxates were dissolved in rapeseed oil and water was then added, with stirring, giving a WOR of 0.25. Thus, the rules of Bancroft and Ostwald are respected here. Reproducing the same experiment but adding more water until the WOR reached 1 resulted in the production of a multiple W/O/W emulsion. In this case, there was a phase inversion, and the Ostwald rule was, therefore, respected.

Salager et al. [36,37] have developed trends and made important recent advances towards understanding emulsion inversion phenomena. We chose to vary the composition parameter. The surfactant was first solubilized in oil and water was then added

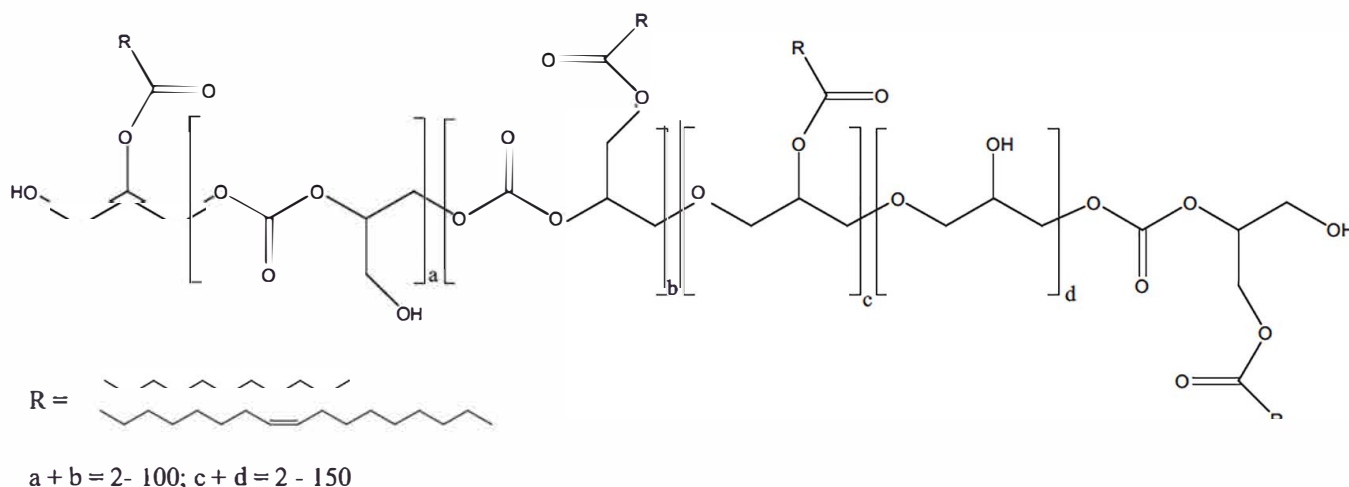


Fig. 6. Proposed structure of esters of oligo-(glycerol carbonate-glycerol ether).

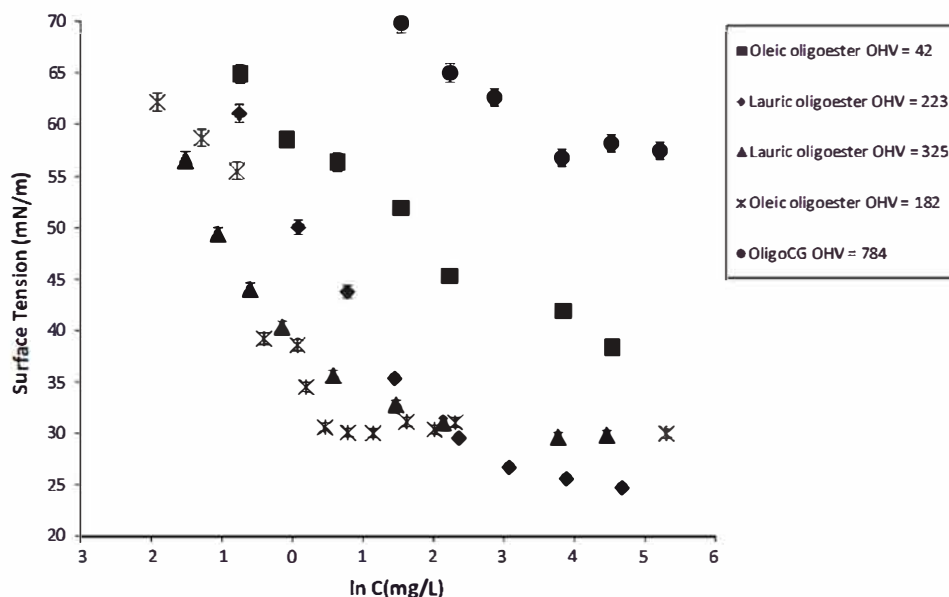


Fig. 7. Surface tension curves of total and partial esters of oligo-(glycerol carbonate-glycerol ether). OHV; hydroxyl value in mg KOH/g.

Table 2
Comparison of the physicochemical parameters of ethoxylated surfactants, glycerol-based surfactants and partial and total esters of oligo-(glycerol carbonate-glycerol ether).

	CMC (mg/L)	CMC (mmol/L)	M_w (g mol ⁻¹)	γ @CMC (mN m ⁻¹)	References
Tween 80 polyoxyethylene (20) sorbitan mono-oleate	15.7 (mixture)	0.012	1310	nd	[29]
Tween 20 polyoxyethylene (20) sorbitan monolaurate	73.7 (mixture)	0.06	1226	38	[29]
C12EO4 4-dodecyl polyethylene monoether	23.5 (pure)	0.065	362	35.2	[30]
	15.7 (mixture)	0.0433			[31]
C12EO8 8-dodecyl polyethylene monoether	37.7 (mixture)	0.07	538	41	[31,32]
C12EO6 6-dodecyl polyethylene monoether	31.9 (mixture)	0.07	450	38.5	[32]
	383 (mixture)	0.085			[31]
3GML Triglycerol monolaurate	78.9 (pure)	0.19	422	31.4	[30]
4GML Tetraglycerol monolaurate	118.0 (pure)	0.24	496	35.2	[30]
5GML Pentaglycerol monolaurate	168.2 (pure)	0.29	570	39.6	[30]
Oleic oligoester OHV = 182	1.5 (mixture)			30.05	This work
Oleic oligoester OHV = 42	9.5 (mixture)			45.8	This work
Lauric oligoester OHV = 325	0.75 (mixture)			32.8	This work
Lauric oligoester OHV = 223	2.2 (mixture)			26	This work

CMC, critical micelle concentration; M_w , molecular weight; OHV hydroxyl value mg KOH/g. Pure or mixture state of the samples in brackets.

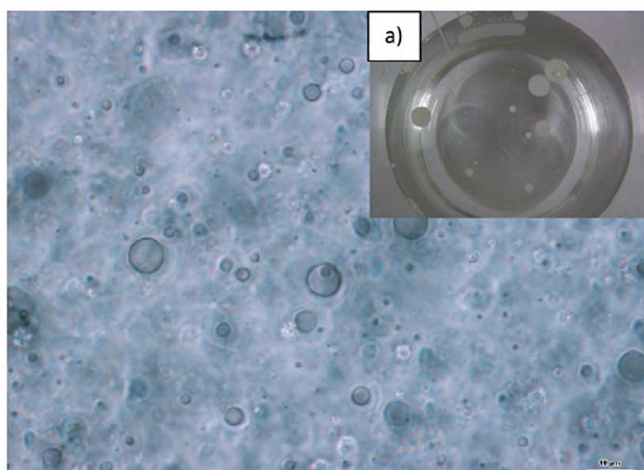


Fig. 8. Micrographs of an O/W emulsion with WOR = 0.25. The scale bar corresponds to 10 μ m. (a) Attempt to disperse a few drops of the emulsion in water.

slowly. This is a Winsor II system and it resulted in a W/O emulsion (Fig. 8). The oil phase was confirmed to be the internal phase, because the emulsion was not dispersible in water, as shown in Fig. 8. The particles observed were between 2 and 3 μ m in size. Adding more water during the emulsification (until a WOR = 1) resulted in the production of a water dispersible multiple emulsion (Fig. 9). Here, the external phase was water and the internal phase was droplets of water in oil. By varying WOR, we triggered a catastrophic phase inversion during the emulsification process. According to the Ostwald packing concept, between a WOR of 0.25 and a WOR of 1, the internal phase of the O/W emulsion became the external phase in a W/O/W multiple emulsion, which was stable for several hours. Emulsification was carried out in a single step, in a very simple classical emulsification process with the oligomeric surfactant: lauric esters of oligocarbonates. It has been reported that multiple emulsions can be prepared by a one step process with a single diblock copolymer [38,39]. Hanson et al. [38] were the first to obtain long term stable double emulsions from synthetic amphiphilic, diblock, copolypeptide surfactants. Hong et al. [39] demonstrated the preparation of stable multiple emulsions by a catastrophic inversion process, using a

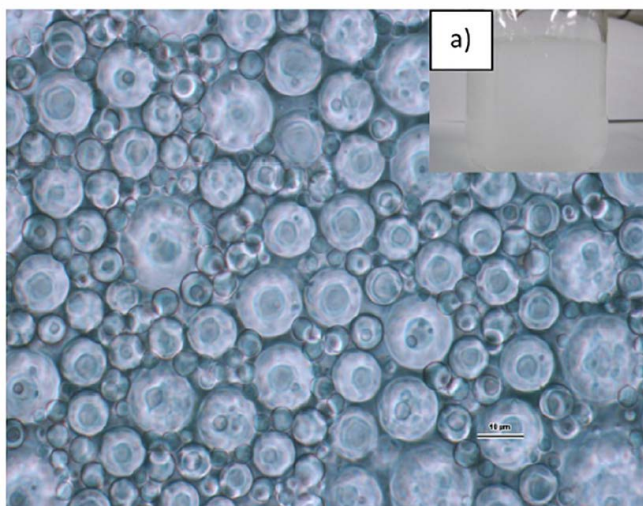


Fig. 9. Micrographs of a W/O/W emulsion with WOR = 1. The scale bar corresponds to 10 μm . (a) Attempt to disperse a few drops of the emulsion in water.

poly(ethylene glycol) *b* polystyrene (PEG *b* PS) copolymer. These systems involve easier formulations and form stable multiple emulsions, but oligocarbonate esters nevertheless present an alternative to amphiphilic diblock polypeptides and ethylene glycol based copolymers.

4. Conclusions

Multifunctional oligomers can be obtained from biobased reactants, such as glycerol and plant oils. Glycerol carbonate, synthesized *in situ* from glycerol [6,20], was here oligomerized into polyhydroxylated oligomers, and assisted by glycerol. Carbonate dioxide's retention was highlighted by the presence of linear carbonate functions on the oligomer skeleton. Linear carbonates bring a nonpolar contribution which is counter balanced by ether units bearing hanging polar hydroxyl groups. The acylation of this oligomerized reaction medium by the reaction of interesterification with plant oils can be modulated and controlled by the hydroxyl values. Partial and total esters of glycerol carbonate oligomers fall into the categories of "oligo gemini" molecules [24–26]. The degree of acylation controls directly the surfactant properties. The non-purified reaction medium, rich in partial esters, gives very low CMC values meaning a possible use of this multifunctional medium at lower mass concentrations than ethoxylated surfactants [29–32]. These findings are of noticeable importance in the domain of the surfactants. Indeed, until now it has been reported that oligomeric surfactants are the most effective surfactants, compared to monomeric or polymeric surfactants [24–26]. The linear structure based on a polyhydroxylated glycerol carbonate glycerol oligomeric skeleton partially functionalized by pendant fatty acids is the key concept, in the findings presented in this study. The resulting amphiphilic structure resembles to a repetition of gemini units, which is a structure with a high interfacial activity [24].

The effectiveness of the use of partial esters of oligo (glycerol carbonate glycerol) as surface active multifunctional system was demonstrated by their ability to stabilize inverse emulsions and multiple emulsions by catastrophic phase inversion. Further physico-chemical studies could explain more fully the mechanisms for interface stabilization. Indeed in industrial domains such as cosmetics, pharmaceuticals, or paint and coatings, complex emulsi-

fied systems are needed and glycerol biobased oligomeric surfactants could greatly contribute to their development.

Conflict of interest

The authors have no conflict of interest to declare.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2016.10.072>.

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Supporting information

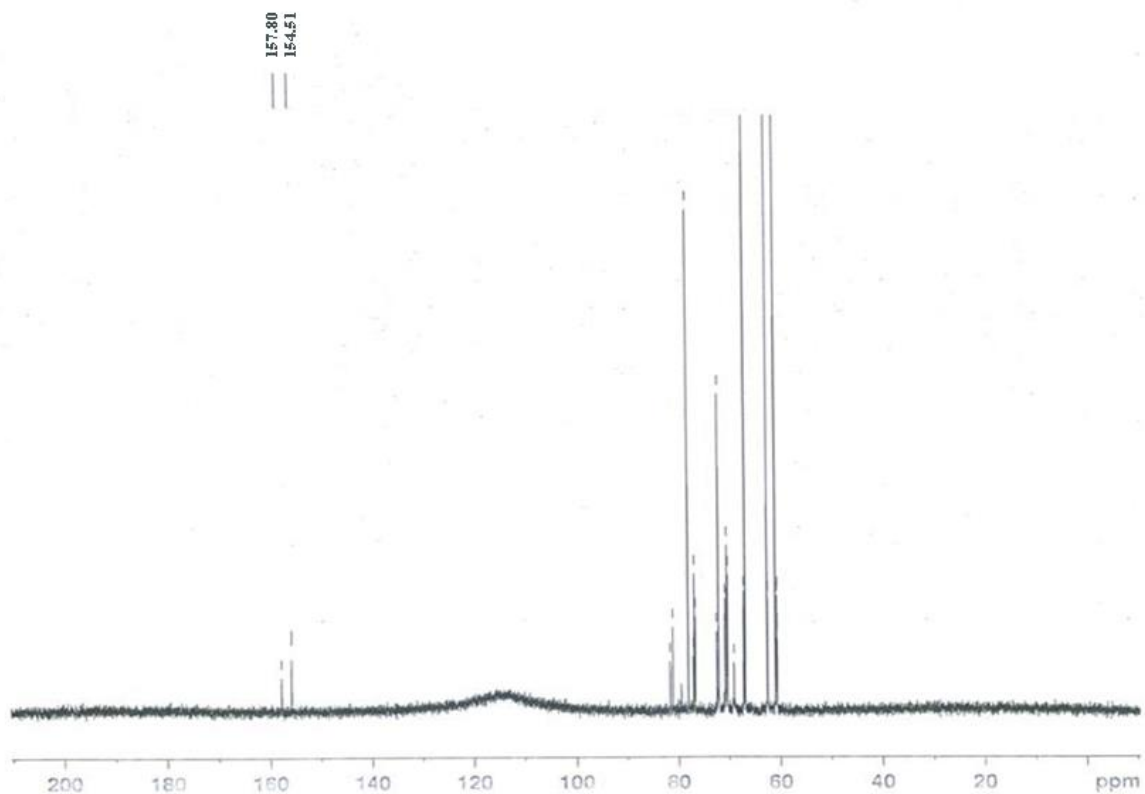


Figure S1: ^{13}C NMR spectrum of oligo-(glycerol carbonate-glycerol ether)

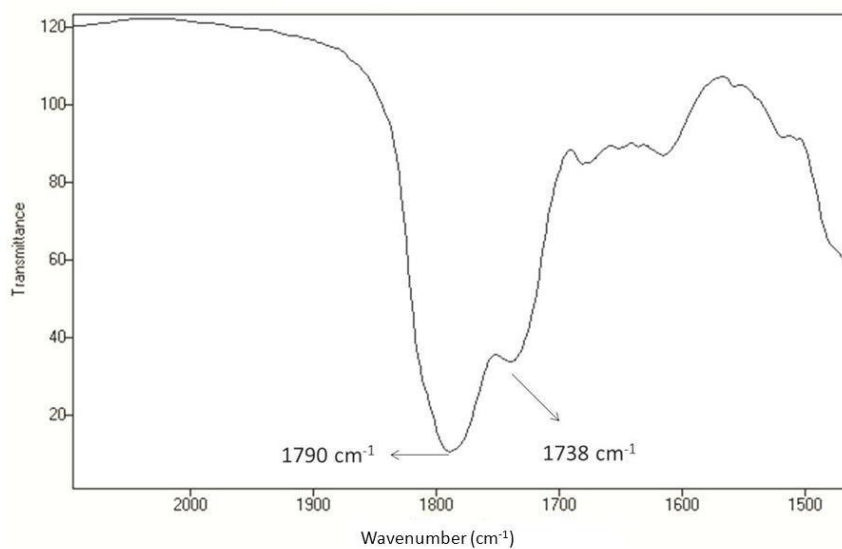


Figure S2: Liquid FTIR spectrum of oligo-(glycerol carbonate-glycerol ether)

m/z (M+23)	Identified motif	Repeated unit
	Linear carbonate	$m = 1$
-189-263-337-411-...	Homo-oligomers	$n = 1 - 8$
-245-319-393-...	Homo-oligomers with 1 terminal ring	$n = 2 - 9$
-301-375-...	Homo-oligomers with 2 terminal rings	$n = 3 - 5$
-307-381-455-529-...	Co-oligomers	$n = 1 - 6, m = 1$
-289-361-437-511-...	Co-oligomers with 1 terminal ring	$n = 1 - 9, m = 1$
-345-419-493-567-...	Co-oligomers with 2 terminal rings	$n = 2 - 7, m = 1$
-407-481-555-629-...	Co-oligomers with 1 terminal ring	$n = 2 - 8, m = 2$
-315-389-463-537-...	Co-oligomers with 2 terminal rings	$n = 1 - 8, m = 2$
-451-525	Co-oligomers	$n = 0 - 2, m = 3$
-433-507-581-655-...	Co-oligomers with 1 or 2 terminal ring(s)	$n = 0 - 6, m = 3$
-415-489-563-637-...	Co-oligomers with 2 terminal rings	$n = 0 - 5, m = 3$
-397-471-545-...	Co-oligomers with more than 2 terminal rings	$n = 0 - 4, m = 3$
-379-453-527-...	Co-oligomers with more than 2 terminal rings	$n = 0 - 4, m = 3$
-435-509	Co-oligomers with more than 2 terminal rings	$n = 1 - 3, m = 3$
-515-589-663	Co-oligomers with more than 2 terminal rings	$n = 0 - 3, m = 4$

Figure S3: Determination of oligomer structure by ESI-TOF mass spectroscopy.