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# Nonionic polyoxazoline surfactants based on renewable source: Synthesis, surface and bulk properties

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**Abstract:** The synthesis of amphiphilic lipid-polyoxazoline based on copolymers (**CO-PO<sub>x</sub><sub>n</sub>**) with narrow distribution has been achieved via cationic ring-opening polymerization of 2-methyl-2-oxazoline (**MO<sub>x</sub>**). Lipid-macroinitiator (**COTs**) was obtained from commercial castor oil (**CO**), widely renewable agricultural resource. **CO-PO<sub>x</sub><sub>n</sub>** with various length segments were synthesized from a macroinitiator **COTs** in order to investigate the effect of the length of the hydrophilic segment on the solution behavior of the nonionic polymer surfactants **CO-PO<sub>x</sub><sub>n</sub>**. The results showed that the critical micelle concentration rised with the increase of **PO<sub>x</sub>** content and inversely surface tension decreased. The average size of aggregates of these structures suggested the formation of vesicles or nonspherical micelles. Star-shaped morphology of **CO-PO<sub>x</sub><sub>n</sub>** in solid state has also been observed using

environmental scanning electron microscopy (ESEM). Additionally energy dispersive X-ray (EDX) analysis demonstrated the presence of **POx** block in the concentric stripes of the texture.

### **Keywords**

Castor oil; lipopolymer; nonionic surfactant; self-organisation; polyoxazoline.

## Introduction

The interest in designing highly specialised synthetic surfactants incorporating blocks coming from renewable resources has increased remarkably during the last few years. Many surfactants are made of natural building blocks like amino acids, sugars and fatty acids. Their low toxicity, good biocompatibility and fast biodegradation are the main reasons for the increasing industrial interest in these compounds. The most important applications for the surfactants are related to their self-organisation in solution. Self-organisation leads to the formation of micelles, liposomes or lyotropic liquid crystalline phases which can be used for the solubilisation of chemicals such as drug carriers or detergents. The preparation of surfactants from renewable sources such as natural oil-based materials and more specifically triglyceride oils have been used for the production of coatings, inks, plasticizers, lubricants and agrochemicals. Among vegetable oils, castor oil (**CO**) represents a promising raw material due to its low cost, low toxicity, and its availability as a renewable agricultural resource. **CO** contains ricinoleic acid (12-hydroxy-cis-9-octadecenoic acid) combining hydroxyl groups and unsaturations [1]. From this starting material and water-soluble polymer, amphiphilic surfactants could be designed. Among numerous water-soluble polymers, polyoxazolines (**POx**s) are attractive for their low acute toxicity [2,3] and have been approved by US Food and Drug Administration (FDA). (**POx**s) have recently emerged in surface chemistry and biomaterials science where they act for instance as nonionic surfactants and could be compared with commercial nonionic polymer ones: Pluronics<sup>®</sup> [4] and analogous PEO based surfactants [5].

Some polyoxazoline surfactants have already been mentioned in the literature with various macromolecular architectures. Amphiphilic block copolymers were synthesized between 2-methyl- or 2-ethyl-2-oxazoline and 2-alkyl-2-oxazoline where the long alkyl chain afforded a hydrophobic character [4,6,7]. Other amphiphilic polyoxazolines were prepared starting from initiators or terminating agents with long alkyl chains and hydrophilic 2-oxazoline [8, 9]. Similar architectures were performed from perfluoro initiator [10]. Some examples of graft copolymers were also referred to poly(2-methyl-2-

oxazoline) and phosphazene [11] or chitine [12]. The large demand for surfactants urgently calls for sustainable surfactants made from renewable raw materials to reduce the impact on the environment and to save fossil resources [13]. In this sense few nonionic polyoxazoline surfactants based on vegetable biomass have been synthesized from glycerol [14] and lipopolymers [15-18]. Schubert et al. have recently reported the synthesis of amphiphilic poly(2-ethyl-2-oxazoline-block-2-“soyalkyl”-2-oxazoline) copolymers from soybean fatty acid [19, 20]. The polyoxazoline block was synthesized using a new oxazoline monomer containing a C18 long unsaturated chain issued from soybean oil.

In this article, we described a new route to synthesize amphiphilic lipid-POx **CO-PO<sub>x</sub><sub>n</sub>** copolymers using commercial castor oil **CO** backbone with various hydrophilic block lengths. Here, hydrophobic group was introduced at the initiation stage of polymerization of 2-methyl-2-oxazoline **MO<sub>x</sub>** (“initiator method”) by a derivative of castor oil (**COTs**). The surface properties of these nonionic polymeric surfactants were also investigated as well as self-ordering of **CO-PO<sub>x</sub><sub>n</sub>** in the solid state.

## Experimental Part

### Experimental Methods

$^1\text{H}$  NMR spectra ( $\delta$ , ppm) were recorded on a Bruker DRX 200 MHz spectrometer with tetramethylsilane as internal standard. Chemical shifts are reported in ppm. Size exclusion chromatography (SEC) was performed on a Spectra-Physics apparatus equipped with an RI Shodex refractive index detector. Two PL-gel mix C columns were used at 70 °C with a 0.8 mL·min<sup>-1</sup> flow rate of DMF (0.1% LiBr), calibrated using polymethylmethacrylate standards. Contact angle measurements were performed on polymer films that were prepared from chloroform solutions. Solutions of copolymer (5/95 w./w.% copolymer/CHCl<sub>3</sub>) was deposited onto glass plates and solvent was evaporated in a vented oven. A G10 optical contact angle measuring instrument from Krüss was used to determine the contact angles of diodomethane as apolar test liquid. The drops of diodomethane were deposited on 3 different areas of the surface with a microsyringe. Results are mean value of three measurements on different parts of the samples. Polymers were analysed by Environmental Scanning Electron Microscope (ESEM) FEI QUANTA 200. The samples were examined without any preparation (samples placed directly onto ESEM stage). The ESEM was operated in low-vacuum mode, at a pressure of 2.87 Torr under a water vapour atmosphere. Others operational parameters were as follows: working distance 10 mm, and operating voltage 15 kV. Elemental analyses (EDX) were realized under the same operational parameters as for imaging. During EDX analysis the elements were both qualitatively and quantitatively measured. The surface activity of the synthesized surfactant was determined using a Krüss digital tensiometer K 12 equipped with a platinum plate. The surface tension was measured by the Wilhelmy plate method. The solutions were transferred into a vessel that was thermostated by circulating water at the desired temperature (298 K). The accuracy of the measurements was 0.1 mN/m. The minimum cross-section area of the surfactant head group,  $a_0$ , was calculated according to equation (1):

$$a_0 = \frac{1}{\Gamma_m N_A} \quad (1)$$

where  $\Gamma_m$  is the maximum value of the surface excess concentration determined from the plot of  $\gamma$  versus the logarithm of the surfactant concentration using the following Gibbs equation:

$$\Gamma_m = -\frac{1}{2.3RT} \cdot \lim_{c \rightarrow \text{cmc}} \frac{d\gamma}{d(\log C)} \quad (2)$$

$N_A$  is the Avogadro number,  $R = 8.32 \text{ J.mol}^{-1}.\text{deg}^{-1}$ ,  $T = 298 \text{ K}$  and  $\gamma$  is expressed in  $\text{N.m}^{-1}$ .

The mean size of micelle was determined by Dynamic light scattering (DLS) using the autocorrelation function of the scattered light with a Malvern photon correlation spectrometer (Zetasizer 3000HS of Malvern Instruments, Malvern, UK). The measurements were carried out at a scattering angle  $90^\circ$  and at constant temperature  $T = 298.15 \text{ K}$ . Hydrophilic–Lipophilic Balance (HLB) values of **CO-PO<sub>x</sub><sub>n</sub>** surfactants were calculated by the commonly used general formula for non-ionic ones:

$$HLB = 20 \frac{M_H}{M_H + M_L}$$

where  $M_H$  and  $M_L$  are the molecular weights of the hydrophilic segment **PO<sub>x</sub><sub>n</sub>** and of the lipophilic segment **CO** of the **CO-PO<sub>x</sub><sub>n</sub>** molecule, respectively.

## Experimental Section

### Materials

Diethyl ether, methanol, chloroform, Milli-Q water, p-toluenesulfonyl chloride (TsCl), castor oil (**CO**), KOH and  $\text{CaH}_2$  were purchased from ACROS and used as received. Pyridine was distilled from KOH under nitrogen. Acetonitrile was dried and distilled according to standard procedures [21]. 2-Methyl-2-oxazoline (**MO<sub>x</sub>**) was dried and distilled from  $\text{CaH}_2$  and stored under a dry nitrogen atmosphere. Deuterated solvents were purchased from SDS and used without further purification.

### Characterization of castor oil: CO

Castor oil (CO) is used as received and its composition is the following [ricinoleic ester (90%), oleic ester (4%), linoleic ester (1%), linolenic ester (1%), stearic ester (1%), palmitic ester (1%), dihydroxystearic ester (1%) and others (1%)].

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.6 and 5.4 (m,  $\text{H}_j$ ), 5.25 (m,  $\text{H}_i$ ), 4.3 and 4.15 (dd,  $J=11.9$  Hz and  $J=4.2$  Hz,  $\text{H}_h$ ), 3.6 (m,  $\text{H}_g$ ), 2.3 (t,  $J=7.4$  Hz,  $\text{H}_e$ ), 2.2 (t,  $J=7.4$  Hz,  $\text{H}_d$ ), 2.05 (m,  $\text{H}_c$ ), 1.7-1.2 (m,  $\text{H}_b$ ), 0.85 (s,  $\text{H}_a$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  173.2 and 172.8 (C=O), 133.1 and 125.5 ( $\text{C}_j$ ), 71.5 ( $\text{C}_g$ ), 68.8 ( $\text{C}_i$ ), 62.6 ( $\text{C}_h$ ), 36.8-22.3 (others carbons), 14.0 ( $\text{C}_a$ ).

### Synthesis of vegetable oil macroinitiator: COTs

A flask equipped with an addition funnel was charged with CO (5.61 g) and pyridine (2.0 mL) dissolved in chloroform (0.5 M, 13 mL). A solution of TsCl (1.33 g, 1.15 eq. in respect to 1/3 of total OH groups of CO) in 42 ml of chloroform was added dropwise under nitrogen atmosphere. After the addition of TsCl, the reactional mixture was stirred for 3.5 h at room temperature. The organic layer was washed with diluted  $\text{CuSO}_4$  solution ( $10 \text{ g}\cdot\text{L}^{-1}$ ), dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated to give COTs. COTs was obtained with a yield close to 70%. OH conversion rate are detailed in the following part.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J=7.5$  Hz,  $\text{H}_l$ ), 7.3 (d,  $J=7.5$  Hz,  $\text{H}_k$ ), 5.6 and 5.4 (m,  $\text{H}_j$ ), 5.25 (m,  $\text{H}_i$ ), 4.5 (m,  $\text{H}_g'$ ), 4.3-4.15 (m,  $\text{H}_h$ ), 3.6 (m,  $\text{H}_g$ ), 2.4 (s,  $\text{H}_f$ ), 2.3 (t,  $J=7.4$  Hz,  $\text{H}_e$ ), 2.2 (t,  $J=7.4$  Hz,  $\text{H}_d$ ), 2.1-1.85 (m,  $\text{H}_c$ ), 1.7-1.1 (m,  $\text{H}_b$ ), 0.8 (m,  $\text{H}_a$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  173.2 and 172.8 (C=O), 144.9 ( $\text{C}_{\text{aromatic}}$ ), 134.6 ( $\text{C}_{\text{aromatic}}$ ), 133.0 ( $\text{C}_j$ ), 129.9 ( $\text{C}_{\text{aromatic}}$ ), 127.7 ( $\text{C}_{\text{aromatic}}$ ), 125.3 ( $\text{C}_j$ ), 71.4 ( $\text{C}_g$ ), 68.8 ( $\text{C}_i$ ), 66.7 ( $\text{C}_g'$ ), 62.0 ( $\text{C}_h$ ), 36.8-21.2 (others carbons), 14.6 ( $\text{C}_a$  with Ts group), 14.0 ( $\text{C}_a$  without modification).



### Typical polymerization of MO<sub>x</sub> from COTs: CO-PO<sub>x</sub><sub>n</sub>

All reactions were carried out under a dry nitrogen atmosphere. COTs and MO<sub>x</sub> were dissolved in dry acetonitrile (4 M). The solution was vigorously stirred at 80°C for 2 days. The reaction product was quenched by addition of an adequate amount of methanolic KOH (10 eq). The flask was kept 4h at 30°C. After cooling,) and dried overnight in vacuum as a pale yellow viscous solid.

The copolymer was isolated by slow precipitation from cold diethyl ether (where the non functionalized CO remained soluble

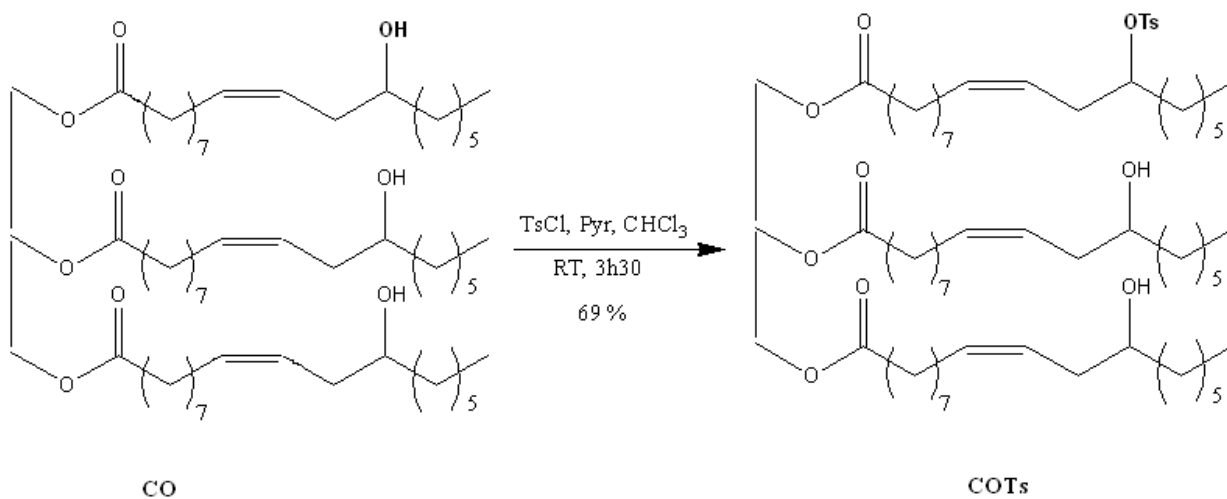
<sup>1</sup>H NMR (CDCl<sub>3</sub>) □ δ H<sub>g</sub>', H<sub>h</sub>, H<sub>i</sub>, H<sub>j</sub> are not visible, 3.6-3.3 (m, CH<sub>2</sub>-CH<sub>2</sub> PO<sub>x</sub> and H<sub>g</sub>), 2.3-2.0 (m, H<sub>c</sub>, H<sub>d</sub>, H<sub>e</sub> and CH<sub>3</sub> PO<sub>x</sub>), 1.7-1.2 (m, H<sub>b</sub>), 0.85 (m, H<sub>a</sub>).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) □ δ 181.2 (C=O PO<sub>x</sub>), 172.6 (C=O CO), C<sub>j</sub> no visible, 71.0 (C<sub>g</sub>), C<sub>h</sub> and C<sub>i</sub> no visible, 49.3-43.8 (CH<sub>2</sub> PO<sub>x</sub>), 32.5-20.6 (others carbons), 14.0 (C<sub>a</sub>).

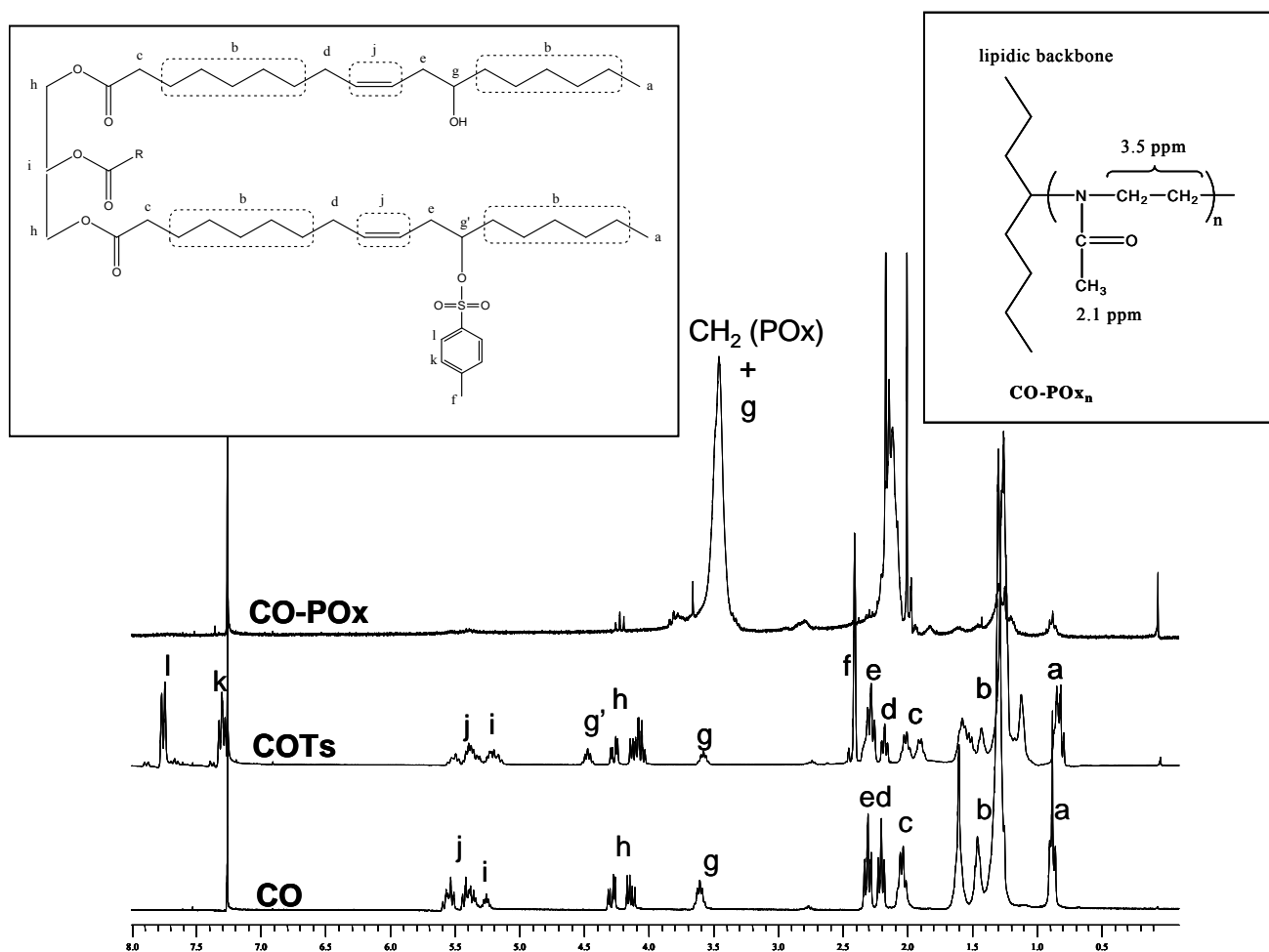
## Results and discussion

### Synthesis of lipid-macroinitiator COTs

The polymerization of oxazoline was investigated using a lipid based macroinitiator. Castor oil **CO** is unique among all oils since it is the only one containing about 90% of C<sub>18</sub> hydroxylated fatty acid ricinoleic acid (12-Hydroxyoleic Acid) which is interesting for further chemical modifications. Its peculiar structure combines one unsaturation with one hydroxyl functions on the same molecule (Scheme 1) [22-26]. Thus, castor Oil **CO** can act as macroinitiator after chemical modification of the OH groups. Herein, hydroxyl group was converted into tosylate initiator **COTs**. In order to obtain compounds bearing surfactant properties with a correct HLB balance, only one OH group of the three ones per triglyceride molecule was modified (Scheme 1). This compound was obtained in one step under mild conditions from **CO** and TsCl (ratio TsCl/OH= 1.15). The chemical modification was checked by <sup>1</sup>H NMR analysis. **COTs** spectrum revealed typical signals of vegetable castor oil **CO** as can be seen in Figure 1. Protons of unsaturated alkene group were observed as a multiplet at 5.6 and 5.4 ppm. Methylene and methine groups of glycerol part appeared at 4.3-4.15 and 5.25 ppm, respectively. Methine groups bearing alcohol oxygen atom were observed at 3.6 ppm. Methylene groups in  $\alpha$  position of alkene or of carbonyl ester appeared at 2.3-2.05 ppm. Terminal methyl group of ricinoleate was detected as a peak at 0.85 ppm. The presence of tosylate group was verified, since the aromatic protons and the methine group bearing an oxygen atom appeared respectively at 7.75-7.3 and 4.5 ppm. Moreover the chemical modification of castor oil **CO** with tosylate group was proved by <sup>13</sup>C NMR analysis with the appearance of aromatic carbons around 130 ppm. Finally, the calculations confirmed that one of the three alcohol groups of castor oil **CO** was transformed in **COTs** taking into account that unmodified oil was eliminated during the purification step.



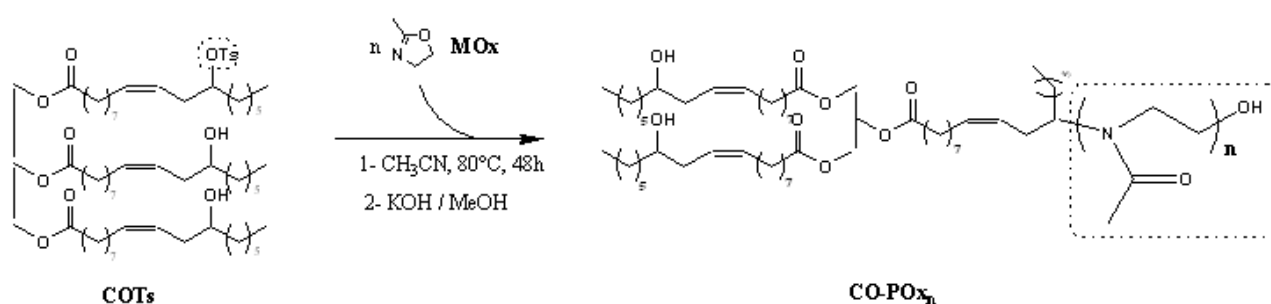
**Scheme 1:** Synthesis of vegetable oil macroinitiator COTs.



**Figure 1.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$  solution) of CO, COTs and CO-PO<sub>x<sub>n</sub></sub> (R=unreactive fatty acid chain).

## Polymerization of MOx based on COTs initiator

The polymerization of **MOx** was achieved using lipophilic macroinitiator **COTs** in refluxing acetonitrile for 2 days as shown in Scheme 2. The polymerization was terminated by adding a large excess of a KOH saturated methanolic solution and was kept at 30°C during 4 h. The copolymer was purified by slow precipitation from cold diethyl ether where the non copolymerized **COTs** remained soluble.



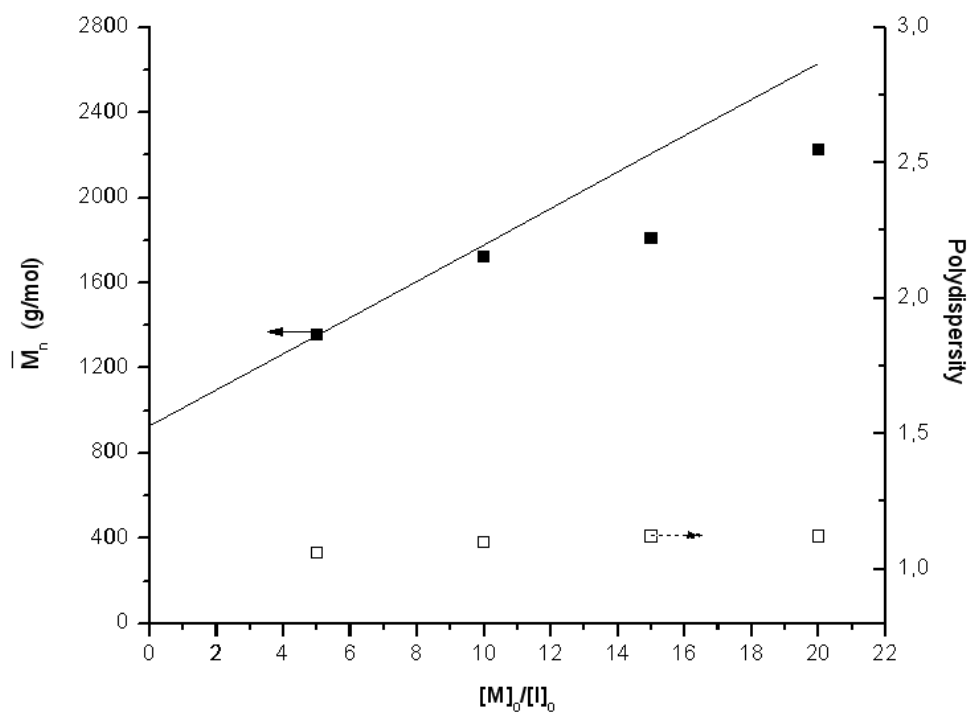
**Scheme 2:** Polymerization of **MOx** based on lipidic macroinitiator **COTs**.

The experimental number-average molecular weights measured by GPC analysis were smaller than the theoretical ones in the most of the cases. The narrow polydispersity were also obtained from GPC and ranged from 1.06 to 1.12 as summarized in Table 1. Until  $\overline{DP}_n$  of 10, the experimental values were consistent with the theoretical ones (Figure 2). For higher molecular weights, the experimental values deviated from the theoretical ones and should be explained by a decrease of initiator efficiency. In addition, the molecular weight versus conversion plot linearly increased with the conversion plot ( $\overline{DP}_n^{\text{th}} = 20$ ), as shown in Figure 3. The experimental values were lower than the theoretical ones and the shift between them might be related to the used PMMA calibration.

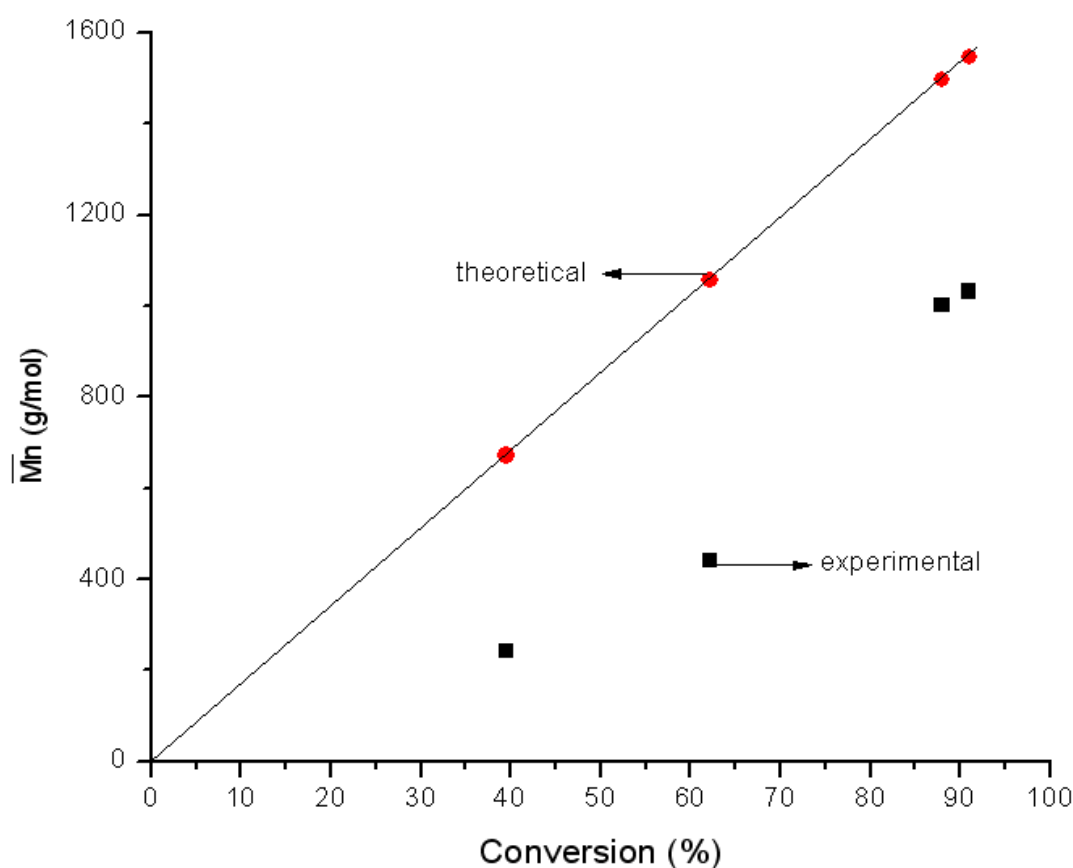
**Table 1:** Polymerization of **MOx** using **COTs** as initiator.

	$\overline{DP}_n^{theo}$	$\overline{DP}_n^{GPC}$ *	$\overline{Mn}_n^{GPC}$ (g.mol <sup>-1</sup> ) *	$\overline{M}_w / \overline{M}_n$ *
<b>CO-PO<sub>x</sub><sub>5</sub></b>	5	5.0	1354	1.0 <sub>6</sub>
<b>CO-PO<sub>x</sub><sub>9,3</sub></b>	10	9.3	1723	1.1 <sub>0</sub>
<b>CO-PO<sub>x</sub><sub>10,3</sub></b>	15	10.3	1810	1.1 <sub>2</sub>
<b>CO-PO<sub>x</sub><sub>15,2</sub></b>	20	15.2	2223	1.1 <sub>2</sub>

\*: Estimated by GPC in DMF based on PMMA standards.



**Figure 2:**  $\overline{M}_n$  and polydispersity obtained by means of GPC for **MO<sub>x</sub>** initiated by **COTs**.



**Figure 3:**  $\overline{M}_n$  versus monomer conversion for the polymerization of **MO<sub>x</sub>** initiated by **COTs** ( $DP_n^{theo} = 20$ ).

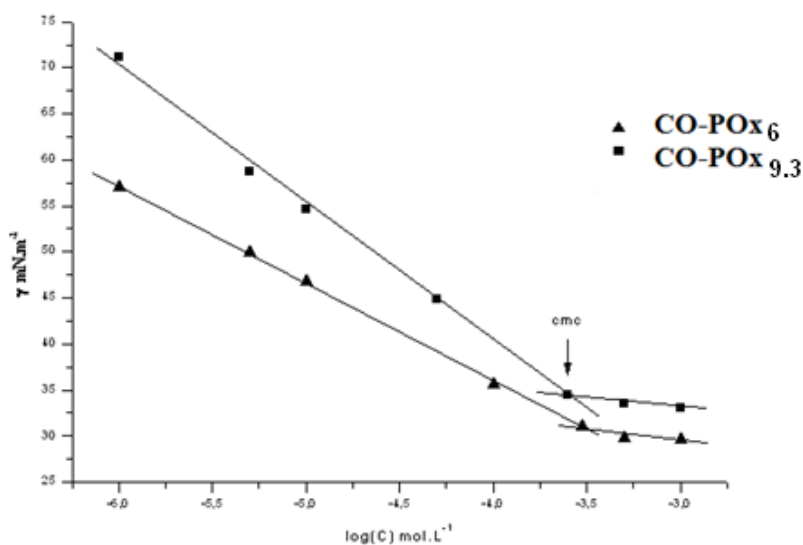
Various lengths of hydrophilic block were synthesized to evaluate the influence of the Hydrophilic-Lipophilic Balance, or HLB, on interfacial properties. This parameter was determined using the general formula applied for nonionic surfactants taking into account the weight fractions of the hydrophilic and of the lipophilic portions of the molecule (see experimental part) [27]. The approximative HLB values calculated for **CO-PO<sub>x6</sub>**, **CO-PO<sub>x9.3</sub>** and **CO-PO<sub>x15.2</sub>** ranged from 7 to 9.2, these values being close to that of usual hydrophilic surfactants.

The proof of the grafting of **PO<sub>x</sub>** segment onto the lipid backbone through an initiator **COTs** was also evaluated by the study of surface properties of the **CO-PO<sub>xn</sub>** compared to **COTs** films by measuring the contact angle of diodomethane drops onto the surface of the films. A remarkable difference existed between **CO-PO<sub>xn</sub>** and **COTs** contact angles with 50° and 15° respectively. This means logically that

hydrophilicity of **CO-PO<sub>x<sub>n</sub></sub>** increased in comparison to **COTs** precursor one and proved the grafting of **PO<sub>x</sub>** onto lipid macroinitiator.

### Self-assembly of **CO-PO<sub>x<sub>n</sub></sub>** in aqueous solution

The surface activity of **CO-PO<sub>x<sub>6</sub></sub>** and **CO-PO<sub>9,3</sub>** were characterized using surface tension measurements. Figure 4 displays the surface tension versus the logarithm of the concentration for **CO-PO<sub>x<sub>6</sub></sub>** and **CO-PO<sub>9,3</sub>** aqueous solutions. The decrease in surface tension with increasing concentration is typical of surface active molecules [27]. This behaviour is explained by the spontaneous adsorption of the amphiphilic molecules from the solution to the solution/air interface. Above the critical micellar concentration, or CMC, there is no longer any change in the surface tension of the solution as the water/air interface becomes saturated. The curves show sharp break enough to allow the accurate evaluation of the CMC, which is taken as the concentration at the intersection of the two linear portions of the  $\gamma = f(\log C)$  plots, where  $\gamma$  and  $c$  are the surface tension and the concentration of the solution, respectively.



**Figure 4:** Change in surface tension with log concentration of **CO-PO<sub>x<sub>6</sub></sub>** and **CO-PO<sub>x<sub>9,3</sub></sub>** at 298K.

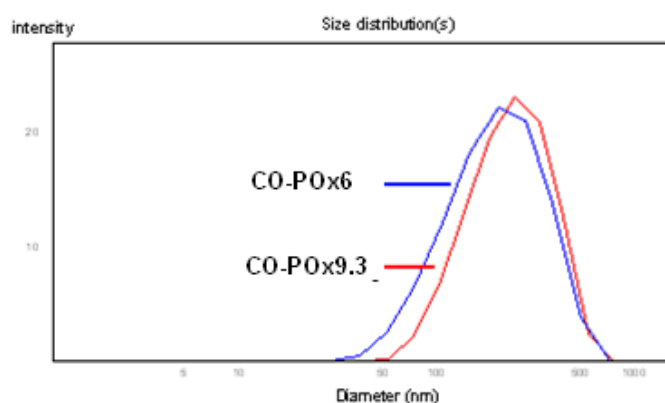
Table 2 lists the values obtained from these plots, CMC,  $\Gamma_m$  (maximum value of the surface excess concentration) and  $a_0$  (minimum head group surface area). The experimental values of CMC of **CO-PO<sub>x6</sub>** and **CO-PO<sub>9,3</sub>** were consistent with those of typical nonionic surfactants which were around  $10^{-4}$  mol.L<sup>-1</sup>. **CO-PO<sub>x6</sub>** and **CO-PO<sub>9,3</sub>** also show a surface tension of 34.5 and 30.0 mN.m<sup>-1</sup>, respectively. Additionally **CO-PO<sub>x6</sub>** exhibits a value of the cross-sectional area of 63 Å<sup>2</sup> while for **CO-PO<sub>9,3</sub>** the value is 88 Å<sup>2</sup>. The chemical nature, structure and length of the polyoxazoline hydrophilic block were essential in determining the surfactant behaviour in solution. Lengthening the polyoxazoline segment in the polar head group results in an increase of the CMC value and in its cross-section at the liquid-gas interface. This behaviour was consistent with the increase in the hydrophilic character of the surfactant molecules, which prevents the micellization. Indeed, the hydration of the headgroup and consequently the degree of repulsive interactions increase with the number of polyoxazoline units. Moreover, the corresponding values of the head group surface area (Table 2) were closed to those of usual surfactant molecules with two hydrocarbon chains [17]. This suggests that the polyoxyazoline group exhibits an extended conformation and penetrates into the water phase as it was characterized from X-ray reflectometry for a polyoxazoline lipopolymer **CO-PO<sub>xn</sub>** [28].

**Table 2.** CMC values, maximum values of the surface excess concentration and surfactant head group surface area ( $a_0$ ).

	$\gamma_{\text{CMC}}$	CMC	HLB	$\Gamma_{\text{max}}$	Head group surface area ( $a_0$ )
	mN.m <sup>-1</sup>	mol.L <sup>-1</sup>		μmol.m <sup>-2</sup>	Å <sup>2</sup>
<b>CO-PO<sub>x6</sub></b>	<b>34.5</b>	<b>2.5 10<sup>-4</sup></b>	<b>7</b>	<b>2.65</b>	<b>63</b>
<b>CO-PO<sub>x9,3</sub></b>	<b>30.0</b>	<b>3.0 10<sup>-4</sup></b>	<b>9.2</b>	<b>1.88</b>	<b>88</b>



DLS measurements indicate that polyoxazoline surfactants **CO-PO<sub>x</sub><sub>n</sub>** have a very strong propensity to form giant micelles or aggregates (Figure 5). The average size of aggregates observed in aqueous solution was about 200-300 nm with a large size distribution. The relatively high diameter, 300 nm, of these structures suggests the formation of vesicles or nonspherical micelles. Further research is currently being carried out to determine the structure and the morphology of these polyoxyazoline surfactant micelles.



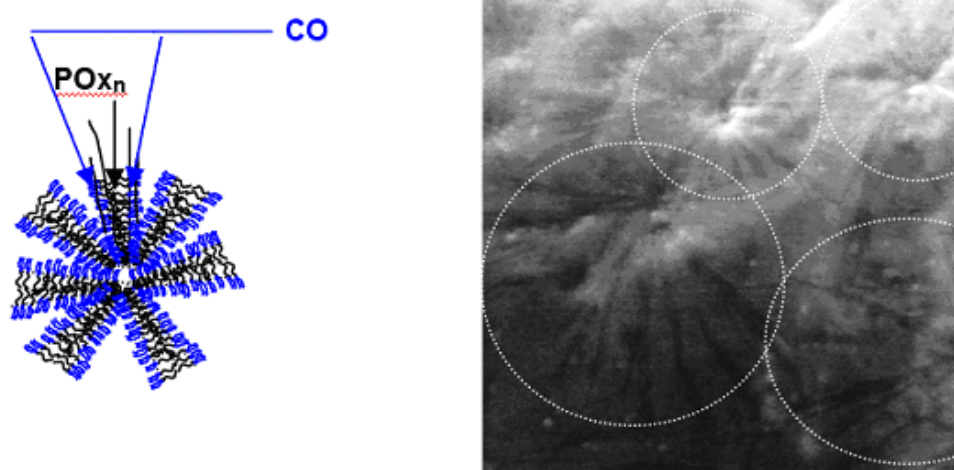
**Figure 5:** Distribution of hydrodynamic radius ( $R_h$ ) for **CO-PO<sub>x</sub><sub>6</sub>** and **CO-PO<sub>x</sub><sub>9.3</sub>** at 298K.

### Cooperative organization of CO-PO<sub>x</sub><sub>n</sub> in solid state

To determine the organization in the bulk and identify the ordered nanopattern of **CO-PO<sub>x</sub><sub>n</sub>** the segregation of lipophilic and polyoxazoline parts was studied by evaporation from concentrated aqueous solution as previously mentioned in the case of poly(2-oxazoline) multiblock copolymers deposited onto surfaces [29, 30]. The nanopatterns result from the precipitation of one part of amphiphilic surfactant. The evaporated solvent and the limit of solubility of the less soluble part induced its precipitation and the formation of nanopatterns since the other part remains still soluble. In our case environmental scanning electron microscopy (ESEM) and energy dispersive X-ray (EDX) analysis were used. During ESEM analysis the pressure in the chamber of the microscope slowly rose to avoid any degradation and

let gradual evaporation of water contained in the sample. In a first step, **CO-PO<sub>9,3</sub>** sample was analysed after spraying water at the surface to favor the self-organization. A variety of ESEM images of the **CO-PO<sub>9,3</sub>** were taken and one of them is shown in Figure 6. Under a pressure of 0.87 torr, no pattern appeared on the surface of the sample while under 2.87 torr some star-shaped morphologies with numerous stripes distributed in the radial direction were observed. The number and the length of stripes per star-shaped morphology varied as well as the size of the patterns ranged from 50 to 200  $\mu\text{m}$ . Star-shaped patterns were spontaneously generated by drying under pressure and illustrate the influence of the evaporation in the cooperative organization in the bulk.

By EDX analysis, nitrogen elemental percentage was quantified and gave information about the spatial distribution of **PO<sub>x</sub>** in the sample because only polyoxazoline unit contains nitrogen atom in the surfactant structure. Compared to nitrogen elemental percentage in EDX analysis, the value measured in arms was up to 6 folder higher than matrix one. Thus the hydrophilic **PO<sub>x</sub>** block was mainly isolated in the concentric surface stripes (black zone) and of course the fatty acid chains were localized in the matrix.



**Figure 6:** ESEM images of **CO-PO<sub>x9,3</sub>** in solid state.

## Conclusions

Nonionic polymer surfactants **CO-POX<sub>n</sub>** based on vegetable oil (castor oil) **CO** and poly(2-methyl-2-oxazoline) were synthesized with narrow polydispersity. From GPC study, the low molecular weights were consistent with theoretical values whereas a deviation appeared to the higher molecular weights.. The hydrophilic-lipophilic balance of the **CO-POX<sub>n</sub>** surfactants and their surface tension values correspond to those of usual nonionic surfactants. Thus the influence of surfactant HLB on the CMC was confirmed with higher values of CMC for longer polyoxazoline hydrophilic chains. The average size of aggregates of these structures suggests the formation of vesicles or nonspherical micelles. The cooperative organization by precipitation of **CO-POX<sub>n</sub>** was also shown in solid state with ESEM-EDX analysis which revealed a star-shaped morphologies where polyoxazoline **POx** was mainly localized in stripes.

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