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Thermal and structural characterization of a new surfactant based on 4-hydroxycoumarin by Differential Scanning Calorimeter (DSC) and Polarizing Optical Microscope (POM)

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Abstract

In this study, we synthesized new substituted coumarins, with the structure confirmed using ^{1}H nuclear magnetic resonance. Differential Scanning Calorimetry (DSC) and Polarizing Optical Microscope (POM) analysis were used to monitor the thermal behavior of the coumarin and its mixtures. DSC revealed a unique glass transition temperature for the first two products, the glass transition temperature of the third could not be determined.The variation in molecule density increases or decreases with increasing temperature, this was detected by the MOP. We see for instance small aggregates with a phase change that occurs between 25°C and 40°C, this phenomenon results in the formation of (micelles).This study is different from the others available because telomers using heterocycles are the speciality of our laboratory, several routes have been set to improve their synthesis and in particular the coumarin series.The latter are analogues of active substances. For example, thiophene series analogues of paullones have been evaluated on MCF-7 breast cancer cells.For Alzheimer's disease, the synthesis of numerous analogues of Tacrine, used as a treatment, have been carried out and the activities have been tested. Similarly, coumarin analogues have been evaluated for ROS (reactive oxygen species) reduction and phosphatase inhibition.

Keywords: Coumarin, nanomaterials, monomer, isotropic phase, Polarizing Optical Microscope, glass transition temperature.

1. Introduction

Coumarin and its derivatives have been used as light-sensitive materials for the preparation of micelles, vesicles and other photoresist polymer nanoparticles [1-11]. This is due to the presence of heterocycles within their structures, which gives access to a wide range of applications, mainly: biotechnology, biomedicine (anticoagulant, anticancer, antibiotic, antibacterial, anti-inflammatory, analgesic and anti-HIV activities) [1, 12-20], photochemical, food, pharmaceutical and cosmetic industries [21-23].

In recent years, researchers have been attracted to coumarin-based polymer nanoparticles, and photochemical processes are now used in fields ranging from microelectronics to stereo-lithography, energy, optics, coatings, adhesives and finally intelligent materials. [24-29].These smart materials are used in biointerfaces, for the transport of molecules and ions, in smart coatings (for systems that release active ingredients) and in corona virus applications. [11, 30-32].These smart solutions represent a class of materials that can stabilise, destabilise or reversecolloidal dispersions (emulsions, foams and suspensions) [33-37].

This phenomenon opens up new avenues in biochemistry by offering the possibility of exposing or concealing metal functions embedded in a heat-sensitive polymer, itself grafted onto the surface of a colloidal particle [38, 39]. These nanoparticles are influenced by three steps: separation of the target substance (trapping the virus between two phases), chemical or mechanical recovery of the phases and recovery of the target substance from the enriched phase (the crucial step).

Recently, a group of researchers used reversible photodimerisation of 7-hydroxy-coumarin to prepare new single-chain nanoparticles (Figure. 1)[40-43].

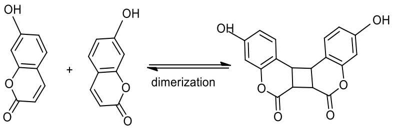

Figure. 1 Intra-chain photo-cross-linking of grafted photo-stimulable polymers [44-51].

This nanoscale structuring is composed of telomeres, which can influence the properties by changing their organisation. This helps us to make these telomeres capable of adapting to the environment to which they will be exposed during their application. Such telomeres are then called "intelligent molecules".

The change in aggregate size and/or architecture, structure and morphology is related to physical or chemical parameters, such as pH [33-37]. This can transform a micelle into tiny hollow spheres that enclose the solution or interchange the blocks that make up the core and crown respectively (Figure. 2).

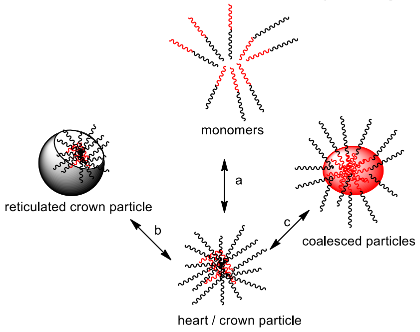

Figure. 2modifications and phase changes of particles [33-37]

Our study will focus on the stabilization of colloidal suspensions.The important point of these smart telomeres is the reversibility of the macroscopic changes they can undergo with a return to their initial state (figure 6, 7 and 8).

In this study, three coumarin based monomers were synthesized, whose structure is confirmed by nuclear magnetic resonance ^{1}H. Differential scanning calorimetry (DSC) and polarizing microscopy (MOP) were used to examine the main properties of coumarin solutions and their optical properties.What we foresee in the future is the addition of a chemical element to the solution -Zn for example- which is essentially good for the immune system and plays a fundamental role in health and nutritional well-being.

2. Experience

2.1 Equipment

Dodecanethiol is a colorless oily liquid with a slight foul and variant odor, molecular weight of 202.4 g/mol, the boiling point is between 266 - 283°C its density at 25°C is 0.845 g/ml. The 2-Butanol has a boiling temperature of 100°C, molecular weight of 74.122 g/mol. These products were purchased from Alfa Aesar (one of the leading manufacturers and suppliers of research chemicals, MA, USA). The 37% concentration of hydrochloric acid and methanol brand Fluka purchased from Sigma-Aldrich.

We used 4-hydroxy-coumarin as a starting material for the synthesis of three derivatives. Its preparation can be done by several methods from different phenols, such as:

The method of Jones et al. is applied to 2-hydroxyacetophenone can allow to obtain 4-hydroxy-coumarin in the presence of diethyl sodium carbonate in "one-pot". The reaction is heated under reflux in toluene for a few hours [52].

The measurement of the melting point is given by a Kofler bench.

2.2 Preparation of 4-dodecanethiocoumarin (product 1)

In a 250 ml tricol equipped with a cooler and a thermometer, 50 ml of distilled water is added to 1.17g ($72.22.10^{-4}$ mol) of 4-hydroxy-coumarin under stirring and at 50°C. After one hour 5g (24.70 10-3 mol) of dodecanethiol($C_{12}H_{26}S$) are added dropwise. The reaction medium is heated to 60°C for three hours. Hydrochloric acid is used to make the precipitate appear. The precipitate is filtered on Büchner and washed with water. The

resulting solid is recrystallized in ethanol.
The yield of the reaction is 87%. Melting point of product 1: 210°C.

RMN ^1H: (250 MHz, DMSO-*d6*) :δ_H 1.90 (s, 3H, CH_3), 2.2-2.5 (m, 1H, CH_2-S), 2.5-2.8 (m, CH_2-), 7.31-7.40 (dd, 1H, CH, J = 1.25, 10.202Hz). 7.50 (s, 1H, CH), 12.41 (s, 1H, OH)

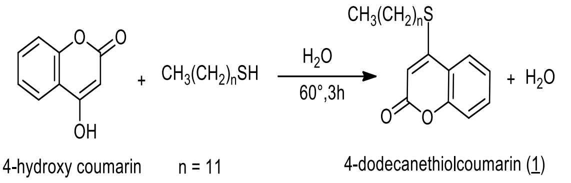

Schéma.1 Preparation of
4- dodecanethiolcoumarin(**1**)

2.2 Preparation of 4-sec-butoxycoumarin (product 2)

In a 250 ml tricol equipped with a refrigerant and a thermometer, 100 ml of distilled water is added to 3.45g of 4-hydroxycoumarin ($21.3.10^{-3}$mol), 10g of 2-butanol ($13.51.10^{-2}$ mol) is added gradually with temperature rising. The solution is stirred for 3 hours and then the temperature is set at 90°C.
We proceed in the same way as the previous reaction by decanting.

RMN ^1H: (250 MHz, DMSO-*d6*) :δ_H1.38 (d, 3H, CH_3), 3.30-3.70 (q, 2H, CH_2) 4.5 (m, 1H, CH), 6.33 (s, 1H, CH), 7.22-7.30 (m, 2H, 2xCH), 7.35-7.40 (dd, 1H, CH, *J* = 1.25 Hz).

The yield of the reaction is 90.22%.
Melting point of product 2 is: 198°C

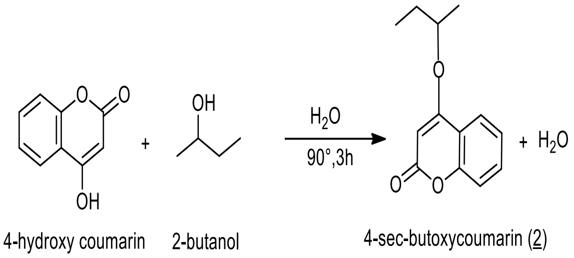

Schéma.2 Preparation of 4-sec-butoxy coumarin (**2**)

2.3 Preparation of 4,7-dihydroxy coumarins (Product 3)

This time, a 250 ml flask is taken directly without refrigeration, 50 ml of distilled water and 2.44 g (15.06.10-3 mol) of 4-hydroxy coumarin are introduced. The temperature of the reaction will be fixed at 0°C with stirring. The handling is left for 3 hours.
At the end of the reaction, the solution is permitted to cool. Afterwards, the solution is poured through a funnel into a beaker on filter paper.
The final product is a white powder, it is 4,7-dihydroxycoumarin.

RMN ^1H : (250 MHz, DMSO-*d6*) : 5.49 (s, 1H, CH), 7.12-7.16 (m, 2H, 2×CH), 7.65-7.70 (d, 1H, CH, *J* = 7.75 Hz), 12.41 (d, 2H, 2xOH).The yield of the reaction is 62.08%. Melting point of product 3: 221°C.

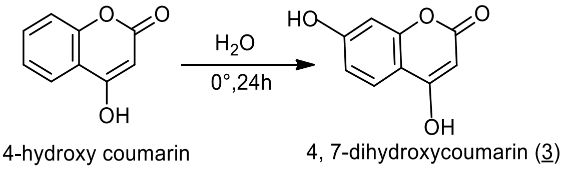

Schéma. 3 Preparation of 4, 7-dihydroxycoumarin (**3**)

3. Characterization

The ^1H nuclear magnetic resonance (NMR) spectra were recorded using a Varian UNITY INOVA 500 instrument, with DMSO-d6 and tetramethylsilane as the external standard. Chemical displacements are given in parts per million (ppm).
The dynamic hardening kinetics was determined using a differential scanning calorimeter (Pyris Diamond-Perkin Elmer instruments).
The operating principle of this device is based on the measurement of the energy required to establish a temperature difference close to zero between the substance (sample intended for measurement) and the inert product of the reference. Both sample and reference furnaces are subjected to the same temperature regime in

a heated and cooled environment at a speed controlled by a computer program (Pyrissoftware version 4.00) [53, 54].
Operation is done under N_2 atmosphere.
Before submitting our samples into the machine, we had set the parameters of this one. The heating rate is 10°C/min (constant speed), the mass of the sample to be put into the hermetic aluminum crucible fixed at 13 mg (machine standard), we submitted our samples in the differential thermal analysis apparatus, the temperature taken between 50 and 450°C.
An isothermal level of 15 minutes at a temperature above T_f and below the temperature of the chemical decomposition, in order to be sure to destroy all the crystalline lamellae, and at the end, a cooling at 10°C/min until the ambient is done (constant speed).

Our surfactants are directly solubilised in an aqueous solution and left under agitation until thermodynamic equilibrium is reached to obtain aggregates.
These aggregates are characterized by structural variables called aggregation parameters (aggregation number, hydrodynamic radius and crown thickness). Other characteristic parameters are the critical micellar concentration (CCM) and the critical aggregation temperature (CAT) [54], which correspond to the concentration and temperature at which the aggregates form. The determination of these parameters involves different analytical techniques: polarising optical microscopy, spectroscopy, light scattering, chromatography, viscometry and tensiometry [54].

Polarized optical microscopy is an ideal tool for determining the morphology of solutions, the observation limit of objects is of the order of micrometer. Observations by polarized light optical microscope have been performed from 25°C to 80°C, passing through 40°C. Phase diagrams are established by monitoring the morphology of the solution by varying the temperature (from 25°C to 80°C) at a well determined concentration [53,55].

4. Results and Discussion

4.1 Determination of physical and thermal properties by DSC

a) Treatment of product **1**

The melting of 4-dodecanethiocoumarin **(**Product **1)** takes place over a more or less wide temperature range depending on the amount of product (figure. 3). In this figure, the melting temperature ($T_f$is taken between 215 and 220.45°C). It is taken at the maximum of the endotherm of the DSC curve, which corresponds to the melting of Product**1**.
In our case, fusion is an endothermic transition which, on heating, has caused product **1** to change from its solid crystalline state to a liquid state. The melting point is not well defined (215-220.45°C), in fact crystallites of different sizes do not melt at the same temperature. For this reason, we can see the slightly wide peak pointing to the right. The enthalpy of fusion is the energy necessary for fusion and is calculated by integration of the DSC peak as a function of time, it is the hatched surface, the crystallinity rate is calculated from the ratio between the enthalpy of fusion of the sample ΔH_f calculated previously and that of the same material entirely crystallized $\Delta H_f°$ (ΔH_f/ $\Delta H_f°$), ΔH_f is equal to 1875J/g.Another change of state seen at a temperature of 230°C. This behaviour is indicative of Product **1**which can react with the solvent and induces a smaller increase in the temperature of the solution. Thus, the glass transition temperature (*Tg*) increases by 12°C (*Tg* = 230°C), with a mass loss of 52%, which confirms the loss of mobility of the chain after the reaction.
The wider glass transition region also suggests that the degree of cross-linking or dimerization of the thiol of the individual chains may vary, which is consistent with the slight increase in temperature (figure. 3).

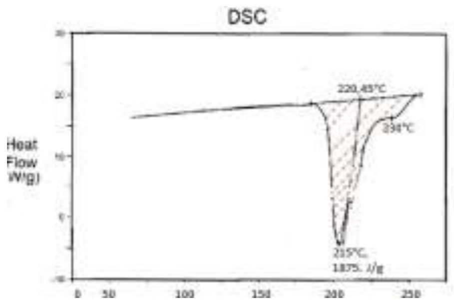

Figure. 3 DSC curve of 4-dodecanethiocoumarin, product **1**

b) Treatment of product **2**

The solid sec-butoxy, 4-coumarin **(**product **2**) melts at 167 °C, this absorbs more heat to be able to increase its temperature at the same rate as the reference. The endothermic phase transition has an energy of 145 J/g (figure. 4). Similarly, the sample can undergo exothermic processes, such as crystallization, this is noticed around 360°C when it transmits heat to the system (ΔH_f= 3251 J/g). Figure 3, shows a curve that increases with a circular trajectory around this temperature, if we assume that the temperature 450°C is that of recrystallization *Tc* (exothermic peak) represented by the small drawing in the center of figure 3, so beyond this temperature the curve is symmetrical and the energy will be higher than 3251 J/g.

280°C will be the glass transition temperature of product **2**.

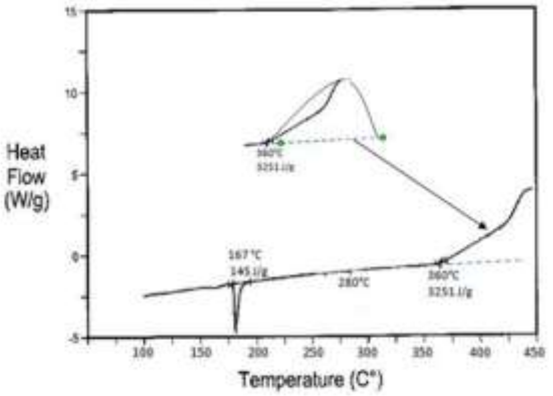

Figure. 4 DSC curve of 4-sec-butoxycoumarin, the product **2**

c) Treatment of the product **3**

Figure. 5 shows three peaks, the first peak is an unknown product that melts at 130°C, the latter can only be impurities, the presence of two peaks at 210°C and 244°C, even after a second heating, is not due to the evaporation of the solvent (ΔH = -5874 J/g). They correspond respectively to the dissolution of di-coumarin ether which we assume to be a secondary product and 4,7-dihydroxy-coumarin respectively. Thermal decomposition will start after 198°C and is maximal at 244°C. The curve stabilizes from 475°C.

The very sharp endothermic crest with a maximum at 244 °C, mentions that the resulting 4,7-dihydroxy-coumarin is thermoplastic, it is necessary to note the good correlation between these DSC results and those given in the bibliography.

The emulsion of 4,7-dihydroxy-coumarin shows a certain weight loss of 2%, which is due to the solvent. From this figure (Figure. 5), it is impossible to determine the glass transition temperature *Tg*. The thermogram is different to those given by the two previous products **1** and **2**.

It is very interesting to mention that the T_f temperature of 4,7-dihydroxy-coumarin remains unchanged even after a second heating.

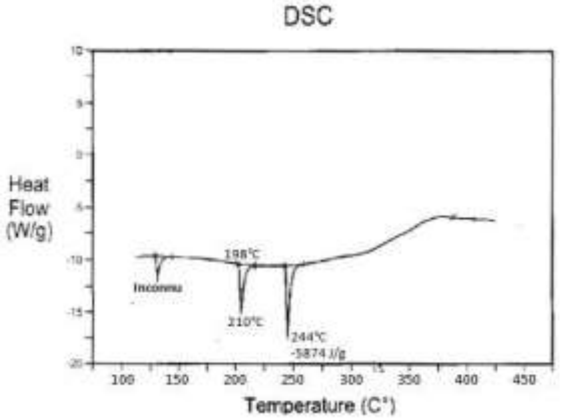

Figure. 5 DSC of 4,7-dihydroxycoumarins, the product **3**

4.2 Polarizing Optical Microscope (POM)

a) Morphology of the solution of product **1**

Figure. 6a of sample 1 shows an example of small crystals (droplets) dispersed in the solution with beautiful iridescent colors. When heated to 40°C (figure. 6b), a phase separation phenomenon with a change in color appeared (the solution became clear). Indeed, the product loses its initial properties and tends towards a mesomorph where the material is represented by two characteristic phases; this phenomenon is translated by the regrouping of crystals (droplets) in the solution and the appearance of small aggregates [56 - 61].

At 60°C, aggregates are formed.

b) Morphology of the solution of product 2

At 25°C, the solution is dark concentrated green with two black spots (figure. 7a). These nanostructures change and alter its organizations by influencing the properties. [56-61].

During the first heating at 40°C, the micelles (black spots) appear a bit like waves, almost instantaneously, the product chooses the shape that requires less energy by concentrating a bit more (figure. 7b).

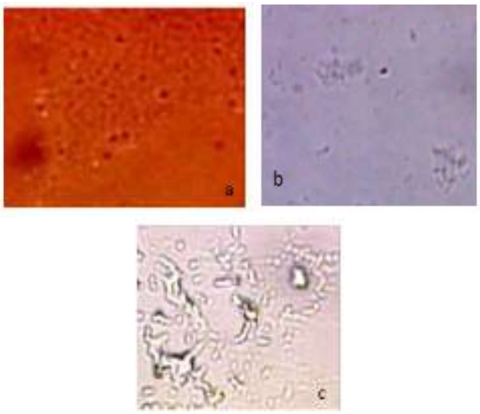

Figure. 6a) dispersed molecules at 25°C.
b, c) formation of micelles at 40 and aggregates at 60°C.

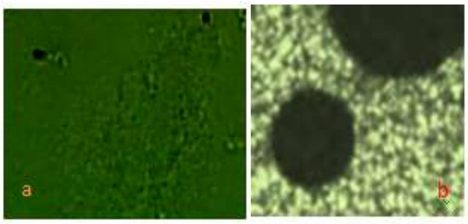

Figure. 7 a) Molecules dispersed between 25° and 40C.
b) As the temperature rises, black spots (aggregates) appear around 60°C.

c) Morphology of the product 3

Figure. 8a shows a large variation in the density of molecules, with sizes increasing as the temperature increases. At 40°C small aggregates can be seen (formation of micelles). The product transforms completely to an isotropic phase (figure. 8c).

We continued to heat up to 100°C, to make sure that there is only one isotropic phase.

The product becomes black [56-61].

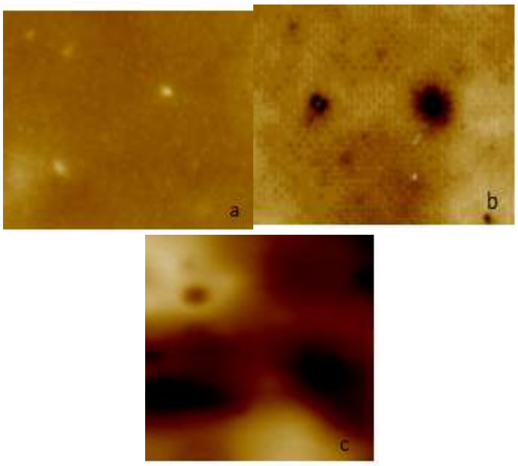

Figure. 8 a) Dispersed molecules at 25°C
b) At 40, phase change with formation of black spots (aggregates).
c) As the temperature increases, the number of aggregates increases.

5. Conclusion

In this work, we examined the thermal and optical properties of oligomers to extend their industrial applications.

First, we synthesized three surfactants in the chemistry laboratory. The synthesis was interesting in terms of manipulations. It gave a very satisfactory result, with a good yield.

This practical part was very complete.

In order to follow the evolution of the thermal behavior and to examine the phase transitions and to see also the thermodynamic behavior during heating and cooling.

The morphology of the phases obtained is therefore directly related to the nature of the product and the experimental conditions of obtaining it.

What we have found is that our products are strong with remarkable properties. Our materials have given us characterization results that slow down the degradation of oligomeric chains. The different products have remained intact despite the time that has passed since their synthesis.

The synthesized samples can find uses as anticorrosive paints to be used in strongly basic or acidic media at relatively high temperatures for up to six months without modification. The field of nanoparticles is not yet mastered; many works can be envisaged in order to improve the conditions of synthesis of these systems to obtain materials of choice.

6. Perspective

In Algeria, an estimated 15,000 people suffer from end-stage renal failure. This is due to the quality of treatment techniques which are the main causes of the increase in the number of patients with this chronic pathology.

One of the perspectives of this work is to prepare a coumarin molecule which, by increasing its concentration, forms aggregates in the kidney.

These molecules filter directly into the bloodstream without passing through analytical techniques. The experiments will be like a survey proposed to the Ministry of Health, which will in turn help us publish the results and take stock of the patients at national level.

Acknowledgements

Collate acknowledgements in a separate section at the end of the article before the references and do not, therefore, include them on the title page, as a footnote to the title or otherwise. List here those individuals who provided help during the research (e.g., providing language help, writing assistance or proof reading the article, etc.).

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