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Physicochemical Properties and Proposed Mechanism in the Obtainment of 4-Hidroxycoumarin Conjugated Polymers Using MALDI-T of Analysis

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ABSTRACT

The mechanism for the poly-condensation event of conjugated polymers with ending 4-hydroxycoumarin has been proposed. It happened under H_2SO_4 acidic conditions only using enolic-coumarins without any substituent at third position. It was studied using Matrix assisted laser desorption/ionization time-of-flight (MALDI-Tof) mass spectrometry. Besides, some physicochemical properties were analyzed using Thermo-gravimetric (TGA), X-ray and UV-Vis analysis.

***Keywords*:** Self-condensation mechanism, MALDI-Tof, X-ray, TGA, UV-Vis,telechelic polymer, applications

I. INTRODUCTION

Fragmentation of analyte molecules upon laser irradiation can be substantially reduced by embedding them in a light absorbing matrix. As a result, intact analyte molecules are desorbed and ionized along with the matrix and can be analyzed in a mass spectrometer. This soft ionization technique is mostly combined with time-of-flight mass analyzers. So, Tof-MS not only presents the advantage of being capable to provide a complete mass spectrum per event, but also it has virtually unlimited mass range, needs small amount of analyte, and the equipment has a relatively low cost.[1-6]

In the last years, coumarins polymers have emerged as structures with important nonlinear optical (NLO) properties. This field is concerned with the interactions of electromagnetic fields and different material such as coumarins polymers to produce compounds with changes in phase, frequency or amplitude. The main applications of these materials with nonlinear optical properties are in doublers of frequency for lasers, optical communications, computers and laser resistance devices.[7]

X-ray scattering are largely used to calculate the periodicity and the thickness of constituent phases in the one-dimensional model for semi-crystalline compounds. The decrease of the periodicity was undoubtedly observed with the increase of the isothermal crystallization time, while the ambiguity in the attribution of the phases to the amorphous and crystal thickness was source of large debate.[5, 6]Also stability and thermal behavior can be used to determine the sample moisture content, hydration level, and decomposition temperature.

In thermogravimetry (TGA), the change in sample mass is measured by a thermo-balance as a function of temperature or time. In a related method, differential thermal analysis (DTA), the temperature difference between a sample and a reference material is measured.[8, 9]Furthermore the composition of polymer materials can be determined by measuring their infrared spectra using a Fourier transform infrared (FT-IR) spectrometer and then comparing the results with a commercially available or specifically prepared spectral data base.[10, 11]As coumarins have chemical, biologics and physicochemical advantages, they result attractive to be incorporated into a polymeric chain. Taking in account our previous work [12] where semi-telechelic polymers with a functional group 4-hydroxycoumarin were prepared, we try to elucidate the mechanism of synthesis involucrate and some physicochemical properties of these compounds. Herein, we describe the polymers preparation using different synthetic pathways and the employment of thermo-gravimetric and spectroscopies analyses.

II. EXPERIMENTAL

Samples

All identified polymers were made in a single reaction in a 125 ml round-bottom flask equipped with a stir bar. 4-hidroxicoumarin and the other coumarins employed in each reaction (200 mg, 1.2 mmol) were added to 20 ml of acetone, or butanone, or cyclehexanone (3.6 mol). Then, increased concentrations of sulfuric acid: 0.5%, 1%, 2%, 3%, 5%, 10%, 20% and 30% v/v, were added successively under argon atmosphere and air atmosphere. This yellow solution was stirred at 80° C for 12 h (when we used toluene as co-solvent, temperature reaches 105 °C and in *p*-xilene co-solvent 138 °C). After cooled to room temperature, sodium carbonate 10% v/v solution was added, and the mixture was stirred for 20 min whit ethylic ether. Organic layer was then separated and wash tree times with distillated water. After dried with anhydrous sodium sulfate, the solution was concentrated giving yellow-orange oil which was chromatographed on silica gel (1:9 ethyl acetate / hexane) to afford products as intense orange viscous oil.

MALDI-Tof/Tof MS and LDI-Tof/Tof MS **Analysis**

See reference [12] for details.

Diffraction X-Ray

The initial structural identification and characterization of the sample was carried out by laboratory XRPD (CuKα, λ: 1.5418 Å). XRPD diagrams were collected in a Rigaku D-Max-IIIC diffractometer with Bragg-Brentano geometry by using monochromatic CuK□ radiation (Ni filter) in a continuous mode from angular range $2° < 2\ \theta < 40°$. In order to allow the ordering of the hydrocarbonates chains, the sample was put in a holder and kept horizontal for 24 hours.

Thermal Analysis

Thermogravimetric (TGA) and differential thermal analysis (DTA) curves were obtained with a Shimadzu TGA-51 Thermal Analyzer and DTA-50 Thermal Analyzer, using platinum pans, flowing air at 50 ml/min and a heating rate of 10 °C/min from room temperature to 900 °C.

Uv-Vis Analysis

UV-Visible diffuse reflectance spectra of the collected material were recorded on a Cary Varian 5E spectrophotometer equipped with a PTFE-coated integration sphere. The optical absorption spectra were measured in a transmission mode on the same spectrophotometer using a quartz tube.

Energy Minimization Simulation

The Gabedit software package [13] was used to draw the polymeric molecule. The geometry was initially optimized using the classic quasi-Newton method, followed by semi-empirical optimization using the software MOPAC 2009,[14, 15] as implemented in Gabedit. This conformation was used to obtain the parameters and topology files for the GROMACS software package.[16, 17] It is afford a graphic interphase for computational chemistry packages. We used the following parameters:

Minimum RMS gradient: 0.10000
Step interval: 2.00000
Frame interval: 10
Terminate steps: 10000
Heating rate: 0
Target temperature: 300° K
Properties: π-bond orders and steric energy summary

III. RESULTS AND DISCUSSION

Synthesis and Structural Elucidation

Coumarins with different chemical groups and pattern of substitution and several concentration of sulfuric acid were usedin order to obtain polymers. The reaction products were characterized by MALDI-MS and LDI-MS (i.e., without needing the presence of a secondary molecule as photo-sensitizer or matrix in the sample). Using 4-hydroxycoumarin (which shows keto-enol behavior) as starting material the expected polymers were obtained (**Fig. 1**).

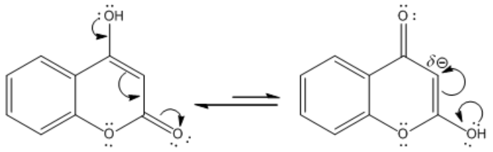


Fig.1. Keto-enolic equilibrium of 4-hydroxycoumarin showing the most negative carbon at C-3.

We also envisaged the synthesis of several polymers with higher building block weight using different ketones, like butanone, but none polymerization was observed by LDI-MS analysis of the reaction mixture. The reaction of 4-hydroxycoumarin in acetone with H_2SO_4 produce polymers with difference of 40 Da and the higher molecular weight detected was 562.6 Da.[12]Using other solvents with substantial higher boiling point like toluene and *p*-xylene, in the presence of acetone, it was observed the same pattern of 40 mass units repetitions of the main chain and new compounds with higher molecular weight (**Fig. 2**).

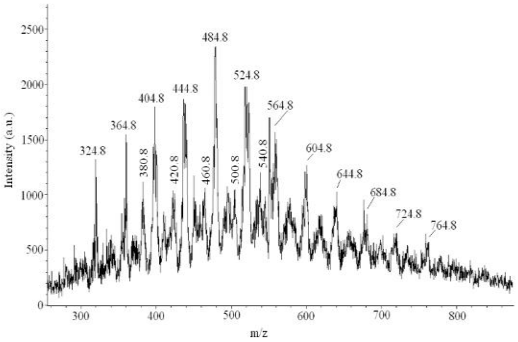
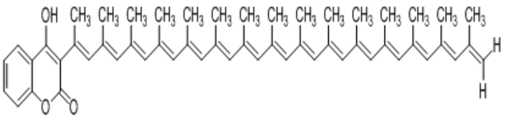


Fig. 2. Positive ion MALDI mass spectrum of reaction product of 4-hydroxycoumarin with H_2SO_4 5% in acetone and *p*-xilene; matrix employed: pirene.

For example, signal at *m/z* 764.8 can be assigned to a polymer with the following structure (with fifteen units of propene building block):



These results clearly indicate that an increasein the reaction temperature produce chain elongation with higher molecular weight polymers. Other coumarins were used in acidic acetone. The positive ion LDI mass spectrum of 6-hydroxycoumarin before the reaction is shown in **Fig. 3a**. Some intense signals are detected $[M + H]^+$ at *m/z* 163.13, $[M + Na]^+$ at *m/z* 185.17, $[M + K]^+$ at *m/z* 201.17, $[2M + Na]^+$ at *m/z* 347.32 and $[2M + K]^+$ at *m/z* 363.22). After the reaction (**Fig. 3b.**) no polymerization products were detected, but the reactant is no longer observed indicating that some reaction is taking place.

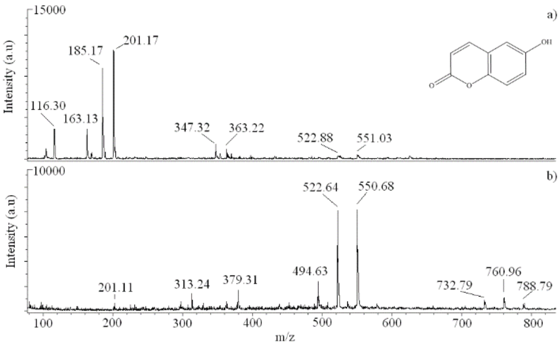


Fig. 3. Positive ion LDI mass spectra of 6-hydroxycoumarin with H_2SO_4 5% in acetone a) before the reaction b) reaction product.

A similar behavior was observed when 4-hydroxy-3-nitrocoumarin was studied. In this case the signals detected for the reactants were $[M + H]^+$ at *m/z* 208.25, $[M + Na]^+$ at *m/z* 230.25, $[M + K]^+$ at *m/z* 246.27, $[2M + Na]^+$ at *m/z* 437.32, $[2M + K]^+$ at *m/z* 453.34 and $[3M + K]^+$ at *m/z* 660.27 (**Fig. 4a.**). After the reaction takes place, when these compounds were used, those signals were not longer observed, however not evidence of polymerization was detected either (**Fig. 4b.**). This evidence suggests that phenol-coumarins that cannot form enolates like 6-hydroxicoumarin or when position three is occupied like 4-hydroxy-3-nitrocoumarin, were not able to form these materials, denoting the main role of keto-enol equilibrium presents in 4-hydroxycoumarin.

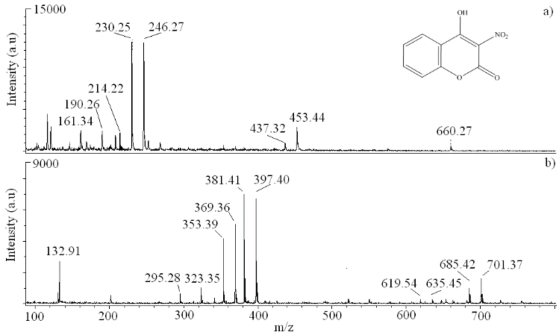


Fig. 4. Positive ion LDI mass spectra of 4-hydroxy-3-nitrocoumarin with H_2SO_4 5% in acetone a) before the reaction b) reaction product.

Proposed Mechanism for the Poly-Condensation Event

Respect to the origin of the fragments of 40 mass units and oligomeric chain, the followingbehavior is proposed (**Fig. 5**). In first time, we suggest the enolization of the solvent propanone with the consequent polarization of the oxygen atom. This phenomenon would occur spontaneously thanks to the acidity provided by the surrounding medium (H_2SO_4 5% has given the best yields), that generate a positive charge in the oxygen atom. An event like this would cause an environment devoid of electrons over the carbon adjacent, generating a potential electrophile, which would be able to suffer a nucleophilic attack. As we know, the aromatic compound 4-hydroxycoumarin is capable to submit forms keto-enolic, being located at position three of this core themost negative electron density. Therefore, this α-carbon adjacent to a carbonyl group could react with a polarized acetone molecule and condensewith different monomers of solvent. This reactionwould be able to extend the length of the strings by a cationic type polymerization. Finally, by loss of multiples water molecules, these chains become on polymers formed by repetitive units of propene. Furthermore, the new extended system might be the driving force for this dehydration.

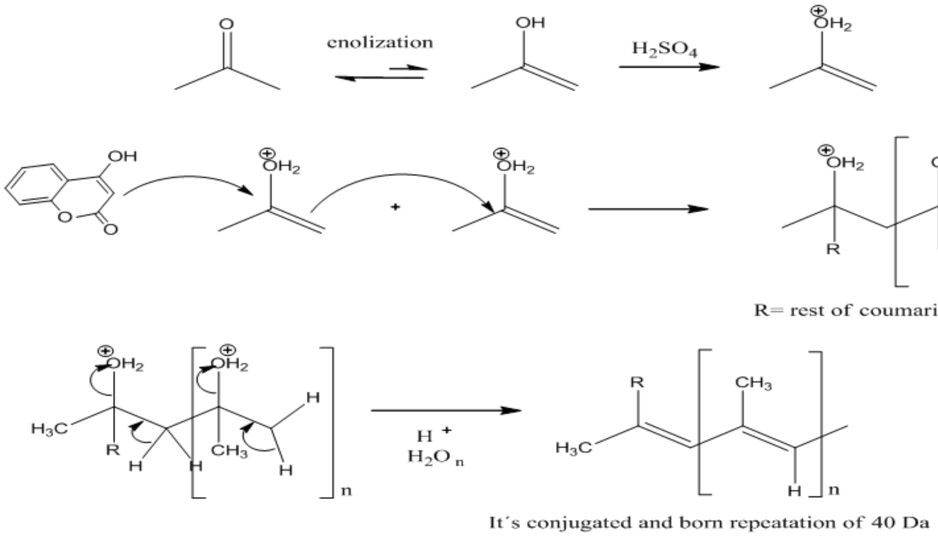


Fig. 5. Proposed mechanism for the poly-condensation event.

X Ray Diffraction Studies

To achieve an approximation of the macromolecular structure of these products an X-ray diffraction study was realized. **Fig. 6** shows the patterns of the glass sample holder (black) and this new material (red). Here, we can see the presence of two broad peaks centered in values of interplanar distances 5.4 Å and 7.4 Å, with a considerable intensity respect to the glass sample holder. The appearance of these peaks indicates the existence of one phase with some degree of order in the planes, which could be related to partial ordering of the hydrocarbon chains (combs of 40 mass units). The peak width at half height, which reaches approximately 6 Å, suggests thatthis arrangement is not complete, but occurs partially in the different zones within the semi-hard material.

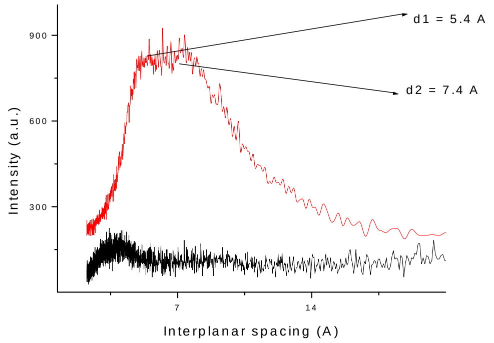


Fig. 6. X-ray diffraction pattern of collected material, employing length wave of = 1.5418 Å, *CuK*at room temperature.

Thermo-Gravimetric Analysis (TGA and DTA)

Fig. 7 describes the thermal behavior of the polymers obtained by calcination of the sample at 900 °C. Black line shows the TGA curve, two main mass losses can be observed. The first of these is between 60 °C and 400 °C, which corresponds to 86.3% of the total mass sample, followed by a second event that occurs between 400 °C and 600 °C, associated with a 12.6% loss of mass.This second event shows two exothermic peaks centeredat 467 °C and 568 °C in DTAcurves (red line), typicallyobserved in decomposition processes. Apparently, the TGA analysis shows that this material breaks down fast.

The differential analysis show that the first process occurs with a downward peak (300 °C) corresponding to an endothermic event, which is typical when aromatic compounds are presents (such as coumarin), because their start taking heat to break the aromatic system.

Regarding the thermal nature of the DTA peaks associatedwith the first decomposition, they present a complex pattern, which shows the existence of two exothermic peaks (339 °C and 393 °C).

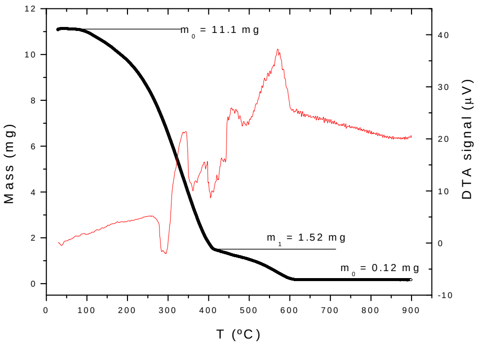


Fig. 7. Thermogram of the obtained material at the range of room temperature to 900 °C. In black: curve of TGA analysis. Red: DTA analysis.

UV-Vis Study

Coumarins show strong absorption in the UV-Vis region, nearly at 355 nm. The UV spectrum shows two considerable peaks at 230 and 266 nm with an excellent molar extinction coefficient of 1 x 10^5 for 230 nm(**Fig. 8**). This value gives potential applications as organic nonlinear optical material to these products.[18]

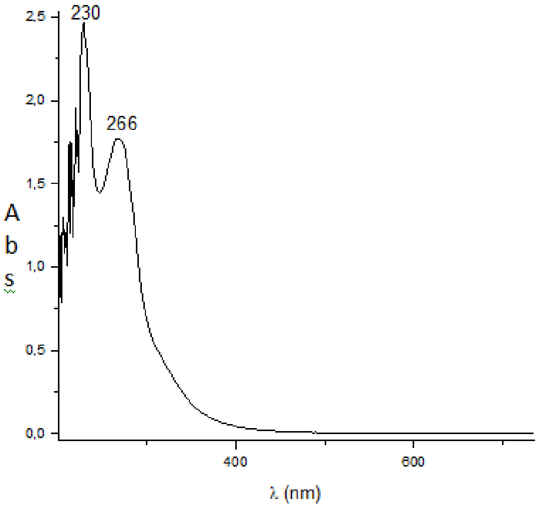


Figure 8. UV-Vis spectrum of collected material with 10^{-3} mM concentration and= 1 x 10^5 for 230 nm.

Energy Minimization Simulation Study

Observing the UV-Visible spectrum (**Fig. 8**)which showed absorption at 266 nm as a larger wavelength value, it is appears anomalous considering the number of conjugated double bonds presents. This phenomenon can be rationalized considering a possible steric inhibition of resonance due to the distance of separationfor the methyl groups in the side chain, which generates some steric hindrance. Using computer calculation was possible demonstrate that it is not possible to achieve a perfect coplanarity of all double bonds presents in the polyene chain (**Fig. 9**); as a matter of fact, some angle values were different to the 180° for *trans*-configurations and for those 120° expected in optimal sp^2hybridizations (this could be the reason for the hypsochromic shift observed).

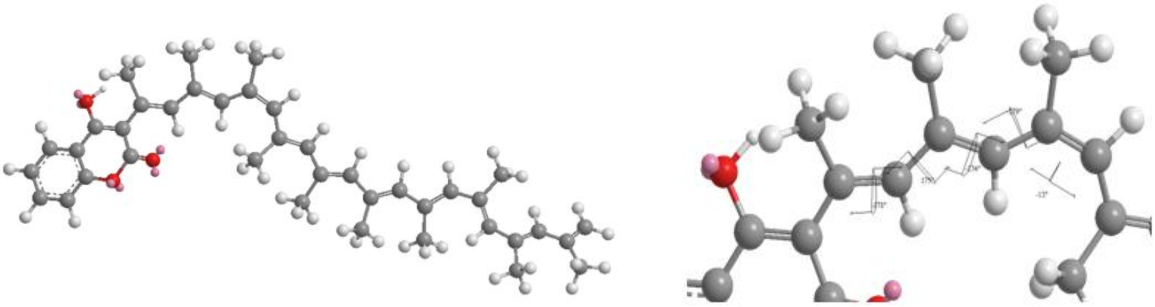


Figure 9. a) Tridimensional conformation of complete polymer obtained showing the lack of planarity. **b)** Zoom in showing anomalous values of dihedral angles.

Materials Solubility

During the process of synthesis there was not formed precipitate. After isolation and identification, the solubility of the material in the most common organic solvents was tested.These polymers are soluble in hexane, cyclohexane, DMF, diethyl ether, petroleum ether, carbon tetrachloride, chloroform, dichloromethane, ethyl acetate and methanol at room temperature, and logically in acetone. On the other hand, these samples are not soluble in water both at room temperature and boiling water. Finally, the sample was subjected to carbonization by incineration, and the resulting residue could not be dissolved in any of the previously mentioned solvents, including boiling water.

IV. CONCLUSIONS

MALDI-Tof spectra show that the main repeating unit in the obtained compound is a propene group which derives from dehydration of propanone solvent under H_2SO_4 acidic condition, but when other ketones are used no products were obtained. In the same way, coumarins that cannot form enolates or when position three is occupied were incapable to form these polymers. Moreover, this new material proved to have some degree of macromolecular order and elastic behavior, with potential applications on the field of nonlinear optics due to its extended conjugated system and its considerable molar extinction coefficient.

V. FUNDING

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