J. Mater. Environ. Sci. 6 (4) (2015) 1137-1141
ISSN : 2028-2508
CODEN: JMESCN

Synthesis and characterization of conjugated olygomers by acetone self-condensation end-functionalized with 4-hydroxycoumarin

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Received 07 Oct 2014, Revised 18 Nov 2014, Accepted 19 Nov 2014

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Abstract

A conjugated olygomer with ending 4-hydroxycoumarin has been prepared by condensation of acetone using sulfuric acid as a catalyst. The resulting polymer was characterized by Matrix Assisted Laser desorption/ionization Time-of-flight (MALDI-Tof) and Fourier Transformation Infrared Spectroscopy (FT-IR) methods.

Keywords: acetone, 4-hydroxycoumarin, MALDI Tof, self-condensation, telechelic olygomers

1. Introduction

In recent years, Matrix Assisted Laser desorption/ionization Time-of-flight Mass Spectrometry (MALDI-Tof MS) has become a routine analytical tool for the structural analysis and characterization of polymers. Peaks in the spectra, of this soft ionization technique, are originated from intact polymer molecule ions, and, therefore, allow structural identification of each single oligomer [1]. Also MALDI-Tof MS has increased the use of mass spectrometry for large molecules analysis and has revealed itself to be a powerful method for the characterization of both natural and synthetic polymers [2-9].

Coumarin (2H-1-benzopyran-2-one) moiety is present in a naturally occurring family of compounds distributed in a wide variety of plants, micro-organisms and some animal species. This moiety consists of an aromatic ring fused to a condensed lactone ring, being coumarins in general freely soluble in ethanol, chloroform, diethyl ether and oils and slightly soluble in water [10]. Frequently, coumarins can be hidroxylated in different positions, i.e., 4-hydroxycoumarin or 7-hydroxycoumarin (*umbelliferone*). Many compounds show biological activity, including antifungal, antibacterial and, the most well-known, anticoagulant activity [11-13].

Coumarins have been widely applied in analytical chemistry as luminescent probes, indicators and others as optical brightening agents in the textile industry, sensitizers in copying techniques, aroma-producing substances in foodstuffs, printing, and perfumery industries, organic reagents in laser technology, toxic chemicals in agriculture, and pharmaceutical preparations in medicine (i.e., evaluated for cancer treatment and HIV inhibitors) [14, 15]. Conjugated polymers have gained much interest as a novel class of semi-conductors and are frequently studied because of their interesting optical and electronic properties. One of the most important factors of controlling physical properties is the band gap, which is a current topic of research. Polymers with a low band gap are, in particular, desired in optoelectronic applications such as LEDS or solar cells [16, 17]. Coumarin derivatives are one kind of significant organic fluorescent chromophores, widely used to synthesize laser dyes and organic nonlinear optical material. Unfortunately, little attention has been paid to the incorporation of coumarins into polymers. A series of novel coumarin contained in monomers and polymers has been synthesized and characterized, i.e. polyamides derived from 6-ethynylphenyl coumarin dicarboxylic acid and aliphatic diamines, polyesters based on 6-(3´-hydroxy)-phenylcoumarin-3-carboxylic acid and 6,6'-biscoumarinyl-3,3'-dicarboxylic acid, and polynorbornene bearing 7-substituted coumarin in the side chain [14].

A major concern of polymer and material science is designing functional materials with physical features tuned to match the needs of expanding technology. In particular, end-functional polymers have an important economic position because of their possible applications as components in the synthesis of block copolymers, thermoplastic elastomers, polymer networks, surfactants, macromonomers, etc. According to the IUPAC, semi-telechelic polymers are defined as polymeric molecules with reactive end groups that have the capacity to enter into further polymerization or other reactions. Reactive end-groups in semi-telechelic polymers come from the initiator or the terminating or chain-transfer agents in chain polymerizations, but not from monomer(s) as in polycondensations and polyadditions. Funtionalization of polymer chain ends can also take place in post-polymerization reactions [18, 19].

Aldol simple condensations can be done usually in presence of alkali [20]. Also, acetone self condensation can be appeared under acidic conditions [21-23] and taking into account the chemical, biologic and physical advantages of coumarins is attractive to incorporate these moieties into a polymeric chain. Here, we report the synthesis and characterization of conjugated olygomers with 4-hydroxycoumarin (at the end) in acetone using acidic conditions.

2. Experimental methods

2.1. Synthesis: All identified olygomers were made in a single reaction in a 100 ml round-bottomed flask equipped with a stir bar. 4-hydroxycoumarin (200 mg, 1.2 mmol) was added to 20 ml of acetone (3.6 mol). Then sulfuric acid 5% v/v (and other acids like HCl or H_3PO_4) was added successively under argon atmosphere and air atmosphere. This yellow solution was stirred at 80 °C for 12 h. After cooled at room temperature, sodium carbonate 10% v/v solution was added, and the mixture was stirred for 20 min with ethyl ether. Organic layer was then separated and washed tree times with distillated water. After dried with anhydrous sodium sulfate the solution was concentrated given a yellow-orange oil, which then was chromatographed on silica gel (1:9 AcOEt / *n*-hexane) to afford products as intense orange viscous oil.

2.2.MALDI-Tof/Tof MS and LDI-Tof/Tof MS analysis

Ultraviolet matrix assisted laser desorption-ionization mass spectrometry (UV–MALDI MS) and ultraviolet laser desorption-ionization mass spectrometry (UV–LDI MS) were performed on the Bruker Ultraflex Daltonics Tof/Tof mass spectrometer. Mass spectra were acquired in linear positive and negative ion modes and with the LIFT device in the MS/MS mode. Stock solutions of polymers were prepared in methanol. External mass calibration was made using *β*-cyclodextrin (MW 1134) with *n*Ho as matrix in positive and negative ion mode. The matrix signal was used as an additional standard for calibration in both ion modes. Sample solutions were spotted on a MTP 384 target plate polished steel from Bruker Daltonics (Leipzig, Germany). For UV–MALDI MS matrix solutions were prepared by dissolving *n*Ho (1 mg/ml) in acetonitrile/water (1:1, v/v) solution, CHCA or SA (2 mg/ml) in methanol, dithranol (2 mg/ml) in $CHCl_3$, citric acid (1 mg/ml) in water. Saturated solutions of anthracene, pyrene and acenaphtene in THF were used as matrices. For UV-MALDI MS experiments dry droplet sample preparation or sandwich method was used according to Nonami *et al.* [24] loading successively 0.5 μl of matrix solution, analyte solution and matrix solution after drying each layer at normal atmosphere and room temperature. The matrix to analyte ratio was 3:1 (v/v) and the matrix and analyte solution loading sequence was: i) matrix, ii) analyte, iii) matrix, iv) matrix. For UV-LDI MS experiments two portions of analyte solution (0.5 μl x 2) were loaded on the probe and dried successively (two dry layers). Desorption/Ionization was obtained by using the frequency-tripled Nd:YAG laser (355-nm). Experiments were performed using firstly the full range setting for laser firing position in order to select the optimal position for data collection, and secondly fixing the laser firing position in the sample sweet spots. The laser power was adjusted to obtain high signal-to-noise ratio (S/N) while ensuring minimal fragmentation of the parent ions and each mass spectrum was generated by averaging 100 lasers pulses per spot. Spectra were obtained and analyzed with the programs FlexControl and FlexAnalysis, respectively.

3. Results and discussion

3.1. Synthesis and structural elucidation using MALDI-Tof

Since coumarins show strong absorption in the UV-Vis region, particularly at 355 nm, laser desorption ionization (LDI) mass spectrometry (LDI-MS), without needing the presence of a secondary molecule as photo-sensitizer or matrix in the sample was also used. The MALDI- and LDI mass spectra obtained in positive ion mode (**Fig. 1**) show several peaks of interest to rationalize the polymerization reaction.

The relevant information is the presence of a family compounds obtained by successive addition of a block of exactly $m/z = 40$ as a repeating unit (i.e., $m/z = 322.3, 362.4, 402.5, 442.5$, etc.) This moiety probably is formed from acetone (MW 58) after losing a water molecule (MW 18). The result of these successive events leads to the formation of the repetitive propene building block (MW 40) and the compounds of the series. The series of signals at *m/z* 340, 380, 420, 460, etc., also underlines the main role of the *m/z* 40 building block. This series also comes from the same process of polymerization, but in this second kind the signals are shifted to higher values in + 16 *m/z* unities. This difference can be explained adding a moiety that includes one oxygen atom additional to the propene building block, in other words an isopropoxy group.

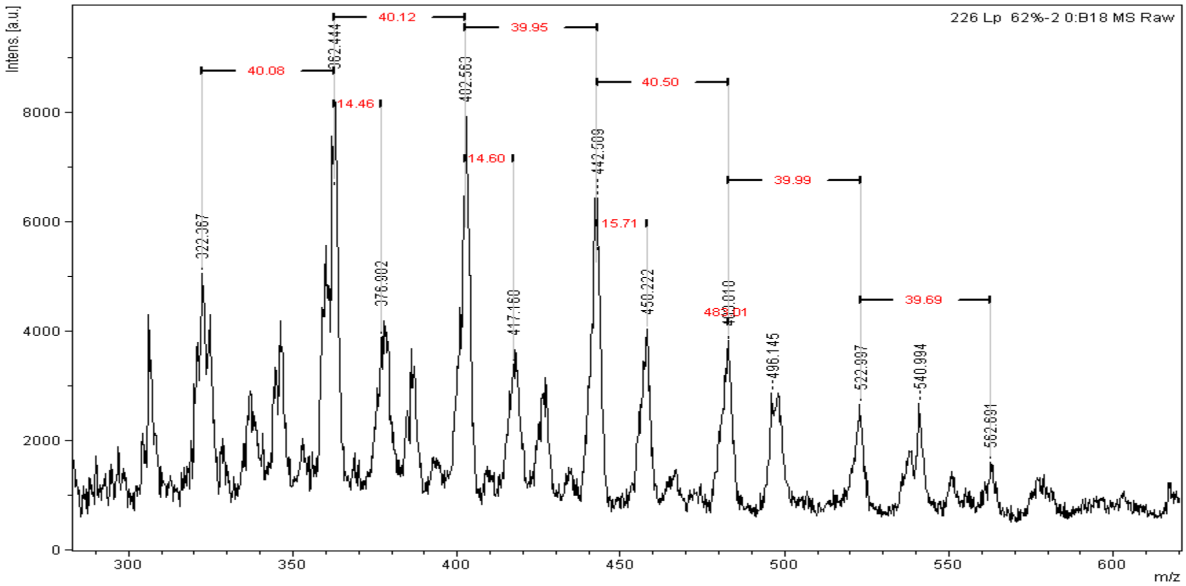
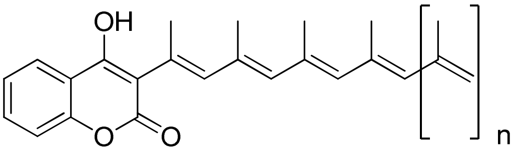
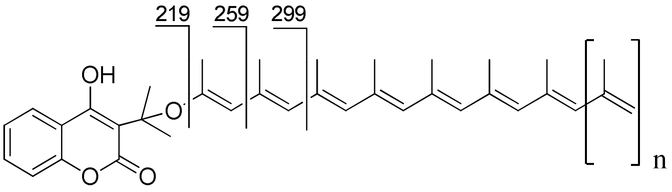


Figure 1. Positive ion mass spectra LDI-MS. Reaction of 4-hydroxycoumarin in acetone with H_2SO_4.

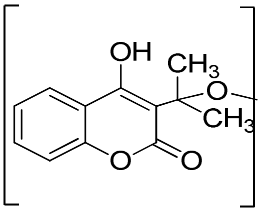
Polymeric chains can be formed by successive incorporation of protonated acetone molecules from the solvent. The most abundant peak in positive mode at *m/z* 362.8 ($[M + H]^+$ *experimental*) can be attributed to the following structure:



Based on these results we can identify two types of polymers that include only one fragment of 4-hydroxycoumarin and different number of blocks from acetone. The first family of compounds is made only by repetitive units of 40 *m/z*, from completely dehydrated acetone molecules. Another family of polyenes produced may include an extra oxygen atom, possibly coming from one molecule of protonated acetone as the isopropoxy moiety [$(CH_3)_2CO$-]. For example fragment at *m/z* = 540.9 shows one extra oxygen atom as follows:



These olygomers with isopropoxy moiety present in the chain can also be supported by the LDI-MS experiments conducted in negative ion mode. For example **Fig. 2** shows an intense peak at *m/z* 219.89, assigned to the following structure:



When other acids like hydrochloric or phosphoric are used, polymerization products are not observed. For example, when 4-hydroxycoumarin was used in the presence of HCl and acetone, none polymerization was observed by LDI-MS analysis of the reaction mixture. However, some reaction is taking place since signals of reactant ($[M + H]^+$ at *m/z* 163.04, $[M + Na]^+$ at *m/z* 185.07, $[M + K]^+$ at *m/z* 201.08, $[2M + Na]^+$ at *m/z* 347.19 and $[2M + K]^+$ at *m/z* 363.15, are observed after the process (*supplementary material*).

3.2 FT-IR spectroscopy characterization

Finally, to confirm the molecular structure and the aggregate of 4-hydroxycoumarin fragment a FT-IR spectroscopic study was made. Here, we can see the spectrum that encompasses the range from 200 to 4000 cm^{-1} (**Fig. 3**), it was possible to observe a typical signal of carbonyl group from a conjugated lactone (1740 cm^{-1}) denoting the presence of the coumarin end group. Other typical signals from the propene chain are the very strong peak near 2950 cm^{-1} corresponding to the C-H bonds stretching from methyl and vinyl groups, and the characteristic band at 1640 cm^{-1} corresponding to C=C bond. This IR spectrum of 4-hydroxycoumarin superposed with the spectrum obtained for these olygomers, denoting the incorporation of 4-hydroxycoumarin at the polyene main chain, making the incorporation of coumarins a tool for develop semi-telechelic prepolymers.

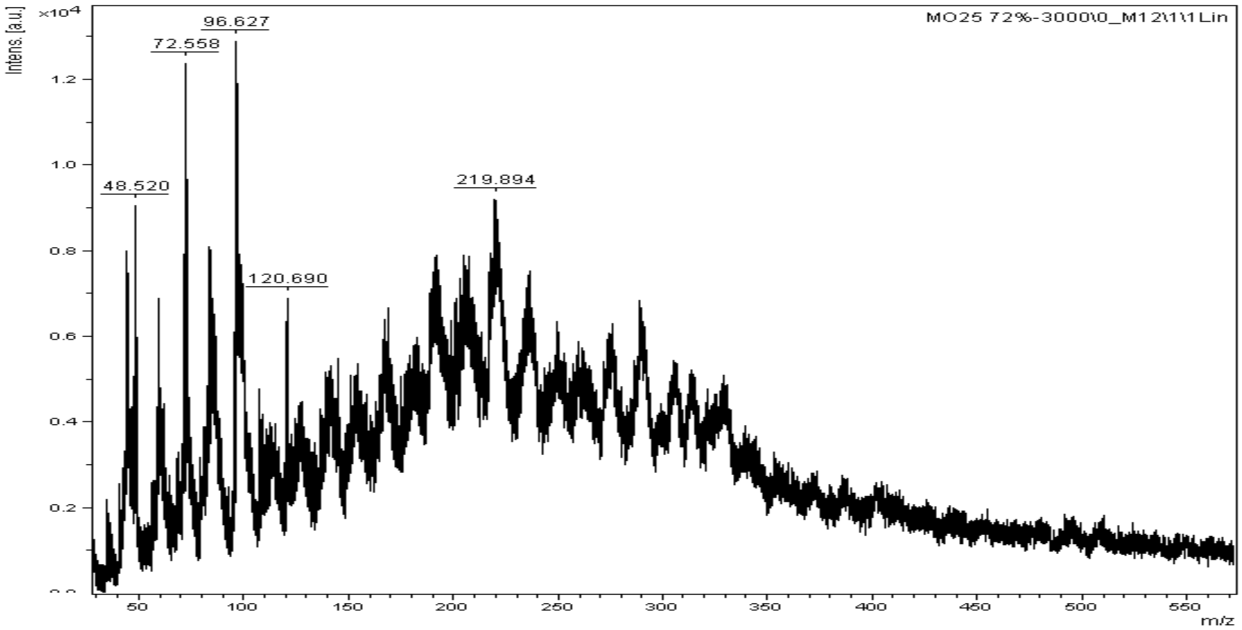


Figure 2. Negative ion LDI mass spectrum.

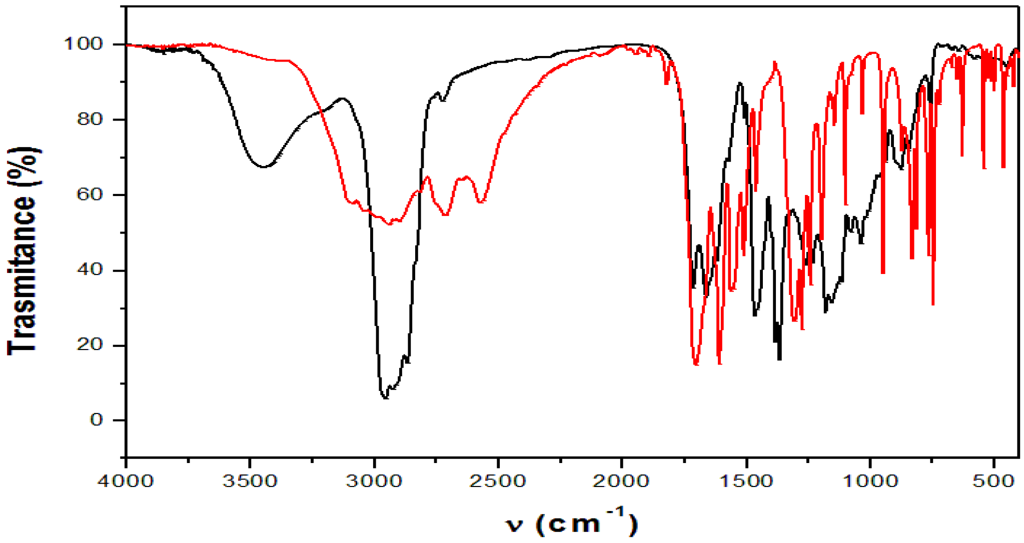


Figure 3. FT-IR spectrum of collected material obtained (black) superposed with FT-IR spectrum of 4-hydroxycoumarin (red).

Conclusion

In summary, MALDI-Tof mass spectra clearly show different olygomers in which the main repeating unit is a propene group (*m/z* = 40), derives from self-condensation and dehydration of acetone in acidic conditions. Also, MALDI-Tof mass spectra show at the end of these chains an ending group of 4-hydroxycoumarin. Furthermore, these results are consistent with FT-IR spectroscopy, where it was determined the presence of 4-hydroxycoumarin structure incorporate to a polyene chain. These results show semi-telechelic olygomers with a functional group 4-hydroxycoumarin at the end of the conjugated propene chain, with potential applications as organic nonlinear optical material.

Acknowledgements-Financial supports from CONICET (PIP 00628), UBA (EX 0088), PCI-A/025750/09, UNSL (Project 7301 and 2-1412), ANPCyT (PICT-10714, 9759), are gratefully acknowledged. We wish to thank to Drs. Larregola, Brusau and Funes for their help. H.A.G. thanks CONICET for postdoctoral fellowship. G.P., C.R.P., C.E.T. and R.E.B are research members of CONICET.

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