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Synthesis and Characterization of Oligo-azomethine by Thermal Condensation Using New Type of Monomers

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Summary

The synthesis and characterization of a variety of aromatic oligo-azomethine, by thermal polymerization of news monomer catalyzed by concentrated HCl, is reported. The new oligo-azomethine has been characterized using Uv-visible, infrared, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Other techniques such as elemental analysis and thermo-gravimetric analysis are also presented. The oligomeric material was synthesized by condensation between the ester group and the amine group. Surprisingly the oligomeric material retains the OCH_2CH_3 groups and it becomes bound to the C=N groups. The new type of monomers (aminophenyl ester) allow, at the first time, to introduce substituent covalent bonds to carbon atom of imine groups.

Introduction

The poly(imines) are an example of conjugated polymers, also known as poly(azomethines) or as Schiff Base polymers. The first variety of them exhibit a complicated chemistry due to their high molecular weight [1]. In recent years, interest towards Poly(imines) has increased due to their proven capacity to act as good materials; as reagents or as a supports in a diversity of applications, for example, poly(imines) have been used as reagents to obtain hybrid materials by the linkage of polypirrol to the backbone of the polymer[2]. Also, some poly(imines) with dendrimere properties are an excellent supports for coordination of metallic ions [3]. On the other hand, similar to polyaniline doping, imine groups, C=N- in poly(imines), can take a proton, yielding cationic backbones that have different anions, which retain interesting properties. Some articles in literature mention the protonation of poly(imines) with heteropolyanion with Keggin structure, which have catalytic properties [4,5]. The classical synthetic route to prepare a poly(imines) occurs by means of condensation between diamines and dialhehydes or diamines and diketones. However, the majority of them involve reactions between substituted aromatic dialdehydes, such as terepthaldehyde or isophtalaldehyde, with substituted phenylendiamines.[1,6-12]. Usually, the resulting products, substituted in aromatic rings, show very low solubility in organic solvents which makes the characterization and the preparation of thin films difficult. However, there are some reagents that allow

to increase the solubility, for example, aromatic poly(imines) become soluble by the addition of gallium (III) chloride or di-*m*-cresyl phosphate,[13] yielding the gallium (III) complexes. Another way is through the incorporation of different substituents in the aromatic ring, such as methyl[12], alkoxo [11, 14-16] or trifluoromethyl [17]. The main characteristic of these polymers is that they have electronic delocalization, which confers them interesting chemical-physical properties, *v. gr.*: mechanicals, electroluminescent, nonlinear optical and liquid-crystalline phase properties[6,7,18].

In this paper, we report the synthesis and characterization of aromatic oligo-azomethine, prepared with new monomers, which allow, for the first time, to introduce substituents in the carbon atom of the imine groups. The oligo-azomethine was prepared by thermal polymerization of ethyl 2-(*3*-aminophenyl) acetate using small ammounts of concentrated HCl as the catalizer. The new oligo-azomethine has been characterized by a conventional spectroscopic method. Other techniques, such as elemental analysis, thermo-gravimetric analysis, are also presented.

Experimental Section

Chemicals

All reagents were obtained from comercial sources. *3´*-aminoacetophenone (98%) and morpholine (99%) were purchased from Merck. Sulfur powder (99.98%) was obtained from Sigma-Aldrich. HCl (37%), KOH (99%), anhydrous Na_2SO_4 and spectroscopic KBr from Merck. Solvents as chloroform, $CHCl_3$; petroleum ether; diethyl ether, Et_2O; acetone, $(Me)_2CO$; tetrahydrofuran, THF; toluene, C_6H_5Me; dimethylsulfoxide, DMSO and dimethylformamide, DMF were obtained from Fisher Scientific. All reagents and solvents were used without previous purification.

The I.R. spectra were recorded on KBr pellets in a NEXUS FT-IR apparatus. The UV-vis spectra were registered in a UNICAM UV 500 equipment using DMF as the solvent. NMR spectra were registered on a 400 MHz Bruker apparatus using TMS as the internal solvent.

Thermo-gravimetricanalyses (TGA) was recorded under a nitrogen atmosphere with STA 625 Thermal Analyzer at 10°C/min.

Synthesis of monomer

The monomer, ethyl 2-(3-aminophenyl)acetate, Scheme 1, was prepared according to King et. al.[19]. The procedure was complicated and was modified by us. In a round-bottom flask connected to a refrigerant tube 20.00 g (0.163 mole) of 3´-aminoacetophenone, 11.85 g (0.370 mole) of sulphur and 25.8 g (0.30 mole) of morpholine (99%) were added. The reaction mixture was refluxed for 2 hours and was allowed to stand at room temperature. The red mixture obtained was solubilized with 300 mL $CHCl_3$ and washed three times with water. The $CHCl_3$ was removed by vacuum, in the Rotary Evaporator equipment, and the orange residue was refluxed at 85-90°C with 50 mL HCl 30% for 6 hours. Next, the mixture was cooled, filtered and removed from the water by a high vacuum using an oil-bath at around 60°C. The orange residue was taken to a pH= 8-9 by the addition of 40 mL of a KOH solution, 8.33 mol/L, and later removed the water and morpholine by high vacuuming in an oil-bath around 82°C. HCl 37% was added to the obtained viscous liquid, until the dissolution was complete. Once again the water was removed by high vacuuming,

using an oil-bath at 85°C. The viscous residue, corresponding to the impure product, was dissolved in $CHCl_3$ and washed with KOH, 8.33 mol/L solution until the washed solution reached pH 9.0-10.0. The organic extract was dried with anhydrous Na_2SO_4. The red oil was purified in a chromatographic column of silica gel using a 1:2 (v:v) $CHCl_3/Et_2O$ mixture as the eluent and the first red-yellow fraction corresponded to the pure product. Rotary Evaporator equipment was used to remove the eluent mixture. Yield 48.0 %.

Thermal polymerization

Synthesis of oligo-azomethine: In a 10 mL flask, 0.4 g of ethyl 2-(3-aminophenyl)acetate were heated at 200 °C in an oil-bath in the presence of air. Then, 3 drops of HCl 37%, were added, and the temperature of the reaction mixture was increased to about 215-230°C for 20 min. Then, it was kept at room temperature. The crude product was washed several times with $CHCl_3$, petroleum ether, Et_2O and Me_2CO. The oligomeric material was dissolved in DMF and precipitated with Me_2CO. The brown solid obtained was separated by centrifugation, washed with Me_2CO and kept mixed with petroleum ether to increase the compactness degree. Finally, the product was filtered and dried during several days at around 30-35°C. Yield: (Weight oligo-azomethine against weight monomer), 41.5%.

Results and Discussion

The synthesis of monomer have complicated the procedure does not allow raising the yield of the reaction to over 48% due to multiple steps in the purification process. The I. R. spectrum in KBr of the monomer exhibits characteristic stretching signals: νN-H at 3414 cm^{-1}, the aromatic νC-H at 3043 cm^{-1}, the aliphatic νC-H at 2979 cm^{-1} and 2925 cm^{-1}, the carbonyl ester νC=O at 1717 cm^{-1}, the aromatic νC=C at 1600 cm^{-1} and νC-O, 1157 cm^{-1}, typical of the amino-ester. Additionally, the spectrum shows the absorptions of out-of-plane deformatyions, γC-H at 815 cm^{-1} and 691 cm^{-1}, which corresponds to the aromatic ring 1,3-disubstituted. The ^{1}H-NMR spectrum, in $CDCl_3$, exhibits a triplet resonance at 1.30 ppm and a quartet at 4.20 ppm corresponding to the $-OCH_2CH_3$ group. A singlet at 3.60 ppm and another broad peak at 3.70 ppm are assigned to the $-CH_2C=O$ group, linked to the aromatic ring, and the H_2N- group, respectively. Finally, a multiplet corresponding to the aromatic 1,3-disubstitute pattern is observed in the 6.50-7.2 ppm range. The integral of each signal is in perfect agreement with the structure of Scheme 1. Using a thermic condensation reaction, Scheme 1, catalyzed by small ammounts of concentrated HCl, ethyl 2-(3-aminophenyl)acetate may be polymerized with a 41,5 % of yield. The process involves the loss of H_2O molecules between both groups >C=O and H_2N- present in the monomer, to give an oligomeric chain. The thermal synthesis of the oligo-azomethine has a low yield, due to two reasons. On one hand, using a temperature of 200-230°C, may indicate that the polymerization process was not complete, which means that, evidently, the catalyst HCl, suffered vaporization; on the other hand, all byproducts of smaller molecular mass, were eliminated during the washing and purification processes. Surprisingly, the polymer molecule retains the OCH_2CH_3 groups on the imine core, >C=N-. The obtained product corresponds to a new type of poly(imine) and the method used is the access route to obtain a great family of these compounds.

Generally, the poly(imines) reported have substituents on the aromatic ring. However, this new type of monomer allows, for the first time, to introduce covalent bond substituents covalent to the carbon atom of the imine groups.
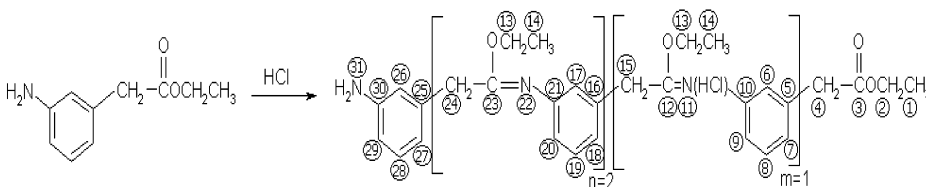
Scheme 1

Figure 1 shows the main absorptions associated to the oligo-azomethine in the I. R. spectrum which are: the stretching of the amine group, νN-H at 3425 cm^{-1}; the terminal carbonyl ester group, νC=O at 1720 cm^{-1}; the aromatic ring, νC=C at 1611 cm^{-1}; the aliphatic groups νCH$_2$ at 1444 cm^{-1} and the terminal ester group, νC-O at 1171 cm^{-1}. The absorption pattern, γC-H, of out-of-plane deformation of the aromatic ring 1,3-disubstituted, were observed at 778 and 693 cm^{-1}, respectively. Nevertheless, the most important absorption corresponds to the imine group, νC=N at 1663 cm^{-1} that contains the CH$_3$CH$_2$O- group. In poly(imines) reported in literature, the νC=N absorption is located at ca. 1600 cm^{-1} and can be displaced to bigger frecuencies by protonation of nitrogen of imines, and by the effect of substituents type electron-withdrawing in the aromatic ring[11,13 20,21]. The high frecuency in the C=N absorption found in this oligo-azomethine, 1663 cm^{-1}, can be attributed to i) the positive formal charge on nitrogen, ii) complete or partial conjugation rupture in the polymeric system iii) the presence of OCH$_2$CH$_3$ group bonds to the carbon of the imine groups which, causes the O-C-N bond angle to increase, and, therefore, causing the shortening of the C=N bond.
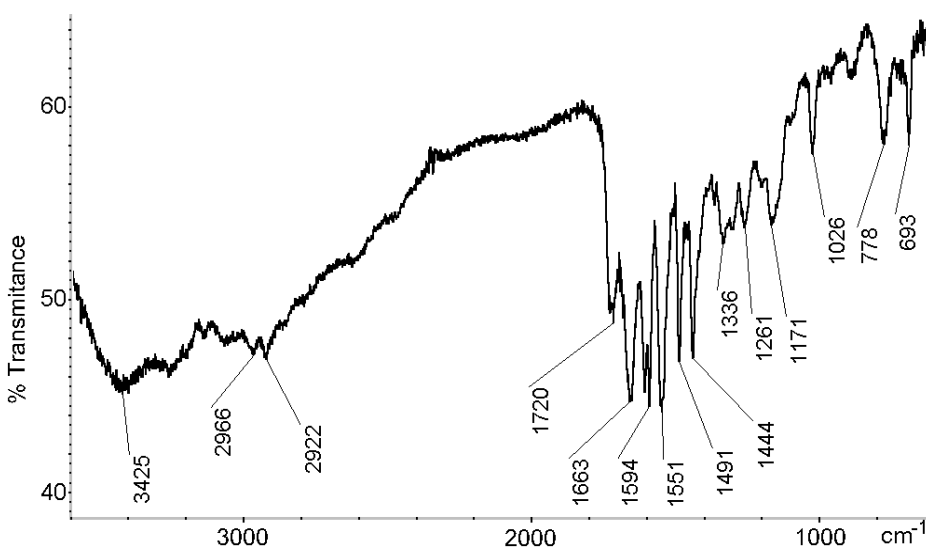

Figure 1: FT-IR spectrum of oligo-azomethine

Table 1 shows the different signals of H[1]-NMR and ^{13}C-NMR spectra of oligo-azomethine. Figure 2 shows the bi-dimensional HMBC spectrum. Figure 3 shows the DEPT-135 spectrum of oligo-azomethine recorded in DMSO-d_6. The signals were assigned with help of CHEM-3D Software. According to spectroscopic data and elemental analysis, we have proposed the structure shown in Scheme 1.

Table 1: Resonances associated at differents protons and carbons of oligo-azomethine spectra

	1,14 CH$_3$	2 CH$_2$	3 O=C-O	4 CH$_2$	5,16,25,10,21,30 Caromatic	6,17,26,8,19,28,9,20,29 CHaromatic
[1]H	1.22-1.17	4.08-4.06	---	3.52	---	7.55-6.94
[13]C	14.53	60.73	171.47	40.99	139.75-117.89	

	11 =N$^+$H	12,23 O-C=N	13 CH$_2$	15 CH$_2$	24 CH$_2$
[1]H	10.30-10.23	---	3.26-3.24	3.71-3.52	3.71-3.52
[13]C	---	169.42	43.82	43.306	40.646

In the HMBC spectrum (figure 2) the broad resonance located at 1.20 ppm in ^{1}H-NMR spectrum, was assigned to all methyl groups, H_1 or H_{14} protons, coupling with the methylene groups, H_2 or H_{13} protons, and this signal is related to with those of C_2 and C_{13}, observed in the respective spectrum of ^{13}C NMR, located at 60.73 and 43.82 ppm, respectively.
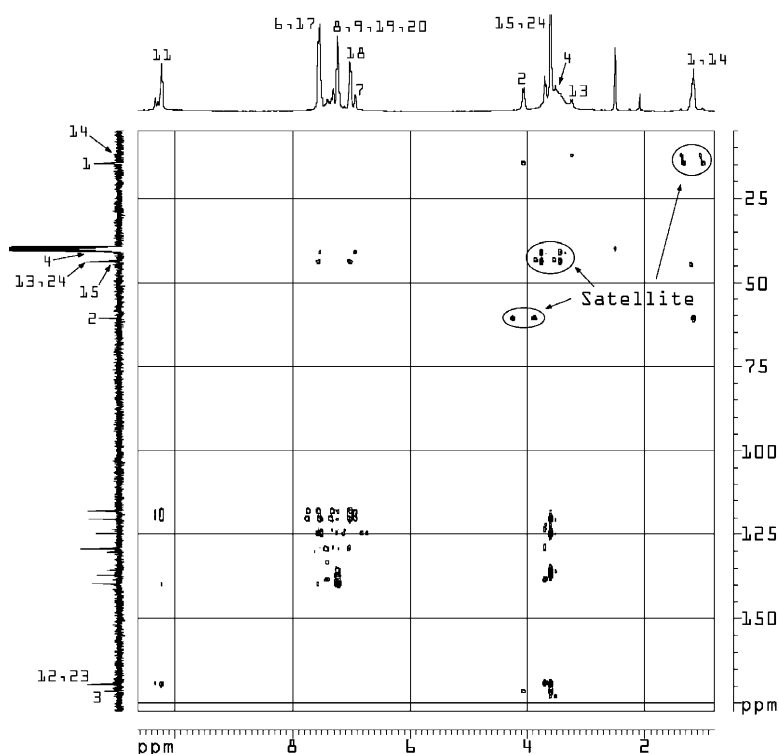

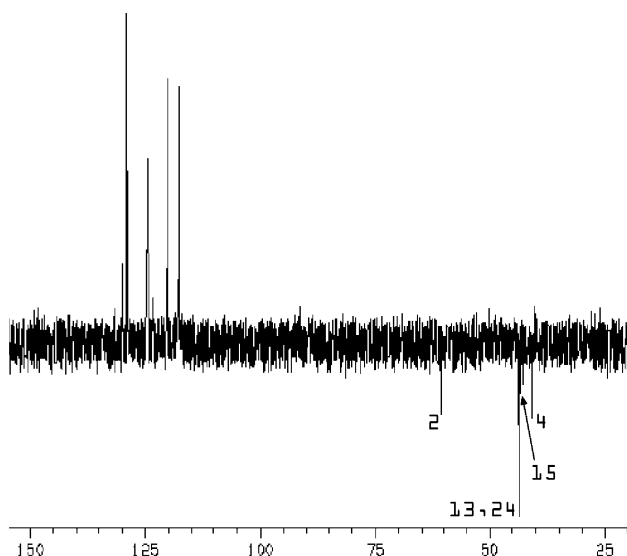Figure 2: HMBC bi-dimensional spectrum of oligo-azomethine

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Figure 3: DEPT-135 spectrum of oligo-azomethine

On the other hand, the resonant group of resonances located in the 3.24-4.08 ppm range in ^{1}H-NMR, correspond to various methylene groups. The first one, centred at 3.25 ppm, assigned to H_{13} protons, is related only to the C_{14} signal located at 13.0 ppm in the ^{13}C NMR spectrum. The second one at 3.51 ppm due to H_4 protons, is related with both, the carbon atoms of the aromatic ring and the carbonyl group C_3 located at 171.47 ppm in the ^{13}C-NMR spectrum. The third and fourth group of signals of the methylene groups, corresponding to H_{15} and H_{24} are centred at 3.67 and 3.71 ppm, respectively. Both are related to C_{23}, C_{12} carbon atoms (imine groups) and to the aromatic carbons. These atoms, C_{23} and C_{12}, give very proximate signals at ca. 169.42 ppm, due to the slightly different imine groups in the ^{13}C-NMR spectrum. The fifth proton signal at 4.06 ppm, corresponding to the H_2 resonances is related to C_1, at 14.53 ppm, and to C_3, 171.47 ppm, carbon atoms signal in the ^{13}C-NMR spectrum. The five different assigned frequencies of methylen groups and, observed in the ^{1}H-NMR spectrum, agree with the resonances found in the DEPT-135 spectrum (figure 3). The circled signals have been attributed to satellite signals.

The frequency groups located in the 6.94-7.55 ppm range were assigned to aromatic protons. The most important characteristic of this set of signals is their relation to the neighboring carbons specially with those of the methylene groups, v. gr.: the pairs H_6 and H_7 resonances at 7.54 and 6.94 ppm, respectively are related to C_4 at 40.99 ppm in the ^{13}C-NMR spectrum and, the pairs H_{17} and H_{18} centred resonances at 7.54 ppm, are related to C_{15} at 43.30 ppm in the ^{13}C-NMR spectrum. The imine H_{11} proton located at 10.30 ppm is related to the aromatic carbons and with the imine carbon C_{12}, centred at 169.42 ppm in the ^{13}C-NMR spectrum.

On the other hand, the composition percentage of each atom in the oligo-azomethine, table 2, was calculated considering the polymerization degree shown in the Scheme 1, n=2 and m=1, these values, "m" and "n", were obtained from the signal integrals of hydrogen methylene centered at 4.07 ppm, hydrogen methyl centered at 1.20 ppm and hydrogen imine centered at 10.27 ppm in the ^{1}H-NMR spectrum, and they are in agreement with the findings in the elemental analysis.

Table 2: Elemental Analysis of oligo-azomethine

	% C	% H	% N	% Cl	% O[1]
Calculated	68.70	6.77	8.01	5.07	11.45
Found	65.36	5.41	8.92	5.07	15.24

[1]Oxygen was determined by the difference in total % of elemental analysis

The presence of 5.07% of chloride indicates that some of the imine groups are protonated, which is confirmed by the presence of two signals that correspond to imine groups, C_{12}, C_{23}, centred at 169.42 ppm in the ^{13}CNMR spectrum.

The UV-vis spectrum of the poly(imine), in DMF (figure 4), exhibits an intense absorption band centred at 272 nm attributed to π-π* to internal transition in the aromatic ring. Two shoulders placed at 288 nm and 300 nm, probably due to the n-π* transitions present on the C=N or C=O chromopheres, Scheme 1. The Band Gap found in solution, proves to be particularly interesting ca. 3.8 eV. This value is higher than the Band Gap of analogue poly(imines) reported in literature.
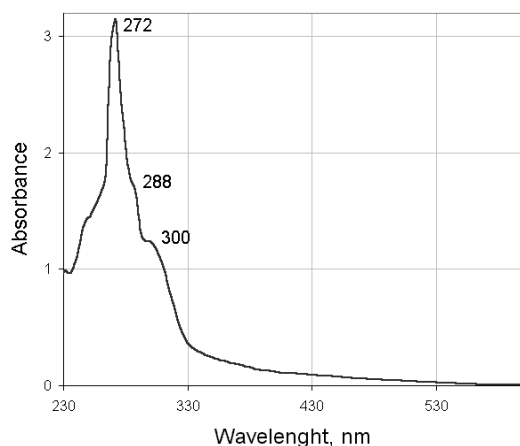

Figure 4: Abpsortion spectrum of oligo-azomethine in solution

The TGA thermograms of oligo-azomethine in a nitrogen atmosphere exhibit two steps (figure 5). The first step shows a 5% mass loss due to temperatures higher than 180°C. The second step shows a 30% mass loss at 307°C, reaching the maximum value at over 500°C. The thermogram shows that the thermal stability of our compound is lower than the thermal stability of poly(imines) described in literature [13,21], possibly due to the lower molecular size of this oligo-azomethine.
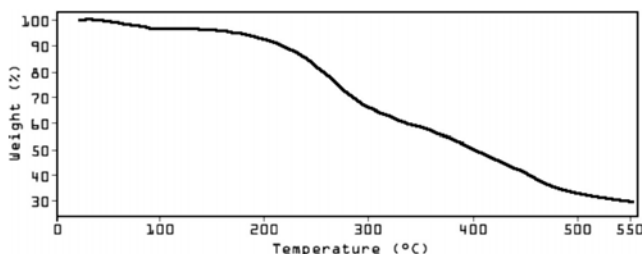

Figure 5: Thermograms of oligo-azomethine

It is important to mention that the oligo-azomethine is insoluble in acetone, ethylic ether, THF, toluene, but is soluble in DMF and DMSO. On the other hand, if its synthesis conditions are changed by addition of higher amounts of the catalizer, a poly(imine) is obtained. If a small polymer sample is heated up to 90°C the polymer can be stretched several meters using a glass needle, thus adopting a thread form. The stretching can continue until the temperature decreases, causing the thread to break. Moreover, this poly(imine) is soluble in DMSO and DMF, these solvents allow to obtain transparent, homogeneous and thin films. The augmented solubility of the oligo-azomethine and the poly(imine) can be attributed to the incorporation of the ethoxy group on the carbon located in the imine groups. The results of characterization and molecular weight of the polymer will be reported later.

Conclusions

We reported the synthesis and characterization of a new oligo-azomethine by means of thermal condensation of ethyl 2-(3-aminophenyl)acetate catalyzed by small ammounts of concentrated HCl. The most important characteristics of the obtained oligomeric material are: i) the oligomer is a tetramer where monomer units are connected by an imine bond, $>C=N-$, ii) the new feature is that the oligomeric material retains the OCH_2CH_3 group on the carbon located in the imine groups, iii) the oligomeric is soluble in DMF and DMSO.

Finally, this investigation represents the resurgence of poly(imine)s, because the new monomer as aminophenyl ester constitutes a new pathway for the synthesis of new series of poly(imine)s. Its possible to obtain a great family of these polymers by changes: i) on the nature of the functional groups bonded to carbonyl carbon of the ester group ii) on the hydrocarbon chain located between the aromatic ring and the carbonyl group and iii) in the position of the amino group on the aromatic ring. In fact, in the first case it might be possible to consider other groups, such as -R, -OR, -NH$_2$, -NHR or -NR$_2$ with different chain lengths methylen ($-CH_2-)_n$. In the second case, it might be possible to consider chain length too.

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