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Synthesis and Characterization Of Oligo(azomethine) Hybrids. Part II

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Summary

The synthesis and characterization of aromatic oligo(azomethines) hybrids by thermal oligomerization of a new monomers is reported. The new oligo(azomethines) have been characterized using, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, elemental analysis, thermo gravimetric and viscosimetric measurements. These oligomers were synthesized by the intermolecular reaction between the ester group and the amine group, and the resulting products contain simultaneously imine, amide and carboxylic acid groups. The soluble oligomers were fractionated and it was possible to obtain a materials of different solubility and molecular size. The oligomers have high thermal stability that reached a loss of mass even of 10% at 460ºC.

Introduction

Poly(imines) are conjugated polymers known as poly(azomethines). One of the first reported polymers date from 1923, when Adams et. al. [1] treated benzidine or dianisidine with terephtaldehyde, obtaining insoluble polymers of high molecular weight. In 1938 Steinkopf et. al. [2], reported a new method. They condensed hidrazine with terephtaldehyde in the melted state. The polymers resulted, once again, insoluble and infusible. Marvel et. al. [3, 4], prepared poly(imines) in solution, treating aromatic dialdehyde with o-phenyldiamines in various solvents, such as: benzene, acetic acid, and dimethylacetamide. However, the poly(imines) prepared in melted state are obtained with a higher molecular weight than the ones prepared in solution. During the last 17 years, substituted poly(imines) in the aromatic ring with substituents of different chain length, such as alcoxo, trifluoromethyl and alkyl groups have been reported [5-10]. In general, the poly(imines) reported have been obtained by condensation from dialdehydes, as terepthaldehyde or isophtaldehyde with substituted phenylendiamines, resulting substituted in the aromatic ring. The polymers of high molecular weight are of low solubility in organic solvents, which makes the formation of films difficult [11-14]. The main characteristic of these materials is that they have electronic delocalization, which confers interesting physical and chemical properties, such as: fibrilar [6], luminescent [15,16], nonlinear optical [11,17], liquid-crystalline [18], semiconductivity [7], support of heteropolyanions with catalytic properties [19-21] and dendrimers as chelants of metallic ions [22].

In a previous paper we have reported the synthesis and characterization of a oligo(azomethine), obtained by the thermal condensation of aminophenyl ester[23]. In this case it was possible to prepare, from a new type of monomer, a substituted tetramer in the carbon atom of imine groups. In this paper we have changed the oligomerization conditions and from ethyl 2-(3-aminophenyl)acetate and 2-(3-aminophenyl)acetic acid was possible to obtain a new structure of oligomers. Decreasing the amount of the catalyst and adding it at the beginning of the oligomerization reaction is possible to obtain hybrid materials that contain imine, amide and carboxylic acid groups. Moreover, we studied the nucleophilic effect of amine groups on the carbonyl-ethoxo groups and its relation with the thermal stability, molecular dimension and molecular structure of the new oligomers. The characterization using spectroscopy methods, elemental analysis, and properties such as thermal stability and viscosimetric measurement are reported.

Experimental Section

The I.R. spectra were recorded on KBr pellets in a NEXUS FT-IR apparatus. NMR spectra, in DMSO-d_6 with internal TMS, were registered on a 400 MHz Bruker apparatus. Thermo-gravimetric analyses (TGA) were recorded under nitrogen atmosphere with STA 625 Thermal Analyzer operating at 10ºC/min. Intrinsic viscosity ($[\eta]$) of each oligomer was determined using Ostwald type capillary dilution viscosimeter in DMF at 298 ºK without kinetic energy corrections. Intrinsic viscosities were obtained using the Solomon-Gotessman equation [24].

Synthesis of the monomers

The monomers, ethyl 2-(3-aminophenyl) acetate and 2-(3-aminophenyl) acetic acid were prepared by us and reported in a previous paper [23, 25]. Ethyl 2-(3-aminophenyl) acetate hydrochloride was obtained adding concentrated HCl on a solution of the corresponding free base in diethyl ether, then the product was filtered, washed with diethyl ether.

Thermal Oligomerization

Thermal oligomerization of ethyl 2-(3-aminophenyl) acetate, ethyl 2-(3-aminophenyl) acetate hydrochloride and 2-(3-aminophenyl) acetic acid were done under same conditions and modified according to the previous paper [23]. In example, the oligomerization of ethyl 2-(3-aminophenyl) acetate is described as followed: in a 10 mL flask, 2.13 g of monomer and 0.22 g of 37 % aqueous HCl (mol ratio = 5.47) were added, then the temperature of the reaction mixture was increased to about 220-230 ºC for 20 min under stirring and then was allowed to stand at room temperature. The oligomeric material was washed several times with hot solvents as chloroform, hexanes, diethyl ether and acetone. Finally, the product was washed with methanol, filtered and washed again with diethyl ether. This reaction yield 0.092 g of oligomeric material, labeled as oligo 1. Likewise, from the oligomerization of ethyl 2-(3-aminophenyl) acetate hydrochloride and from 2-(3-aminophenyl) acetic acid were obtained, 0.28 g of oligo 3 and 0.29 g of oligo 4, respectively. A second fraction of oligomer was separated from methanol washing fraction corresponding to the oligomerization of ethyl 2-(3-aminophenyl) acetate. In order to provoke precipitation, on 20 mL of this last solution, 11 mL of diethyl ether were added; the product was filtered and washed with diethyl ether. This gummy oligomeric fraction was treated with petroleum ether in order to increase the compactness level. This procedure yield 0.12 g of oligomeric fraction, labeled as oligo 2.

Results and Discussion

In a previous paper we have reported a thermal intermolecular condensation reaction for oligomerizing ethyl 2-(3-aminophenyl) acetate, catalyzed by concentrated HCl. In fact, when the monomer/catalyst ratio was 2:1 and the catalyst is added at 215ºC, a substituted oligo(azomethine), containing ethoxo groups on the imine carbon, was obtained [23]. Now, we reported analogous reaction adding the catalyst at the beginning of the reaction with a ratio monomer/catalyst increased to 5.47. The obtained results indicate that the products have an oligomeric character and contain imine groups that tautomerize partially to yield the amide group.

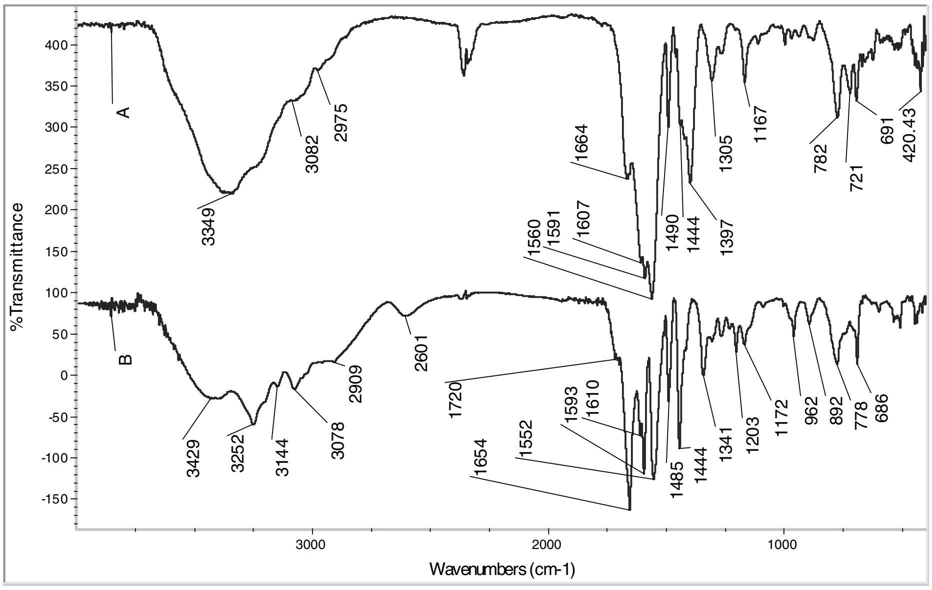


Figure 1: IR spectra of a) oligo[ethyl 2-(3-aminophenyl)acetate], oligo 1, and b) oligo[2-(3-aminophenyl)acetic acid], oligo 4.

Figure 1 shows the absorptions bands of two of these oligomers in the IR spectra. The principal stretching modes are: i) the overlapped bands of amine and O-H groups, ν(N-H) and ν(O-H), centered at 3349 cm^{-1} in oligo 1 and 3252 cm^{-1}, 3429 cm^{-1} in oligo 4, ii) the carbonyl of amide groups, νC=O, located at 1664 cm^{-1} in oligo 1 and

1654 cm^{-1} in oligo 4, iii) the aromatic, ν(C=C) at 1607 cm^{-1} in oligo 1 and 1610 cm^{-1} in oligo 4. On the other hand, the absorption pattern of deformation out of plane , γ(C-H), typical in the aromatic rings with 1,3-disubstitution were observed at 773 cm^{-1} and 691 cm^{-1} in oligo 1 and 778 cm^{-1} and 686 cm^{-1} in oligo 4. The protonated amine group, ν(NH_3^+) was observed in oligo 4 at 2601 cm^{-1}. The IR spectra of oligo 2 and oligo 3 exhibit similar functional features than those found in oligo 1, figure 1a. A stretching absorption band of low intensity, partially overlapped with the amide stretching was observed in the IR spectrum of oligo 4 at 1720 cm^{-1}, Figure 1b. This absorption was assigned to carbonyl group corresponding to carboxylic acid located in one of the extremes of the chain. In the other spectra, oligo 1-3, probably, the absorption band corresponding to the carboxylic acid, are completely overlapped with the carbonyl absorption of amide group.

Table 1 shows the different signals of ^{1}H-NMR and ^{13}C-NMR spectra of oligo 1 and oligo 4 and figure 2 shows the bidimensional HMBC spectrum of oligo 1 recorded in DMSO-d_6. The signals were assigned with the help of CHEM-3D software.

Table 1: Resonances associated at different hydrogen (H) and carbons (C) of oligo 1 and oligo 4 spectra.

Oligo 1	-CH_2 C(R)=NH$^{(+)}$-	-CH_2- C(R)=N-	-CH_2- CONH-	-CH_2- COOH	-C (R) =NH$^{(+)}$
^{1}H (ppm)	3.18	3.44	3.58	3.28	----
^{13}C (ppm)	39.8	40.2	40.4	40.0	178.2

	-CO-NH-	COOH	C-H aromatic	-C(R) =N-
^{1}H (ppm)	5.2-4.8	5.2-4.8	7.6-6.3	----
^{13}C (ppm)	169.7	178.0	149-111	170

Oligo 4	-CH_2 C(R)=NH$^{(+)}$-	-CH_2- C(R)=N-	-CH_2- CONH-	-CH_2- COOH
^{1}H (ppm)	----	3.62	3.72	3.62
^{13}C (ppm)	----	43.3	43.8	41.4

	-CO-NH-	COOH	C-H aromatic	-C(R) =N-
^{1}H (ppm)	----	----	7.6-6.9	----
^{13}C (ppm	169.1	173.0	140-118	169.5

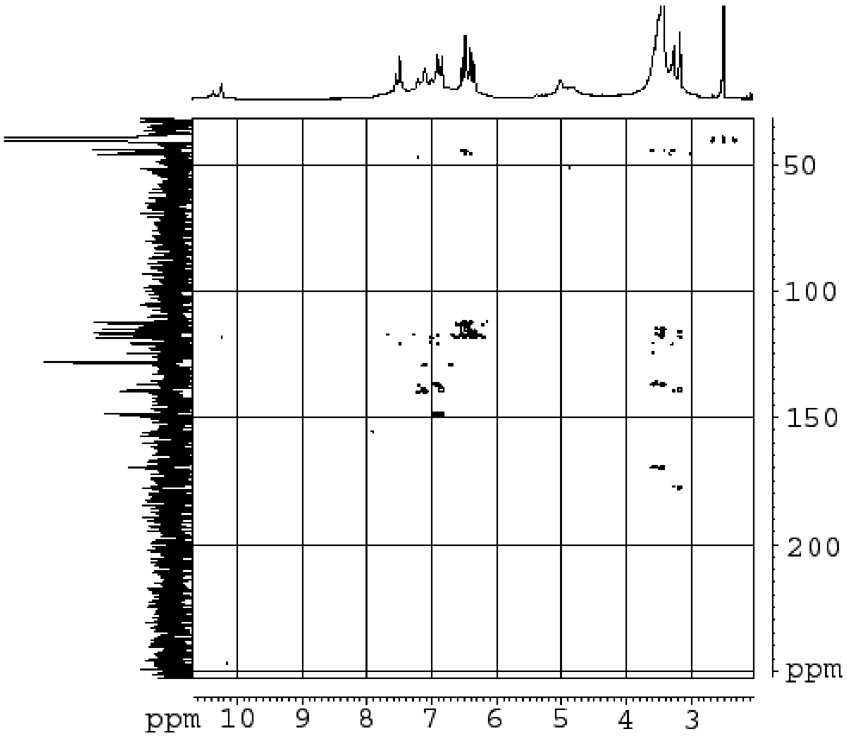


Figure 2: HMBC bidimensional spectrum of oligo(ethyl 2-(3-aminophenyl) acetate), oligo 1.

The ^{1}H-NMR spectrum in the bidimensional HMBC spectrum of oligo 1 shows a group of resonances located in 3.18-3.58 ppm range, assigned to four different methylene groups. Two of these signals are related with two carbonyl groups in the ^{13}C-NMR spectrum, located at 178.0 and 169.7 ppm, assigned to carboxylic acid and amide groups, respectively. The other two methylene groups are related with two imine carbons, located at 178.2 ppm and 170.0 ppm in the ^{13}C-NMR spectrum. Besides, each of these four resonances of methylene hydrogen are related with four methylene carbons located in the 39.8-40.4 ppm range and are also related with the aromatic carbons located in the 149-111 ppm region in the ^{13}C-NMR spectrum. The set of signals located in the 7.6-6.3 ppm range of the ^{1}HNMR spectrum were assigned to aromatic hydrogen resonances. The HMBC bidimensional spectra of oligo 2-4, are similar to figure 2 and the same relations and functional groups were observed in those spectra. However, in the spectra of oligo 3 and oligo 4 the protonated imine is not observed, which was confirmed by the low percentage of chloride in the elemental analysis, Table 2. On the other hand, the HMBC spectra of oligo 1-3 exhibits that the etoxo-carbonyl groups are completely hydrolyzed or substituted during the oligomerization reaction, in this way, similar backbones were obtained when the materials are prepared from the monomer ethyl 2-(3-aminophenyl) acetate, ethyl 2-(3-aminophenyl)acetate hydrochloride and 2-(3-aminophenyl)acetic acid.

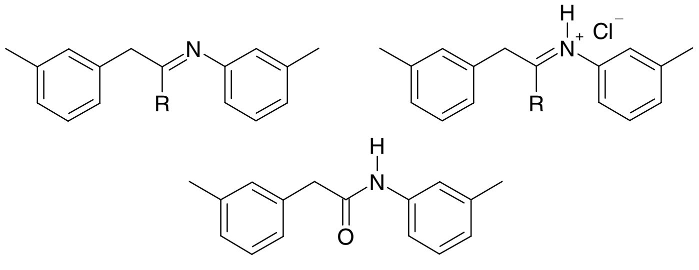
According to these results, the backbone of these four oligomers presents similar structure, containing the same functional groups: i) amide and imine groups, in the repetitive units, Scheme 1a, and ii) amine and carboxylic acid at the end of the chain, Scheme 1b. The chloride anion, originating of the catalyst, HCl, detected in the elemental analysis of each oligomer, Table 2, indicates that there are certain quantity of protonated groups, $-NH_3^+$ and $>C=NH^+$-, yielding a polyelectrolite. For these reasons, the oligomers are solubles in polar solvents. In fact, oligo 1 has low solubility in DMF, but is soluble in DMSO and oligo 2-4 are soluble in both solvents; which allows preparing thin films of these materials. Oligo 1 and oligo 2 have over 1 mole of chloride for repetitive units; furthermore, the elevated contents of oxygen, Table 2, explain his greater affinity to trap water. The properties of the films and the gels observed with different organic solvents will be reported later.

Table 2: Elemental analysis, Viscosities, Empirical Formula of the hybrids oligomers.

Oligomers	% C	% H	% N	% Cl	% O[b]	$[\eta]^a$ dl/g	Empirical Formula
Oligo 1	21.53	1.30	3.19	30.09	43.89	---	$C_8H_{5.80}N_{1.02}Cl_{3.79}O_{12.25}$
Oligo 2	38.08	3.10	5.41	18.11	35.30	0.10	$C_8H_{7.76}N_{0.97}Cl_{1.29}O_{5.57}$
Oligo 3	63.59	5.13	9.29	5.55	16.44	0.02	$C_8H_{7.69}N_{1.00}Cl_{0.24}O_{1.55}$
Oligo 4	63.59	5.19	9.33	5.21	16.88	0.12	$C_8H_{7.84}N_{1.01}Cl_{0.22}O_{1.59}$

a) Oligo 1 had low solubility in DMF and its viscosity it not measured
b) Calculated by difference

Scheme 1



a: Internal functional groups

b: Terminal functional groups

The intrinsic viscosity of the materials were measured using the Solomon-Gotessman equation [24], the observed values indicates that the oligomers 1-4 are low molecular size, Table 2. Oligo 3 exhibits the lowest viscosity value, which indicates that, if the amino group in the monomer is in its hydrochloride form, then, the growth mechanism of the material could be affected due to minor nucleophilic power of the nitrogen atom. Besides, due to the oligo 1 have low solubility in DMF, the molecular dimension could be higher than oligo 2-4. Moreover, as oligo 2 is a fraction separated of oligo 1 and have a similar viscosity to oligo 4, then ethoxo group furthers the growth stage of this oligomer, due to than is a best exiting group that OH group. In this case, the substitution reaction occurred on the carbonyl yield finally the amide group in the oligomeric backbone.

Figure 3 exhibits the thermograms obtained after thermic stability analysis of each oligomer. Here, recalling that oligo 2 is a oligomeric fraction separated after the synthesis of oligo 1, we can see 5 %'s loss of mass down 317 ºC, while in oligo 1, loss of same quantity of mass occur down 390ºC. This observation indicates that the thermal stability decreases proportionally with the molecular dimension or with the amount of HCl.

The thermal stability is different if the oligomeric material was prepared from 2-(3-aminophenyl)acetic acid (oligo 4) or from ethyl 2-(3-aminophenyl)acetate monomer (oligo 2); both oligomers presented similar intrinsic viscosities (table 2) and, in the first case a mass loss 5% occurred at 227ºC and in the second case, some mass loss occurred at 318ºC, indicating that the oligomeric material prepared from the monomer that contains etoxo-carbonyl groups favors thermal stability, which is possible because of a higher number of protonated imine units by hydrochloride in the oligomeric material. If the oligomeric material is prepared from the monomer 2-(3-aminophenyl) acetate hydrochloride, oligo 3, a material of lower thermal stability is obtained, which is in accord with lower molecular dimension or low content of hydrochloride. In general, these oligomeric materials are of high thermal stability, surprisingly, in the case of oligo 1, the loss of mass only reaches at 10% at 460 ºC.

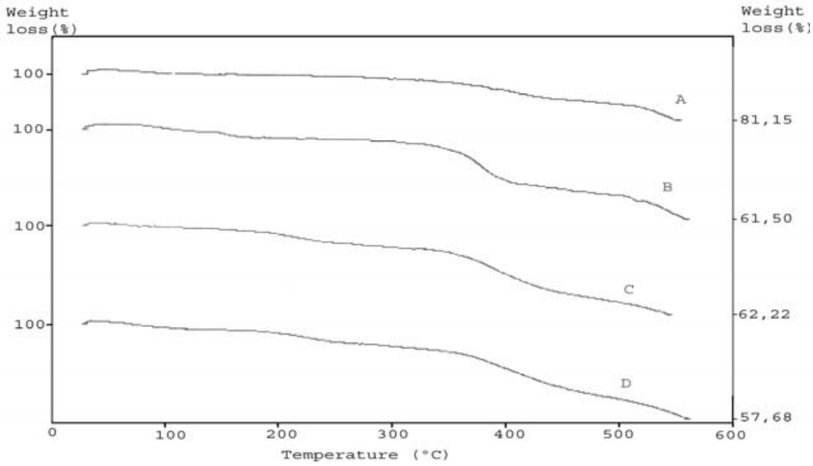


Figure 3: TGA thermograms of: a) oligo 1, b) oligo 2, c) oligo 3 and, d) oligo 4.

Conclusions

We report the synthesis and characterization of oligomeric material obtained by thermal condensation of ethyl 2-(3-aminophenyl) acetate, ethyl 2-(3-aminophenyl) acetate hydrochloride and 2-(3-aminophenyl) acetic acid and catalyzed by concentrated aqueous HCl. By changing the reaction conditions it was possible to prepare hybrid materials whose molecular structure contains i) internal amide and imine functions and ii) terminal amine and carboxylic acid function. These materials presented good solubility, different molecular size and high thermal stability.

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