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New Polyaniline Derivative with Two Central Ester Groups: Synthesis, Characterization, and Theoretical Study

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ABSTRACT: A new polyaniline derivative was prepared to study the formation of quinoid-diimine units in its polymer. The monomer and polymer were experimentally and theoretically characterized. Both polymers have one or two electron-withdrawing groups as side substituents. The polymers' quinoid-diimine unit composition is affected by the electron-withdrawing side groups of aniline. The presence of the quinoid-diimine group diminished for the two electron-withdrawing groups of aniline. The polymer conductivity is different than with respect to polyemeraldine, associated with the quinoid-diimine units' composition. The quinoid-diimine composition is strongly increased in the polymer containing one electron-withdrawing group. Moreover, the polymer presented good solubility in organic solvents and moderate thermal stability.

INTRODUCTION

The expression polyaniline[1] refers to a set of polymers that show a variety of possible compositions with benzenoid-diamine units $(-NH-C_6H_4-NH-)$ and quinoid-diimine units $(-N=C_6H_4=N-)$ in their backbones. When the composition of quinoid-diimine units is 50%, the polymer is called polyemeraldine, which can be doped by inorganic acids to obtain a semiconductor material.[2−8] The polyemeraldine form of polyaniline is of great interest in scientific and technological areas. Specifically, polyemeraldine has been studied in batteries,[9,10] diodes, and transistors,[11−13] and also as a catalyst,[14] blends in selective electrodes,[15] sensors,[11,16,17] biochemical processes,[18] and as alternative skin tissue,[19] among others. However, its poor solubility is a disadvantage for applications in technological areas. The polymer's solubility can be increased using two approaches:[20] (a) doping the polymer with organic acids[21−23] or (b) through the inclusion of side chain substituents in the aromatic rings. However, any of the methods used decrease the electrical conductivity to a greater extent. The side substituents on aniline, particularly the electron-withdrawing groups such as halogens, carboxylic acid, acetic acid, and propionic acid, affect the formation of quinoid-diimine units in the polymer.[24−27] In this sense, these electron-withdrawing substituents decrease the composition of quinoid-diimine units with respect to polyemeraldine, and therefore, semiconducting polymers are obtained, avoiding the total loss of electrical conductivity. Moreover, substituted aniline including other groups such as nitro, cyano, and sulfonic acid groups do not polymerize in acidic media.[28,29] Nevertheless, it has been reported[30] that if one electron-withdrawing group is bonded through alkyl groups to the aniline unit, the

composition of quinoid-diimine units in the polymer increases. In this sense, the increase of quinoid-diimine units in the polymer with electron-withdrawing or electron-donating substituents is the most important factor to obtain semiconducting polymers.

Thus, the aim of this work is to study the effect on the formation of quinoid-diimine units in a polyaniline derivative when two electron-withdrawing groups (diester) are bonded by alkyl groups to aniline (with three bonds). In order to carry out such a study, the synthesis of a ladder-type polyaniline derivative, namely, poly(bis(3-amino-benzyl)malon ester), was performed. The complete characterization using elemental analysis, spectroscopic methods, solubility, and thermal stability is reported. This polymer displays good solubility in organic solvents, which is an advantage for the possible applications in technological areas. Moreover, our study shows that the composition of quinoid-diimine units in the main chain of the polymers is strongly affected by the electron-withdrawing side groups connected to the aniline ring. Specifically, the number of quinoid-diimine units is lower in the case of aniline containing two electron-withdrawing groups. In contrast, the composition of quinoid-diimine is increased in the polymer containing a single electron-withdrawing group. The formation of quinoid-diimine units

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Figure 1. FT-IR of bis(3-amino-benzyl)malon ester on the KBr pellet.

Figure 2. (a) HMBC spectrum of the monomer of ^{1}H against ^{13}C in acetone-d_6 and (b) numbers assigned in the spectrum for carbon and hydrogen in the molecular structure.

in polyaniline derivatives and the effect on electrical conductivity are reported and discussed. Finally, to support all of the results shown herein, DFT calculations were performed over an oligomeric representation of the polymer.

■ EXPERIMENTAL PART

Chemicals. 3-Nitrobenzyl chloride, diethyl malonate (99%), powdered 10% Pt/C catalyst, ammonium persulfate, ethanol, methanol, and ethyl ether were purchased from commercial suppliers and used without further purification.

Physical Measurements. The IR spectra were obtained with a Nicolet Fourier-transform infrared (FT-IR) Nexus spectrophotometer on KBr pellets. Ultraviolet−visible spectroscopy (UV−vis) spectra were recorded in a UV 500 Unicam spectrophotometer, using DMF as the solvent in 1 cm cells. NMR spectra were obtained from DMSO-d_6 solutions using

TMS as internal reference in a 400 MHz Bruker spectrophotometer. Elemental analysis (C, H, and N) was achieved in an EA-1108 Fisons elemental analyzer, and the total quantity of chloride was determined by the ASTM standard method.[31] Thermogravimetric analysis (TGA) was registered under a N_2 atmosphere on a STA 625 thermal analyzer between room temperature and 550 °C at 10 °C/min. Intrinsic viscosity, $[\eta]$, was calculated from DMF solution at 298 K on an Ostwald-type capillary without kinetic energy correction and the $[\eta]$ value was calculated using the Solomon-Gotessman equation.[32] The bulk electrical conductivity of the polymers was measured by a two-disk method using a UT 70A multimeter at ambient temperature.[33]

Synthesis of the Monomer. The synthesis of bis(3-amino-benzyl)malon ester was accomplished in several steps. The full description can be found in the SI.

Polymerization. In a 250 mL round-bottom flask, 2.07 g (5.59 mmol) of bis(3-amino-benzyl)malon ester and 154 mL of aqueous 1 M HCl were mixed. After that, 2.54 g (11.23 mmol) of ammonium persulfate was dissolved in 15 mL of aqueous 1 M HCl at room temperature under stirring for 55 h. The solid product was filtered and washed with large amounts of 1 M HCl until obtaining colorless 1 M HCl. A soluble fraction was separated by solid−liquid extraction with methanol, and then methanol was removed under vacuum. A black polymer was obtained, which was purified by dissolution in 20 mL of methanol and ethyl ether addition until polymer precipitation. Finally, the product was separated from the solvent mixture by centrifugation. The process of purification was performed twice. 650 mg of product was obtained (31% yield).

Theoretical Calculations. The Gaussian 16 computational package[34] was used to perform ground-state geometry optimization calculations employing the Becke's three-parameter hybrid exchange functional and the Lee−Yang−Parr nonlocal correlation functional B3LYP[35] and the 6-31g* basis set for C, H, N, and O atoms.[36] Time-dependent density functional theory (TD-DFT) calculations[37] were also performed using the same functional and basis sets, and the first 120 transitions were calculated. The calculations by the first-principles method were used for obtaining the accurate excitation energies and oscillator strengths of two proposed tetramers. The solvent effects were considered via the conductor−like screening model using dimethylformamide's dielectric constant.

■ RESULTS AND DISCUSSION

The synthesis of bis(3-nitrobenzyl)malon ester was achieved by the addition of 3-nitrobenzyl chloride on previously

Table 1. Elemental Analysis and Empirical Formula of the Polymer

%C	%H	%N	%Cl	%O[a]	empirical formula
56.60	5.21	6.28	16.05	15.86	$C_{21}H_{24.4}N_{2.0}O_{4.4}Cl_{2.02}$

[a]% was determined by difference.

deprotonated diethyl malonate. The reaction mixture was acidified and washed, then extracted with $CHCl_3$ to remove a byproduct formed in the reaction (diethyl-3-nitrobenzyl malonate). In the last step of the synthetic procedure, a dissolution of aqueous KOH was added to precipitate the bis(3-nitrobenzyl) malon ester product, which was separated using filtration and purified by recrystallization. The reaction had a moderate yield (38%) considering that two major products were formed (42% yield for (3-nitrobenzyl)malon ester). The bis(3-nitrobenzyl)malon ester product was reduced with gaseous hydrogen, using Pt absorbed on active carbon as the catalyst. Then, the diamine product (monomer) was purified by TLC, resulting in an orange oil product (0.60 g of monomer was obtained (70% yield)).

The monomer was characterized by elemental analysis and spectroscopic methods. In the mass spectrum, the three main peaks (m/z), with the highest intensity, were at 370, 218, and 107. The signal at mass 370 corresponds to the molecular ion, which corresponds to the molecular mass of the monomer. The FT-IR spectrum exhibited the characteristic bands of the functional groups, e.g., amine (νN−H, 3369.9 cm^{-1}), aliphatic (νC−H, 2980.8 cm^{-1}), carbonyl (νC=O, 1726.0 cm^{-1}), and aromatic (νC=C, 1621.7 cm^{-1}) groups, as shown in Figure 1. In the spectrum obtained by proton nuclear magnetic resonance (^1H NMR), the signals corresponding to aliphatic and aromatic protons are in agreement with the monomer's structure, e.g., in the aromatic zone (at 6.98 ppm (1H,t); 6.60 ppm (1H,s); 6.55 ppm (1H,d); 6.50 ppm (1H,d)) and in the aliphatic zone (at 3.07 ppm ($-CH_2-$, 2H,s); 1.20 ppm ($-CH_3$, 3H,t)). Finally, at 4.15 ppm ($-OCH_2-$, 2H,m) and 4.65 ppm, a broad signal of amine groups (2H,s) are observed.

The heteronuclear multiple bond correlation (HMBC) spectra of ^1H coupled with ^{13}C showed an excellent signal correlation with respect to the functional groups. Figure 2 shows the spectrum with the signals and most important couplings and the molecular structure, showing the hydrogen and carbon associated in the spectrum of the monomer. The couplings that should be emphasized are those related to the quaternary carbon of the monomer. In the ^1H NMR spectrum, the singlet at 3.07 ppm is coupled with the quaternary carbon located at 58 ppm, and moreover, with the carbon of the

Figure 3. (a) HMBC spectrum of the monomer of ^1H against ^{13}C in DMSO-d_6 and (b) proposed segment of the main chain of the polymer.

Figure 4. FT-IR of the polymer on the KBr pellet.

Figure 5. UV–vis spectra of the polymers with two electron-withdrawing groups.

carbonyl group located at 170 ppm, the signal located at 4.15 ppm is coupled with the quaternary carbon located at 58 ppm and with the carbonyl carbon located at 170 ppm. These couplings indicate that the monomer contains two aniline rings.

The monomer was polymerized in aqueous 1.0 M HCl medium using ammonium persulfate as an oxidizing agent. After 55 h, the reaction mixture exhibited a black color, and the solid product was separated by filtration and washed with large amounts of aqueous 1.0 M HCl to remove the monomer, byproducts, and other low molecular weight compounds formed in the reaction medium. Due to the low acid concentration exposure and low temperature used in the ester to the hydrolyzation conditions, the hydrolysis of the ester groups was not observed. Furthermore, any hydrolyzed product was eliminated through the purification process of the obtained polymer. The reaction product was purified by the addition of methanol and reprecipitated by the addition of a minimal amount of ethyl ether. The polymer formed a colloid with the solvent mixture, thus requiring separation by centrifugation. Table 1 shows the polymer's elemental analysis and the empirical formula. The empirical formula agrees with the polymer's repetitive unit (see Figure 3). The excess of oxygen in the elemental analysis is due to the water molecules absorbed by the polymer, whereas the elimination of these

molecules is a difficult process (the obtained product was dried under vacuum for several days at 110 °C before performing the EA). Figure 3 shows the proposed structure of the polymeric backbone and the bidimensional spectrum (HMBC) of ^{1}H coupled with ^{13}C of the polymer. Also, as shown in Figure 3a, the signals associated with the different functional groups are shown. In the ^{1}H NMR spectrum, the signals centered at 1.08 ppm (triplet) and 4.05 ppm (multiplet) were assigned to the methyl and methylene protons of the ethoxy groups, respectively; while the signal centered at 3.06 ppm was assigned to the methylene protons bonded to the aromatic ring. The signals centered at 6.90 ppm (singlet), at 6.95 ppm (doublet), and at 7.24 ppm (doublet) were assigned to aromatic protons. The signal at 2.44 ppm was assigned to DMSO-d_6 (residual solvent) protons. The multiplicity of the signals in the ^{1}H NMR spectrum in the aromatic zone indicates that the monomer was polymerized through nitrogen and at position 4- of the aromatic ring, similar to the process of polymerization of aniline.[3,5]

The polymer's FT-IR spectrum exhibited the characteristic bands of the different functional groups, e.g., amine groups (νNH, 3451.7 cm^{-1}), aliphatic groups (νCH, 2969.3 cm^{-1}), carbonyl groups (νC=O, 1719.9 cm^{-1}), quinoid-diimine groups (νC=N, 1593.9 cm^{-1}), and benzenoid-diamine groups (νC=C, 1566.5 cm^{-1})[38] (see Figure 4). By means of DFT calculations, the vibrations of the proposed representation were calculated. It was observed that the signal observed at 2569.3 cm^{-1} corresponds to the C=C vibration of the groups that are located inside the structure (protected from the outside interactions), and thus they are displaced from the normal vibration region. The presence of quinoid-diimine groups in the main chain was confirmed by UV–visible spectroscopy, *vide infra*.

The polymer is soluble in several organic solvents, such as methanol, acetone, THF, DMF, DMSO, and CH$_3$CN due to the two ester functional groups that are present as side substituents. Moreover, the polymer exhibited a viscosity of 0.32 g/dL, as calculated by Solomon's equation.[32] The value of viscosity and the observation that a gel was formed upon contact of organic solvents indicate that an oligomeric material was formed.

The UV–vis spectrum of the polymer in DMF is shown in Figure 5, where a comparison of the herein synthesized polymer and a reference polymer is shown.[30] The reference

Figure 6. Quinoid-diimine segments in the main chain of the polymer.

Figure 7. Thermal decomposition profile of the synthesized polymer obtained by TGA.

Table 2. Energy (eV), Most Intense Calculated Absorption Wavelength (λ in nm), Oscillator Strength (ƒ), Active Molecular Orbitals (MOs) (H (HOMO), L (LUMO)), and Contributions (%) of the Electronic Transitions from TD-DFT Calculations for Possibility (Pos.) a and b

pos.	λ	eV	f	MOs	%
a	305	4.06	0.119	H-1 → L+1	72
b	595	2.08	0.006	H-1 → L+1	78
	309	4.02	0.243	H-15 → L+1	35
				H-16 → L+1	16
				H-17 → L+1	19

polymer was previously reported[30] (see the structure on top of the curve in Figure 5) and has a single electron-withdrawing group (ester) at a distance of three bonds to the aniline ring, like the herein reported polymer. The absorption bands in the UV region (at 298 nm in the polymer reported herein and at 305 nm in the previous report) were assigned in both cases to the π−π* electronic transition of the phenyl rings in the

polymers; while in the visible region, the absorption bands located at 570 and 600 nm were attributed to quinoid-diimine units present in the main chain of the polymers, which are shown in Figure 6. The reference polymer containing a single electron-withdrawing group exhibits a much greater composition of quinoid-diimine[30] compared to the polymer that contains two electron-withdrawing groups, which was reflected in the UV−vis spectra.

It is necessary to emphasize that polyemeraldine in its deprotonated base form has a quinoid-diimine absorption band located at 634 nm.[3−8] The intensity and broadness of this band agree with those of the previously reported polymer, which contains one electron-withdrawing group. In the case when the polymer contains two electron-withdrawing groups (the herein report), the band assigned to the quinoid-diimine units is smaller compared to the former mentioned polymers (see Figure 5); therefore, this polymer has a lower composition of quinoid-diimine units than polyemeraldine and the reference polymer. The lower composition of quinoid-diimine units is a consequence of the two electron-withdrawing groups present in the monomer, which prevent the formation of quinoid-diimine units in the polymerization process.

On the other hand, it has been described in the literature that aniline monomers substituted by electron-donating groups (such as methyl, propyl, hexyl, α-hydroxo-ethyl, dimethyl, and methoxo) are polymerized in the acidic medium. Thus, it results in a polymer with excellent absorption in the visible region, like the absorption of polyemeraldine in its base form.[38−45] Therefore, we think that the most important variables to obtain semiconducting polymers are the electron-withdrawing and electron-donating side substituents of anilines. In a previous paper,[30] it has been reported that it is possible to combine both properties (electron-donating and electron-withdrawing) to obtain a polymer with improved abundance of quinoid-diimine units. To achieve this preferred structure, it is necessary to have one electron-withdrawing

Figure 8. Molecular orbitals involved in the calculated absorption transitions.

group (ester) at a distance of at least three bonds from the aniline ring. In the case of the obtained polymer, the two electron-withdrawing groups are three-bond distant from the aniline ring, as in the reference polymer; however, the formation of quinod-diimine units is not favored due to the double effect of the two electron-withdrawing groups in the aniline ring. With a 50% abundance of quinoid groups, the protonation by a Bronsted-Lowry acid (doping) is possible because it produces charge carriers (polarons and bipolarons), which are delocalized throughout the polymeric chain, producing electrical conductivity.[46−48] In contrast, if the quinoid-diimine composition is not sufficient, the doping acid does not affect the electrical conductivity since the abundance of the charge carriers is small and/or they are not formed. In fact, the Cl/N molar ratio values calculated in elemental analysis (Table 1) represent a measure of the polymer doping level. In this case, the polymer doping level has a value of 1.0, indicating that the polymer is highly doped by HCl. According to literature, the charge carriers absorb in the UV−vis spectra at a wavelength higher that 700 nm.[45,47−50] In this case, they are not observed in the UV−vis spectrum of this polymer (Figure 5). Furthermore, the small electrical conductivity measured for the polymer ($<10^{-9}$ S cm^{-1}) is in concordance with the low composition of quinoid-diimine groups found by UV−vis spectroscopy. An increased composition of quinoid-diimine units in the polymer could have been possible by the inclusion of other methylene groups bonded to the aniline ring since the electron-donating groups promote the formation of these units, and at the same time, the two electron-withdrawing groups are sufficiently separated from the aniline ring.

Figure 7 shows the thermal decomposition profile obtained by TGA for the polymer. We can assume that the polymer is thermally stable up to 217 °C because no additional mass loss is observed in this temperature region. On the other hand, the sample is totally decomposed at 352 °C. The strong diminution observed in the weight/temperature profile shows two inflection points. The first one, at 246 °C, is due to the decomposition of one ethoxy group and the second one, at 312

°C, is due to the rupture of the two methylene bonds connected to the quaternary carbon. The polyaniline derivative has moderate thermal stability since 8.0% weight loss occurs at 246 °C. To characterize the morphology of the polymer, SEM characterization was performed. It can be observed that the polymer shows certain rugosity in its particle structure (for details, see the SI).

By means of theoretical computations, to show the influence of the quinoid-diimine units over the UV−vis spectra, two different tetramer structures were calculated, one containing only benzenoid-diamine units (possibility **a**) and one containing 50% quinoid-diimine units (possibility **b**). All of the calculations were performed using the B3LYP functional and the 6-31g* basis set for all of the atoms. The frequencies showed only positive values, meaning that a minimum point on the potential energy surface was reached. To correlate the theoretical results with the experimental results, a TD-DFT calculation was carried out for both the theoretically proposed polymer structures. In the case of the polymer containing only benzenoid-diamine units (possibility **a**), a transition with high oscillator strength was observed only at 305 nm, which is composed of a transition that goes from one phenyl ring to another phenyl ring (see Table 2 and Figure 8). In the case of the polymer that contains 50% quinoid-diimine units (possibility **b**), two transitions were observed. One transition is located at 595 nm with a low oscillator strength, which goes from orbitals located over one benzenoid-diamine unit to the quinoid-diimine unit (see Figure 8). The second observed transition is centered at 308 nm and has a high oscillator strength. This transition starts with several different orbitals located over different regions of the polymer and goes to an orbital located over the quinoid-diimine unit. All of the observed results and the good correlation of the UV−vis data with the TD-DFT calculation corroborate that the experimentally obtained polymer contains quinoid-diimine units in between benzenoid-diamine units.

CONCLUSIONS

A new polyaniline derivative was synthesized and characterized. It was shown that when two electron-withdrawing groups (ester) are three-bond distant from the aniline ring, the formation of quinoid-diimine units is not favored due to the double effect of the two electron-withdrawing groups, in comparison with the reference polymer. The quinoid-diimine composition is much lower than required to obtain a polymer with electrical properties like polyemeraldine. The polyaniline derivative exhibits moderate thermal stability since it shows linear weight loss up to 217 °C.

ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c06471.

> Monomer synthesis and SEM images of the oligomer and molecular structure (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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