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Synthesis, Characterization, Thermal Stability and Fluorescence of Hybrid Polymers Prepared from Amino-phenyl esters

C. O. Sánchez[1] (✉), F. Alvarado[1], C. J. Bustos[1], E. Schott[1], N. Gatica[2], K. Valdebenito[2]

[1]Instituto de Química, Facultad de Ciencias, Universidad Austral de Chile, Avda. Los Laureles s/n, Campus Isla Teja, Casilla 567, Valdivia, Chile
E-mail: christiansanchez@uach.cl; Fax: 56-63-221597

[2]Departamento de Polímeros, Facultad de Ciencias Químicas, Universidad de Concepción, Avda. Edmundo Larenas 129, Concepción, Chile
E-mail: nigatica@udec.cl

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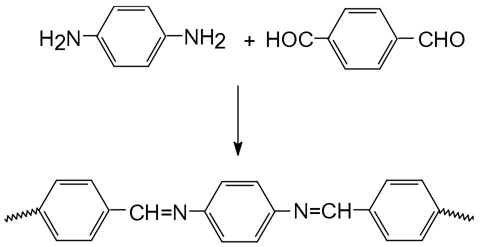
Summary

This paper addresses paper the synthesis, characterization and properties of a new class of materials prepared from amino-phenyl esters. These materials are polymers prepared by self-condensation of the monomer at high temperature, using HCl as catalyst under different pressure conditions. The polymers were characterized by elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, UV-visible and fluorescence spectroscopy. The composition, viscosities and thermal stability were also determined. The results showed that the polymers are hybrid materials because they contain simultaneously amide and imine groups in their backbones. When diminishing the pressure of the reaction medium, the polymers were obtained with higher viscosities, which were related with the composition and the thermal stability. Moreover, the polymers presented fluorescence which was associated to the polymers' different functional groups.

Introduction

Poly(imines) are materials known as poly(azomethines). They have in their backbones imine groups (C=N) that can be protonated with acids (HA) to yield a polyelectrolite (-C=NH$^+$(A$^-$)-). The first poly(imine), poly(p-xylylidene-p-phenylenediamine), named PI, was synthesized by Adams et. al. [1] (scheme 1), and is of easy preparation and high thermal stability [2,3]. However, it is an unsoluble material in organic solvents due to a rigid structure and a high molecular weight.

Some methods used to improve PI solubility include the insertion of flexible bonds between aromatic ring in the polymeric backbone such as oxy, methylene and sulphonyl groups [4-10], as well as the incorporation of side substituents in the aromatic ring, such as methyl, methoxy, chlorine, hydroxy, alkyloxymethyl, and sulfonate groups [11-17].



Scheme 1: Synthesis of Poly(p-xylylidene-p-phenylenediamine), PI

PI and their derivatives have been studied for their dendrimer structures [18,19], liquid-crystalline phase[20], non-linear optical properties [21,22], semiconductivity [23], luminescence [24,25] and as support of heteropolyanions with catalytic properties [26,27].

In a previous paper [28], we prepared a class of materials, hybrid oligomers, using self-condensation of ethyl 3-aminophenyl acetate and 3-aminophenyl acetic acid. Those hybrid oligomers have simultaneously in their backbones amide and imine groups, although they have low viscosity values (0.12-0.02 dL/g). From the point of view of their properties, these hybrid oligomers are interesting materials, since they have spherullitic-type semi-crystallization, gel properties and high thermal stability. In this type of materials, the properties observed depend on the preparation conditions as well as on the viscosity values.

The aim of this work is the preparation of materials with a viscosity higher than found for previously reported oligomers, which can be obtained from another monomer, methyl 3-aminophenyl acetate. The polymerization conditions are also modified by changing the pressure of the reaction medium. The obtained materials were characterized by elemental analysis and spectroscopic methods. The thermal stability and other properties such as fluorescence are also reported.

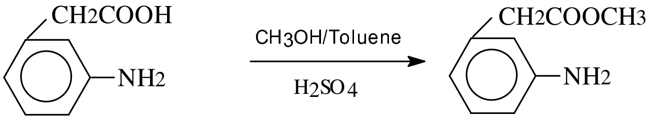
Experimental

Physical measurements

Elemental analysis, C, H, N, were obtained using an EA-1108, Fisons Elemental Analyzer and the total quantity of chloride from the ASTM standard method [29]. IR spectra were recorded on a Nicolet FT-IR Nexus spectrophotometer on KBr pellets. NMR spectra were obtained from DMSO-d_6 solutions using TMS as internal reference on a 400 MHz Bruker spectrophotometer. The UV-Vis and fluorescence spectra were registered from polymeric dissolutions (0.21 mg/mL) using DMF as solvent in a cell of 1 cm of length at room temperature (20ºC). A poly B solution in DMF at 50ºC was prepared and cooled at room temperature, then, the spectra were registered immediately. The UV-vis spectra were registered in a UNICAM UV 500 equipment and the fluorescence spectra were registered in a SFM 25 Fluorescence spectrophotometer Kontron Instruments equipment at a voltage of 400 V. Thermogravimetric analysis, TGA, were registered under N_2 atmosphere on a STA 625 Thermal Analyzer at 10ºC/min. Intrinsic viscosity, [η], was determined from DMF solutions at 25ºC on an Ostwald-type capillary viscometer without kinetic energy correction and the [η] values were calculated using the Solomon-Gotessman equation [30].

Synthesis and Characterization of the Monomer

The precursor, methyl 3-aminophenyl acetate, was prepared from 3-aminophenyl acetic acid [31] according to the following reaction:



4.26 g of 3-aminophenyl acetic acid was refluxed at 80-90ºC for 72 h with 350 mL of methylic alcohol, 5.3 mL of toluene and 3.6 mL of H_2SO_4 98%. The reaction mixture was concentrated by reduced pressure distillation at 80-90ºC up to a volume of 44 mL. Then, the mixture was alkalinized to pH=11-12 with a 4 % NaOH aqueous solution (approximately 65 mL), extracted four times with ethylic ether, dried with Na_2SO_4, and the ether removed by distillation. The product was purified using various chromatography sheets (20 x 20 cm^2) prepared with Silica Gel F_{254} and eluted with ether. The first eluted product (liquid) was methyl 3-aminophenyl acetate. 1.09 g (23.4% yield) of monomer was obtained.

(^{1}H-NMR, $CDCl_3$): 3.73 ppm (s,3H, CH_3); 3.57 ppm (s, 2H, CH_2); 7.14 ppm (t,1H aromatic); 6.65 ppm (m, 3H aromatic); 3.82 ppm (s,2H amine). (FT-IR): νN-H(3467 cm^{-1}, 3380 cm^{-1}); νC-H aromatic (3006 cm^{-1}); νC=O (1742 cm^{-1}); νC=C aromatic (1603 cm^{-1}); δC-O (1296 cm^{-1}, 1163 cm^{-1}); pattern of deformation out-of-plane with 1,3-disubstitution, γC-H (692cm^{-1}, 779 cm^{-1}). Elemental Analysis: Calc.C, 65.44%; H, 6.71%; N, 8.48%. Found, C, 65.02 %; H, 6.31 %; N, 8.23.

Thermal Polymerization of the Monomer

Methyl 3-aminophenyl acetate monomer was polymerized at high temperature using 37% aqueous HCl as catalyst in two different conditions of pressure, at atmosphere and reduced pressure.

Polymerization at Atmosphere Pressure

In a flask, 0.17 g of the monomer and 0.013 g of 37% aqueous HCl were added, then the mixture was heated in an oil-bath at 220-230ºC for 20 min. After that, it was cooled at room temperature, and the polymer was successively washed with chloroform, hexane, ethylic ether, acetone and 5 mL hot methanol. The polymer was dried in vacuum at 80ºC during two days. A total of 0.05 g (29 % Yield) of polymeric product were obtained and called Poly A.

Polymerization at Reduced Pressure

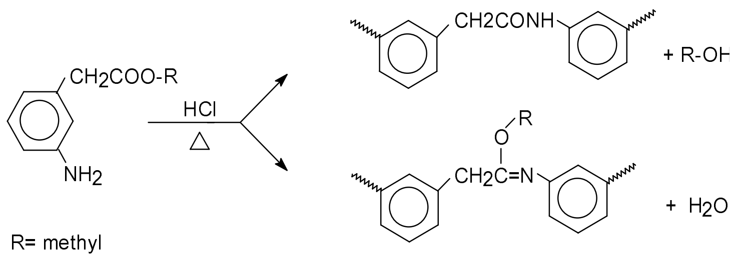
To a flask, 1.09 g of the monomer and 0.091 g of 37% aqueous HCl were added, then the flask was connected to a vacuum pump (10^{-5} mmHg) and heated in a oil-bath at 210-230ºC for 9 min. Subsequently, it was cooled at room temperature, and the polymer was successively washed with chloroform, ethylic ether, hexane, heated acetone and heated methanol. The polymer was dried under vacuum at 80ºC for two days. A total of 0.61 g (56% Yield) of polymeric product was obtained.

Fractionation and Purification of Polymers

The polymer prepared at reduced pressure was fractioned in two polymeric samples of different viscosity. 0.47 g of the polymeric product was added *ca* 6 mL of DMF stirred, filtered through Büchner funnel, and washed successively with methanol, ethylic ether and vacuum dried at 80ºC during two days. 0.10 g of insoluble product in DMF was obtained and named Poly B. Sufficient methanol was added to the soluble fraction in DMF until precipitation of the polymeric product. Then, the mixture of solvents was separated from the polymeric product by centrifugation. The soluble polymeric product was washed several times with ethylic ether and the ether separated by centrifugation. Then the product was vacuum dried at 80ºC for two days. A total of 0.17 g of polymeric product was obtained and named Poly C.

Results and Discussion

The preparation of hybrid materials that simultaneously contain amide and imine groups in their backbones is possible because the amino-phenyl esters monomers can be self-condensed to high temperature using HCl as catalyst. The amide and imine groups are formed by a substitution or addition-elimination mechanism between the amine groups and the alcoxo-carbonyl group, resulting in the release of alcohol and water (Scheme 2).



Scheme 2: Functional groups formed in the self-condensation of aminophenyl ester

In a previous work [28], we prepared, under different reaction conditions, hybrid oligomers obtained from ethyl 3-aminophenyl acetate with viscosity values between 0.02 and 0.12 dL/g. However, if the polymerization reaction is carried out from methyl 3-aminophenyl acetate under different reaction conditions (atmosphere and reduced pressure) in presence of catalyst (HCl) at a high temperature, hybrid materials of higher viscosity are obtained (Table 1). In fact, when methyl 3-aminophenyl acetate is polymerized at atmosphere pressure (Poly A), the viscosity is 0.95 dL/g; and when it is polymerized at reduced pressure (Poly B), the viscosity is 1.23 dL/g. The increase in viscosities with respect to the previously reported oligomers is due to two motives. First, in the reaction of substitution, the methoxy group is the best leaving group than the ethoxo group (the methoxy group is more stable as conjugated base). Second, due to reduced pressure the water and alcohol are eliminated in the course of polymerisation, thus, the equilibrium at high temperature is displaced towards product formation, thus favoring the polymerisation reaction.

On the other hand, the viscosity of poly B is greater than the viscosity of poly A. This result is due to the effect of the reaction's reduced pressure and the high temperature, allowing the quick release of water and alcohol from the reaction medium. Indeed, in the experimental process, we observed that the water and alcohol formed were quickly eliminated and condensed on the equipment. The yield of poly A (29%) is smaller than the yield of the polymer obtained at reduced pressure (56%), because a greater amount of catalyst was used in the synthesis of Poly A, and consequently it can hydrolyze a fraction of the amount of monomer. The formed 3-aminophenyl acetic acid is not very reactive in the reaction of self-condensation, which was confirmed in a previous work [28].

The polymer prepared at reduced pressure was fractioned in two polymeric samples, Poly B and Poly C with different viscosities (Table 1). However, a polymeric fraction from poly A could not be obtained possibly due to the polymer's low polydispersity.

Table 1: Elemental analysis, viscosities, Empirical Formula of polymeric samples

Polymeric samples	%C	%H	%N	%Cl	%O[b]	[η][a] dL/g	Empirical Formula
Poly A	67.15	9.29	8.29	5.47	9.80	0.95	$C_{8.0}H_{13.2}N_{0.9}O_{0.9}Cl_{0.2}$
Poly B	67.02	5.80	10.86	3.55	12.77	1.23	$C_{8.0}H_{8.2}N_{1.1}O_{1.1}Cl_{0.14}$
Poly C	66.99	5.88	9.87	3.94	13.32	1.16	$C_{8.0}H_{8.4}N_{1.0}O_{1.2}Cl_{0.16}$

a) Calculated in DMF at 25°C, b) Calculated by difference

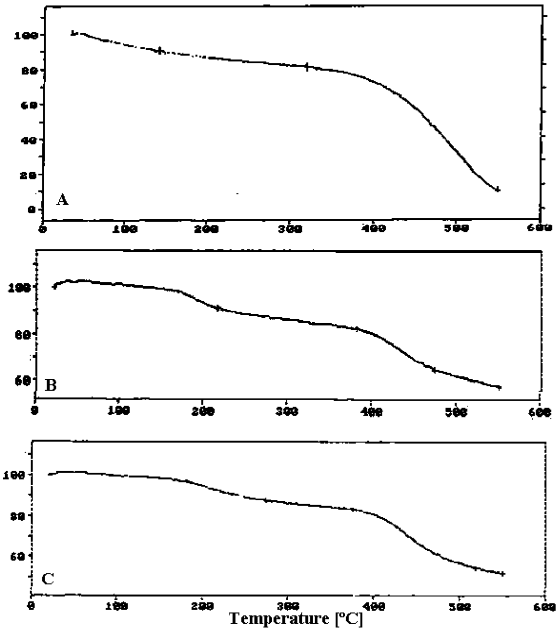
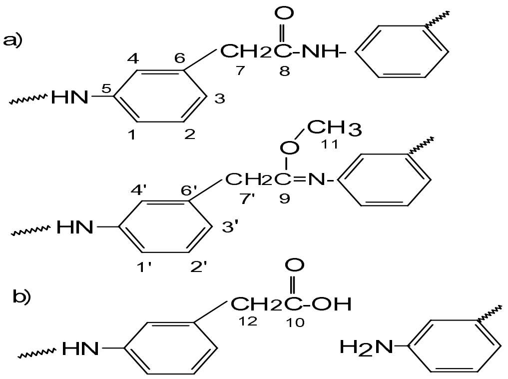


Figure 1: Thermal decomposition profiles of A) Poly A, B) Poly B and C) Poly C

Figure 1 exhibits the polymers` thermal decomposition profiles recorded in nitrogen atmosphere. Poly A presents the lowest thermal stability because it is showed a weight loss of 10% at 140°C; Poly B and Poly C presented a similar profile with a weight loss of 10% at 216ºC and 225ºC, respectively. When the polymer viscosity increases, the thermal stability is higher. However, the thermal stability is lower than that found for the previously reported oligomers [28], which presented a weight loss of 10% at 460ºC. Thus, the thermal stability of this type of materials can also depend on the backbone`s rigid structure, where the rigidity depends on the composition (or amount) of the imine and amide groups in the main chain. In fact, it is know that the imine groups confers high thermal stability to PI (Scheme 1) [2,3].

Table 1 shows the elementary analysis results and the empirical formula of the hybrid materials prepared at atmosphere pressure (Poly A) and reduced pressure (Poly B and Poly C), and Scheme 3 presents the proposed functional groups in the polymers` backbone. The (normalized) empirical formulas of the polymeric samples are similar, and each repeated unit in the polymers contains eight C-atoms, one nitrogen and *ca* one oxygen atom.



Scheme 3: Functional groups proposed for Poly A, B and Poly C: a) Internal functional groups, b) terminal functional group

The bi-dimensional spectrum of Poly A recorded in DMSO-d6 is shown in Figure 2. The signals were assigned with the help of CHEM-3D.The more important signals and its relations are described as the following: The sets of signals located in the 3.20-3.63 ppm range in the ^{1}H-NMR spectrum were assigned to protons of three different methylene groups as well as to the protons of one methoxo group. The protons of each methylene group are related (doublet) with three different carbons located at 41.33, 41.80 and 43.83 ppm in the ^{13}C-NMR spectrum. The protons of the methoxo groups are related (doublet) with one carbon atom located at 51.0 ppm in the ^{13}C-NMR spectrum.

The methylene protons are related with the aromatic carbons located between 117.91 and 139.65 ppm, with 2 carbonyl carbons located at 169.4 ppm, 173.0 ppm, and with one carbon of imine groups located at 169.1 ppm in the ^{13}C-NMR spectrum (see Scheme 3). The sets of signals located in the 6.57-7.50 ppm range in the ^{1}H-NMR spectrum were assigned to aromatic protons, which are related with methylene carbons located at 41.33 ppm and 43.83 ppm and with aromatic carbons located in the 117.91-139.65 ppm range in the ^{13}C-NMR spectrum. The signal located at 10.16 ppm in the ^{1}H-NMR spectrum was assigned to the proton of amide groups (-CONH-), which is related with 3 aromatic carbons and also with one carbonyl carbon located at

169.4 ppm in the ^{13}C-NMR spectrum. The sets of signals located in the 3.3-2.6 ppm range can be associated with the short chains` methylene groups.

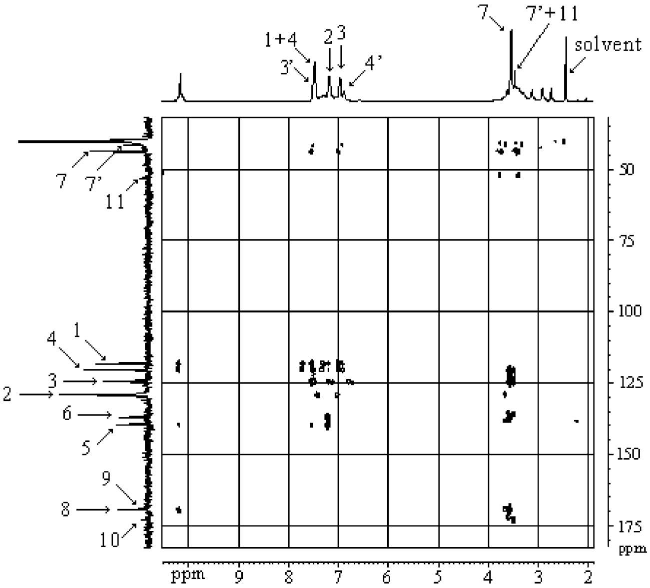


Figure 2: Bi-dimensional spectrum of poly A

The polymeric sample prepared at reduced pressure (Poly B) was insoluble in deutered solvent. However, Poly C (obtained by separation with organic solvents from poly B) was soluble in DMSO-d6 and the corresponding ^{1}H-NMR spectrum is presented in Figure 3. The signal located at 10.1 ppm was assigned to the protons of amide groups (-CONH-) and the singlet signals located at 2.6 ppm and 2.8 ppm were assigned to methylene protons of amide ($-CH_2CONH-$) and imine ($-CH_2C(OR)=N-$) groups, respectively. The signal located at 3.55 ppm was assigned to the methoxo groups that are bonded with the carbon of imine groups. The signals in the 6.3-7.7 ppm range were assigned to the protons of the aromatic ring. The solvent (DMSO-d6) and water absorbed appears at normal chemicals shifts at 2.5 ppm and 3.4 ppm, respectively. It is evident that the chemicals shifts in the two ^{1}H-NMR spectra are different, indicating that the molecular surroundings of the functional groups in the main chain of the two polymers are different. Therefore, the composition and the molecular ordering of the imine and amide groups are different in the backbone of the two polymeric samples.

The polymer composition, measured as percentage of the imine groups, was calculated using a ratio between the integral of the aromatic protons associated to imine groups and the integral of all the aromatic protons. The integral of the aromatic protons associated to imine groups was obtained by subtracting the integral of all the aromatic protons and four times the integral of the protons of amide groups located at 10.1 ppm. In this way, the percentages of imine groups in Poly A and Poly C were 28.4% and 43.0%, respectively. According to the composition, the polymers prepared at reduced pressure have a greater amount of imine groups, which is consistent with the higher thermal stability found for Poly C.

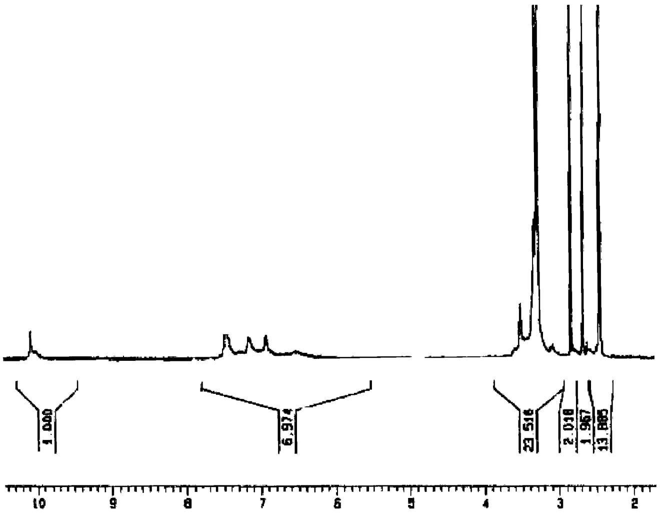


Figure 3: ^{1}H-NMR spectrum of Poly C

The FT-IR bands are consistent with the functional groups of the studied polymers (Figure 4). The principal absorption bands of the polymer prepared at atmospheric pressure (Poly A) and at reduced pressure (Poly B and Poly C) are: ν NH (3422-3436 cm^{-1}); ν OH (3237-3293 cm^{-1}); ν C=O of amide groups (1660-1655 cm^{-1}); ν C=O of carboxylic acid, partially overlapped in Poly A (1721 cm^{-1}); the out-of-plane deformation pattern of 1,3-disubstitution(two bands) (773-768 cm^{-1}); ν C-H aliphatic (2930-2925 cm^{-1}); δ C-H aliphatic (1378-1342, cm^{-1}). In literature the I. R. absorption band of ν (C=N) is reported at 1600-1620 cm^{-1} range [13,14, 21]. However, in the

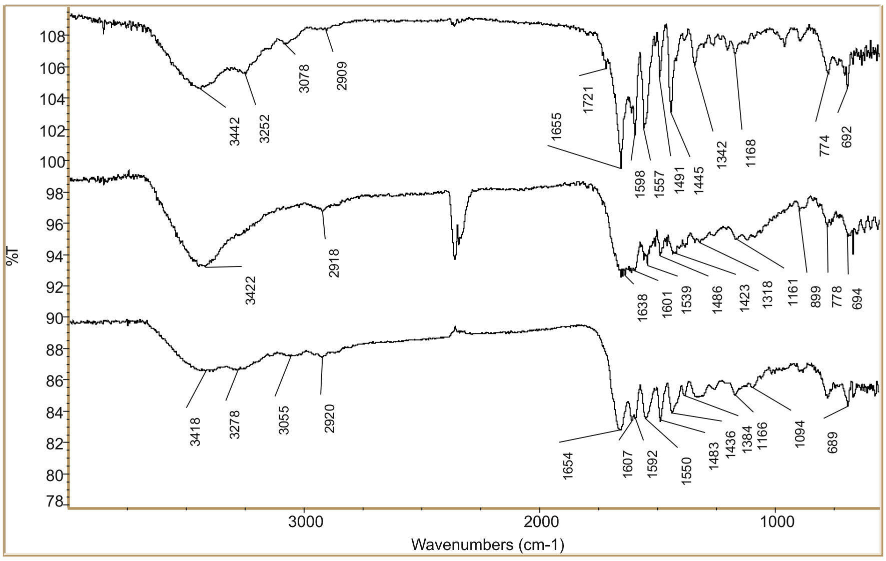
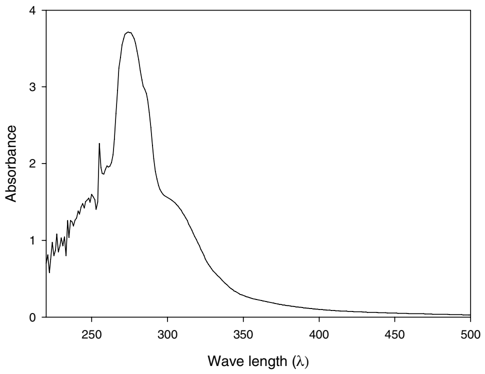


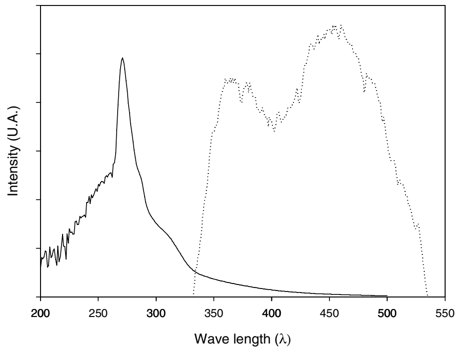
Figure 4: FT-IR spectra of poly A (top spectrum), poly B (middle spectrum) and, poly C (down spectrum)

cases of Poly A, Poly B and Poly C these bands are partially overlapped with ν (C=C and C=O) absorptions. The presence of imine groups in these materials was confirmed by XPS experiments [32].

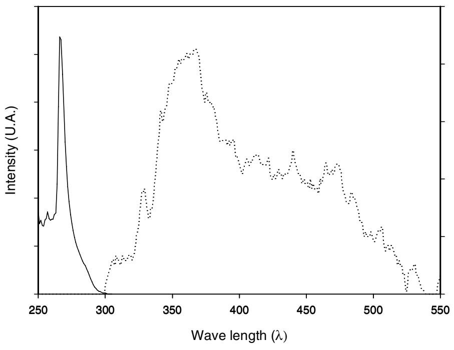
Figure 5 shows the absorption and fluorescence spectra of dissolutions 0.21 mg/mL in DMF of Poly A, Poly B and Poly C. The absorption maxima are observed at the same wavelength (275 nm) in the three polymers. Moreover, a shoulder is observed at *ca*



Poly A



Poly B



Poly C

Figure 5: Absorption and fluorescence spectra of Poly A, Poly B and Poly C (left: absorption, right: fluorescence) in DMF dissolution

300 nm in Poly A and Poly B. These absorptions are assigned to transitions π-π* of the aromatic rings. The absorptions at low wavelength are due to a small conjugation in the backbones of the polymers.

Considering the small conjugation of the studied systems, the polymers prepared at reduced pressure (Poly B and Poly C) exhibit fluorescence at relatively long wavelengths, at 450 nm for Poly B and at 370 nm for Poly C.

The fluorescence in dissolution depends on several factors, namely the intra-chain interactions, bond rotation, and the defects along the chain, which are channels for non-radioactive deactivation of the excited state [33, 34]. The polymeric samples have different viscosities, composition (imine group content), and molecular ordering, complicating the relation between the increases in fluorescence and polymer properties. We think that fluorescence in the polymers depends strongly on the viscosities and the composition of the imine groups because Poly B has a higher fluorescence than Poly C for the same order of increases in the viscosity. Additionally, Poly C has imine groups content higher than Poly A, which doesn’t present fluorescence. The fluorescence could be principally ascribed to the presence of both electron-withdrawing (imine) and electron-donating (methylene) groups along the partially conjugated system.

Conclusions

We have been obtained hybrid materials from methyl 3-aminophenyl acetate monomer. The self-condensation polymerisation reaction of the monomer was carried out at high temperature, atmosphere pressure and reduced pressure using HCl as catalyst. From methyl 3-aminophenyl acetate, polymers with higher viscosities can be prepared decreasing the internal pressure in the reaction medium. At the same time, those polymers with moderate thermal stability have the capacity of fluorescence emission, allowing the later study of these materials in optoelectronics, such as diodes luminescent, which is part of our research equipment work.

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References

1. Adams R, Bullock J, Wilson W (1923) J Am Chem Soc 45:521
2. D’alelio G F, Crivello J V, Dehner T R, Schoenig R K (1967) J Macromol Sci A1(7):1331
3. D’alelio G F, Crivello J V, Schoenig R K, Huemer T F (1967) J Macromol Sci Chem A 1:1321
4. El-Shekeil A G, Khalid M A, Al-Yusuf F A (2001) Macromol Chem Phys 202(15):2971
5. Weng I, Sun W, Jiang L, Shen Z (2000) Macromol Rapid Commun 21(15):1099
6. Banerjee S, Gutch P K, Saxena C J (1995) Polym Sci Part A Polym Chem 33(10):1719
7. Banerjee S, Gutch P K, Saxena C J (1999) Des Monomers Polym 2(2):135
8. Yang H, Natansohn A (1992) Macromolecules 25(21):5798
9. Yang H, Natansohn A (1993) Polymer 34(19):4135
10. Mansour E S, Kassem A A, El-Din H N, El-Toukhy A A (1991) Macromol. Rep. A28:103
11. Yang S J, Jenekhe S A (1995) Macromolecules 28:1180
12. Gopal J, Srinivasan M (1986) J Polym Sci Part A Polym Chem Ed 24:2789

13. Yang C J, Jenekhe S A (1991) Chem Mater 3(5):878
14. Park S R, Kim H, Zin W C, Jung J C (1993) Macromolecules 26(7):1627
15. Lee K S, Wong J C, Jung J C (1989) Makromol Chem 190(7):1547
16. Reinhardt B A, Unroe M R (1991) Polym Commun 32(3):85
17. Lee T S, Kim H, Kumar J, Tripathy S (1998)Macromol Chem Phys 199(7):1445
18. Higuchi M, Shiki S, Yamamoto K (2000) Org Lett 2(20):3079
19. Higuchi M, Shiki S, Ariga K, Yamamoto K (2001) J Amer Chem Soc 123(19): 4414
20. Yang H, Natansohn A (1993) Polymer 34:4135
21. Jenecke S A, Yang C-Y, Vanherzecle H, Meth J S (1991) Chem Mat 3:985
22. Yang C-Y, Jenecke S A (1994) Chem Mat 6:196
23. Lee K S, Won J C, Jung J C (1989) Makromol Chem 190:1547
24. Wang X, Ogino K, Tanaka K, Usui H (2003) Thin Solid Films 438/439:75
25. Yang Z, Sokolik I, Karasz F E (1993) Macromolecules 26:1188
26. kulszewicz- Bajer I, Hasik M, Wielgrs I, Turek W, Lapkowski M, Pron A (1995) Synth Met 69:573
27. kulszewicz- Bajer I, Hasik M, Wielgrs I, Turek W, Lapkowski M, Pron A (1995) Mat Res Bull 30:1571
28. Sánchez C O, Bustos C J, Alvarado F A, Gatica N M, Fernández N (2006) Polymer Bulletin 57:505
29. ASTM Method (1981) 30:103
30. Solomon O, Gottesman B (1967) Makromol Chem 104:177
31. Sánchez C O (2003) J Appl Polym Sci 89:1484
32. Sánchez C O, Bustos C J, Alvarado F A, Schott E E, Gatica N, Bernede J-C (2007) e-polymers (In Press)
33. Jenekhe S A, Osaheni J A (1994) Science 265:765
34. Kim D Y, Cho H N, Kim C Y (2000) Prog Polym Sci 25:1089