POLYIMINES CONTAINING N-HEXYL 3,6-CARBAZOLYL-DIYL AND 1,4-PHENYLENE UNITS IN THE MAIN POLYMER CHAIN

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Three soluble imine polymers based on a combination of two units: 3,6-(N-hexyl) carbazolyldiyl and 1,4-phenylene in the main polymer chain have been synthesized by solution polycondensation method from 1,4-diaminobenzene or 3,6-diamino-N-hexylcarbazole and 3,6-diformyl-N-hexylcarbazole or terephthaldehyde and their structure was analysed by spectroscopic methods. Presence of linear and cyclic oligomers was observed by gel permeation chromatography and assigned after liquid chromatography separation and mass spectroscopy analysis.

INTRODUCTION

Poly (azomethine)s, known as polyimines or Schiff base polymers, or also named polyazines (when hydrazine is used as diamine compound) or polyketanils (when diketones are used as dicarbonyl compounds) are polymers mainly obtained by polycondensation reactions between diamines and dicarbonyl monomers.[1] The interest for fully aromatic and conjugated polyimines renewed in the last years because aromatic poly(azomethine)s are isoelectronic with poly(p-phenylene vinylene)s which are the most known electroluminescent polymers,[2] while polyazines are nitrogen-containing analogues of polyacetylene, the most conducting polymer.[3] Simionescu *et al.*[4-10] have synthesized aromatic polyimines as precursors for conducting polymers by solution polycondensation of aromatic diamine/dialdehyde pairs and also by oxidative polymerization of imine-based monomers containing two oxidizing aromatic end groups (thiophene, pyrrole, naphthalene).

Carbazole is a heterocyclic compound that has been used in the synthesis of many polycondensation or polymerization polymers due to its photoconducting properties and high electron-donating character. Therefore, these polymers possess interesting electro-optical and photochemical properties as well as high thermal stability due to the carbazole conjugated system.[11] However, only few papers are reported about azomethine polymers containing carbazole rings.[12-17]

In this article, novel conjugated polyazomethines containing 3,6-(N-hexyl) carbazolyldiyl and 1,4-phenylene units in the main polymer chain have been synthesized by solution polycondensation method from 1,4-diaminobenzene and 3,6-(N-hexyl) diaminocarbazole) or 3,6-diformyl (N- hexyl) carbazole and terephthaldehyde and their structure was proved by spectroscopic methods.

RESULTS AND DISCUSSION

Three imine polymers have synthesized by solution polycondensation of equimolar mixtures of 3,6-diformyl-N-hexylcarbazole with 1,4-phenylenediamine or 3,6-diamino-N-hexylcarbazole and terephthaldehyde with 3,6-diamino-N-hexylcarbazole (Scheme 1). Polymers **I** and **II** have the same chemical composition but they can be considered as *head-* and-*tail* and *tail-* and-*head* isomers, depending on the position of carbazolyldiyl and phenylene units attached at –CH=N- linkage (Scheme 2).

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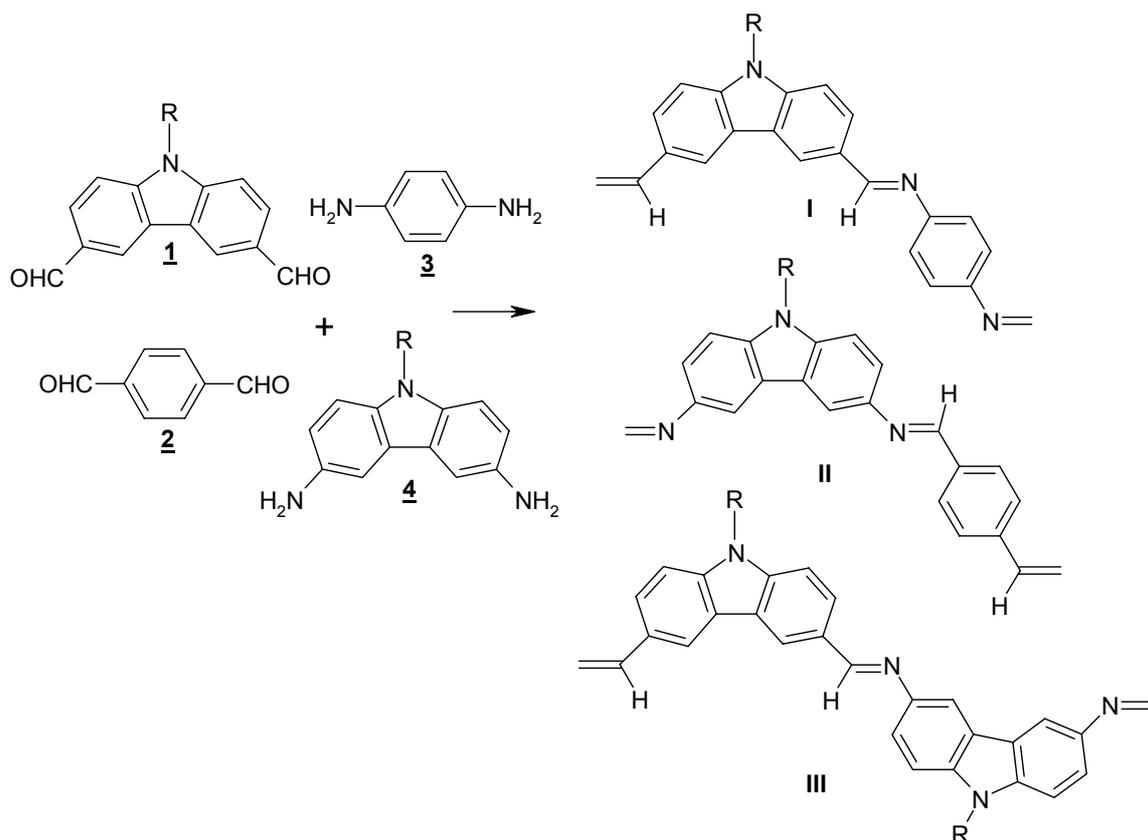
Scheme 1 – Synthesis of carbazole-based polyimines.

The reactions were carried out in chloroform, in homogeneous phase and polymers were separated in high yields by precipitation in methanol. The introduction of flexible alkyl substituents in the main polymer chain using adequate dialdehyde and diamine partners has as effect the increasing of polymer solubility in organic solvents. In addition,

the presence of 3,6-disubstituted carbazole induces a bent conformation for macromolecular chain with benefits on polymer solubility. Thus, the synthesized polymers are soluble in aromatic (toluene), chlorinated (CH_2Cl_2, $CHCl_3$) and aprotic polar solvents (THF, DMF, NMP, DMAc).

Table 1

Synthesis of carbazole-based imine polymers

Polymer	Solvent (mL)	Yield (%)	M_w (PD)	λ max, UV, ($CHCl_3$)	^{1}H-NMR ($CDCl_3$)
I	$CHCl_3$ (7)	78.7	4400 (1.5)	260, 270, 298, 344, 353, 385	10.12 (-CHO); 8.68(-CH=N-); 8.15; 8.03; 7.50; 7.37; 6.74; 4.35/4.23; 1.91; 1.31; 0.87
II	$CHCl_3$ (7)	87.1	6700 (1.3)	280, 305, 345, 378, 422, 450	8.79(-CH=N-); 8.16; 7.53; 7.32; 7.0; 4.34/4.24; 1.88; 1.26; 0.86
III	$CHCl_3$ (7)	94.3	4540 (1.3)	269, 300, 358, 389, 420	10.02 (-CHO); 8.65 (-CH=N-); 8.12; 8.02; 7.51; 7.08; 6.90; 4.52/4.16; 1.86; 1.26; 0.89

[Dialdehyde} = [Diamine] = 0.14 mol.L^{-1}, reaction temperature: 7 h at room temperature and 0.5 h at reflux temperature.

The IR spectra of the polymers (Fig. 1) show the typical absorption band at 1625 cm^{-1} characteristic for the azomethine –CH=N- linkage. The –C=C- aromatic absorption bands appear at 1595 cm^{-1} while 810 and 880 cm^{-1} peaks are assigned to out-of-plane deformation of the C-H bonds in the 1,2,4-trisubstituted benzene rings of

carbazole nucleus. Due to the low molecular weight of the polymer, the terminal –CHO (1680 cm^{-1}) group is also observed, mainly in the spectrum of the polymer **I**. The elementary step in the polycondensation of diamine with dialdehyde is the nucleophilic attack of the amine group on the carbonyl bond followed by dehydration of the

tetrahedral intermediate. Therefore, the rate of reaction is dependent on the diamine nucleophilicity and the electrophilicity of the carbonyl compound. The reactivity of the diamine and dialdehyde compounds, used in this study, is in the order: diamine nucleophilicity; **4** > **3** and dialdehyde electrophilicity; **2** >**1** and this explains the lower molecular weight of the polymer **I** against polymer **II** and presence of stronger absorption peak assigned to –CHO ends. The weight-average molecular weights were determined by GPC (THF as eluent) to be 4400 (**I**) and 6700 (**II**) with the polydispersibilities of 1.5 and 1.3 against the polystyrene standards and presence of some oligomers in the GPC curves was detected.

The ^{1}H-NMR spectrum (CDCl$_3$, 400 MHz, aromatic region) of the polymer **I** (Fig. 2) shows peaks at 8.68 (-CH=N-), 8.15-8.03 (H$_4$), 7.5 (H$_1$), 7.37-7.0 (H phenyl) and (H$_2$) corresponding to imine and aromatic protons, respectively. A weak signal positioned at about 10.12 ppm can be assigned to the oligomer chain ends (-CHO) while signal positioned at 6.74 is assigned to aromatic protons from *ortho* position of phenylene amine ends. Polymer **II** shows a very similar spectrum; a singlet signal at 8.79 ppm for imine protons and three wide peaks positioned at 8.16, 7.5, 7.3 and 7.0 ppm (aromatic protons from carbazole and phenyl rings). The existence of a single signal for imine protons has suggested the presence of only one isomer, probably conformer *anti* which is thermodynamically more stable. The aliphatic region is very similar for both polymer structures and shows four signals at about 4.3 (-N-CH$_2$), 1.9 (-N-C-CH$_2$), 1.3 [(CH$_2$)$_3$] and 0.87 ppm (CH$_3$) assigned to protons from hexyl substituent.

The UV-vis absorption spectra of the two polymers, in chloroform solution, are presented in Fig. 3. They show absorption maxima in the range 250-330 nm characteristic of π -π* transition in aromatic rings while absorptions at higher wavelengths (340-430 nm) are assigned to n- π* transitions of imine groups conjugated with aromatic nuclei. A clear red shifting of the absorption is observed in the case of polymer **II** versus polymer **I** mainly for n- π* absorption.
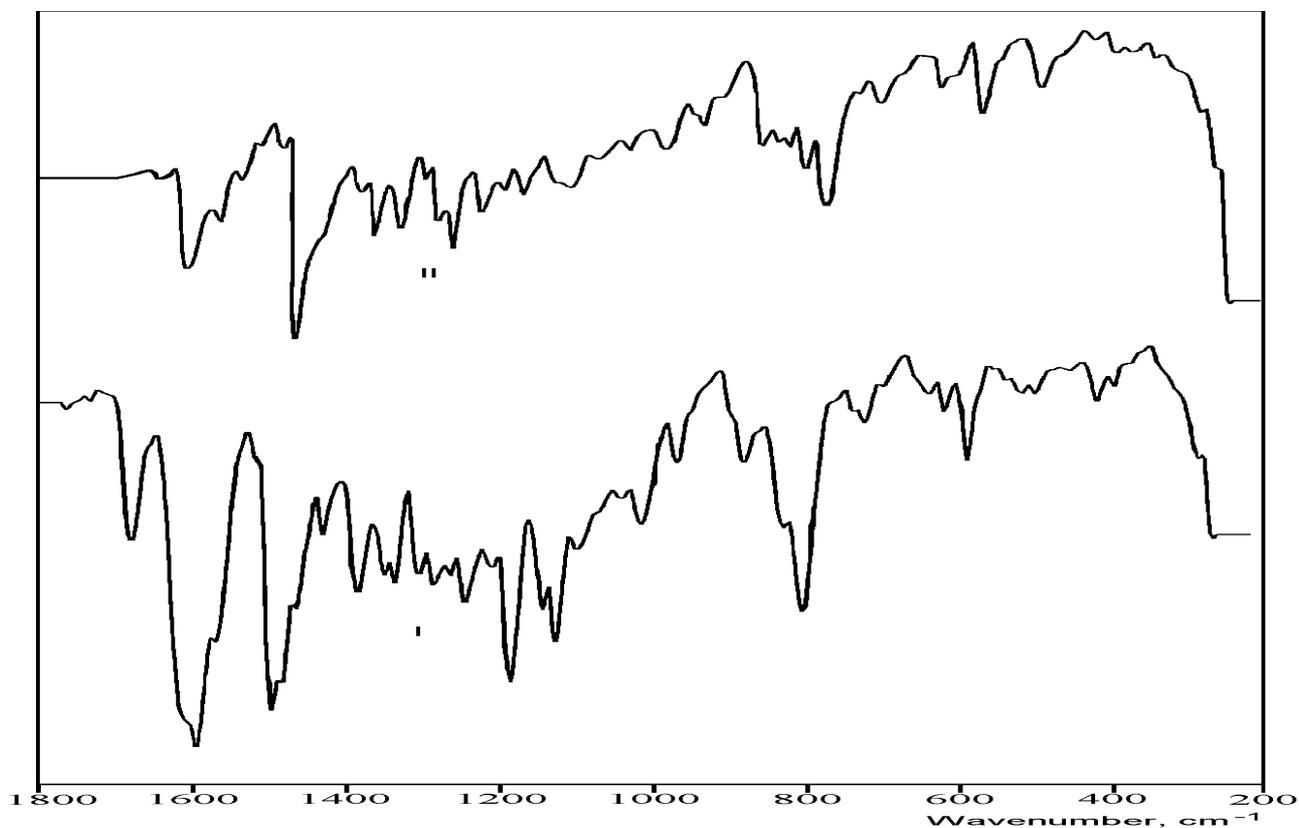

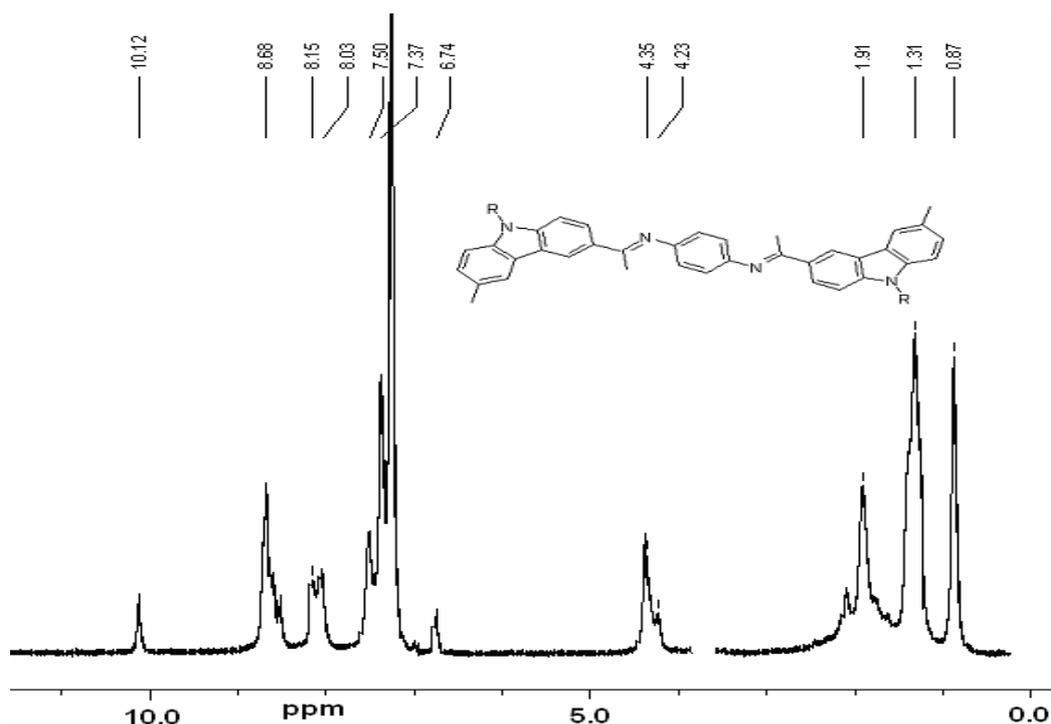Fig. 1 – Infrared spectra (KBr pellet) of polyimines **I** (bottom) and **II** (top).

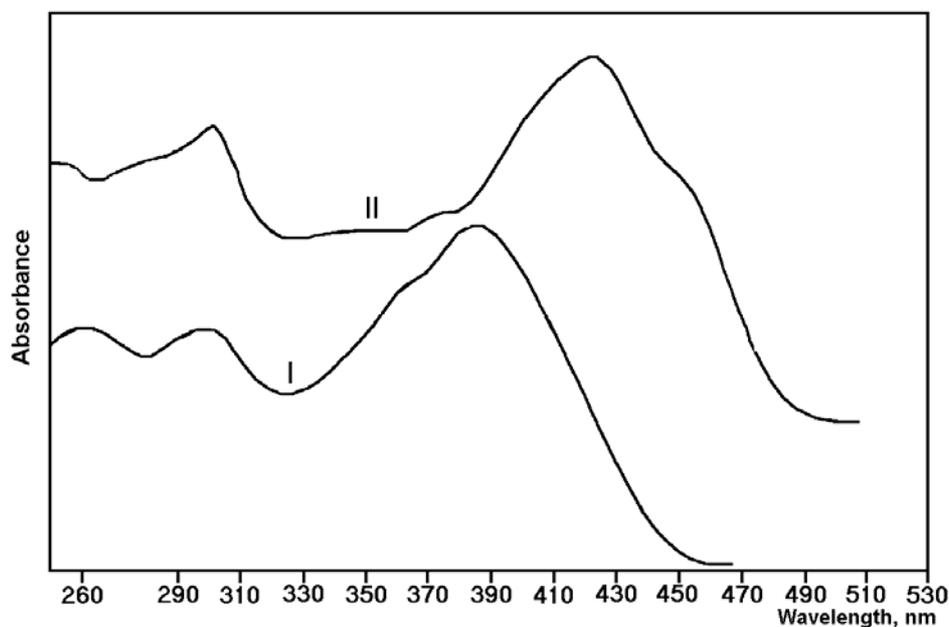Fig. 2 – ^{1}H-NMR (CDCl$_3$, 400 MHz) spectrum of polymer **I**.

Fig. 3 – UV-vis spectra (CHCl$_3$) of polyimines **I** and **II**.

This behavior can be explained considering the sterical structure of the imine derivatives. It is recognized that imine group is not coplanar with neighboring aromatic rings, thus the aromatic ring linked at –N= atom is out of the imine group plane with 40-55 ^{o} while aromatic ring linked at –CH= is out of plane with 10 ^{0} but in opposite sense.[18] This arrangement allows lone electron pair of nitrogen to be in conjugation with amine aromatic ring.

Therefore, in polymer **I**, the lone electron pair of imine nitrogen is conjugated with a phenyl ring while for polymer **II** is in conjugation with carbazole nuclei, the conjugation being more extended and absorption takes place at lower energies (Scheme 2). Both polymers have a good thermal stability in air up to 320 ^{0}C that is mainly due to their aromatic and conjugated structure.
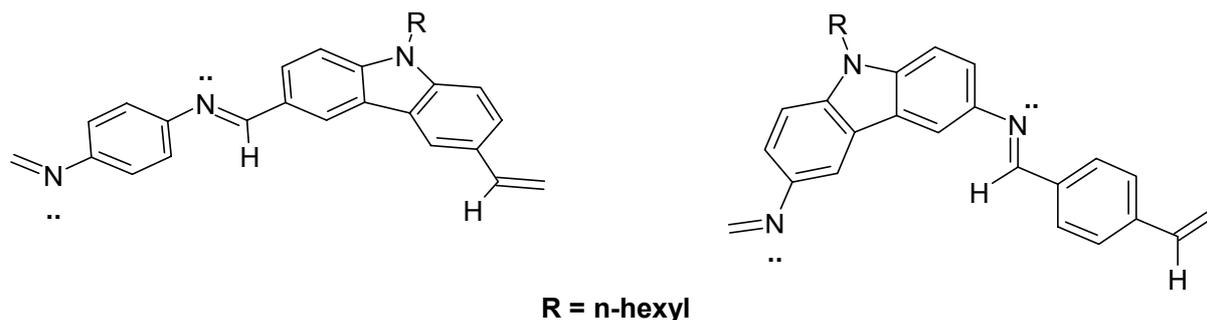
R = n-hexyl

Scheme 2 – Chemical structure of head-to-tail and tail-to-head imine isomers.

A polyimine containing only N-hexyl 3,6-carbazolyldiyl units was synthesized by polycondensation of carbazole based- diamine and dialdehyde compounds. The polymer has a good solubility in common organic solvents; chlorinated, aromatic and aprotic dipolar solvents, and is amorphous. The GPC curve of the polymer is presented in Fig. 4 where besides moderate molecular weight polymer, presence of a strong signal is assigned to oligomers. These oligomers have separated as acetone – soluble fraction and analyzed by liquid chrmatography coupled with mass spectroscopy. The presence of some oligomers was observed also in the GPC curves of polymers **I** and **II** where diamine is a linear compound, but their intensity was lower.
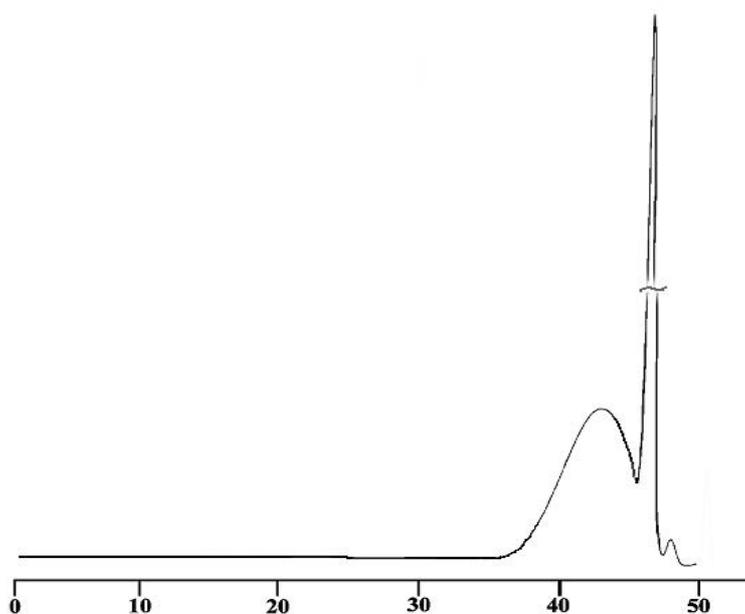
Fig. 4 – GPC curve of polymer **III**.

The liquid chromatography analysis coupled with mass spectroscopy of acetone-soluble fraction shows that oligomers are cyclic and linear products having structures presented in Scheme 3.

In Fig. 5 (a and b) are presented mass spectroscopy data of acetone-soluble fraction, in which it can be observed in the domain 500 – 1500 m/z, three main components with mass molecular ions of 553, 571 and 1105 m/z corresponding to the chemical compounds with MW 552 (**6**, n=1), 570 (**5**) and 1104 (**6**, n=2) Daltons. Higher linear oligomers (**7**, **8**) are in small quantities.

In the synthesis of polymer **III**, both dialdehyde and diamine have the two aryl-CHO and aryl-NH$_2$ bonds projected at about 120 $^{\circ}$ angle from the nitrogen atom of the carbazole ring and hence macrocycles formation can be anticipated to take place. The ring closing is more probable for low macrocyclics (**6**, n= 1, 2) because for larger macrocycle the probability of reaction of CHO and NH2 ends of the same molecule decreses with its length. Polymer **III** shows an UV spectrum as a superposition of the two spectra of polymer **I** and **II** (Table 1).
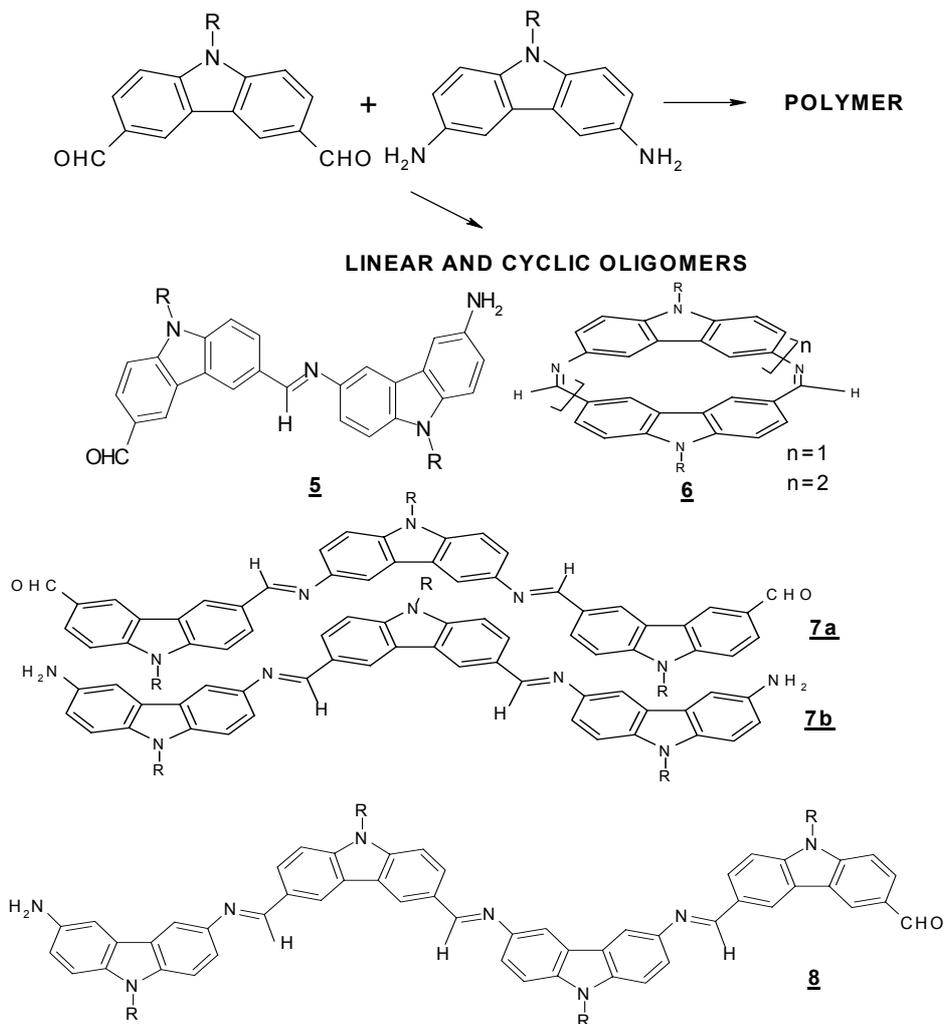
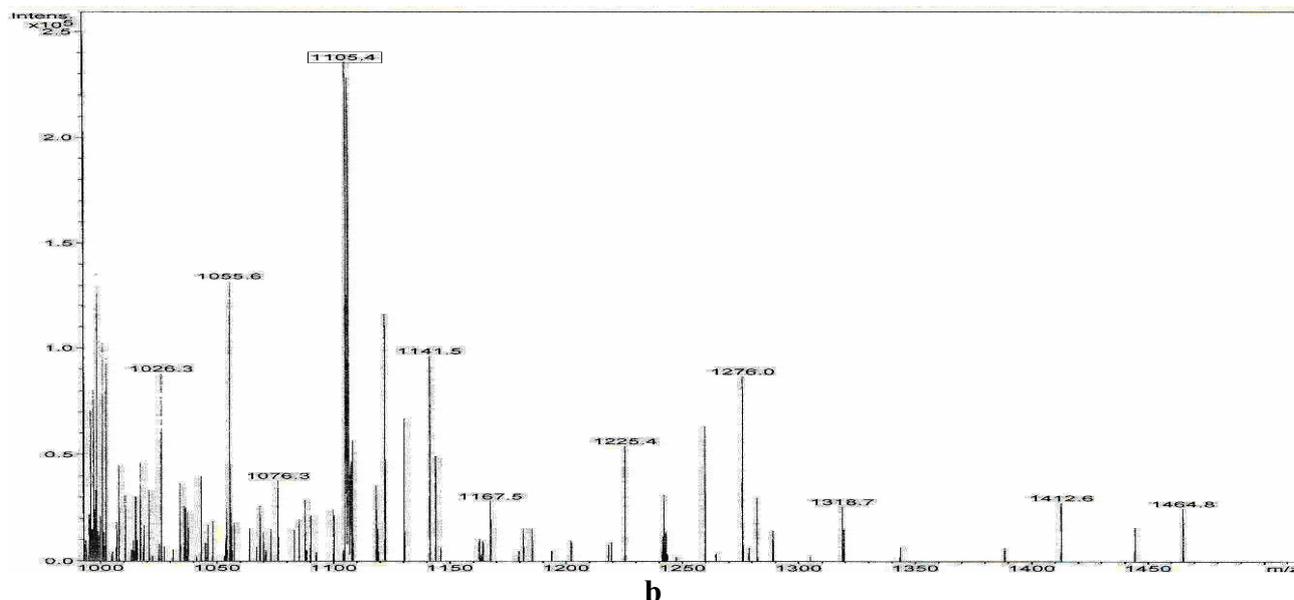Scheme 3 – Structure of the linear and cyclic oligomers obtained in polymerization of **1** with **4**.

a
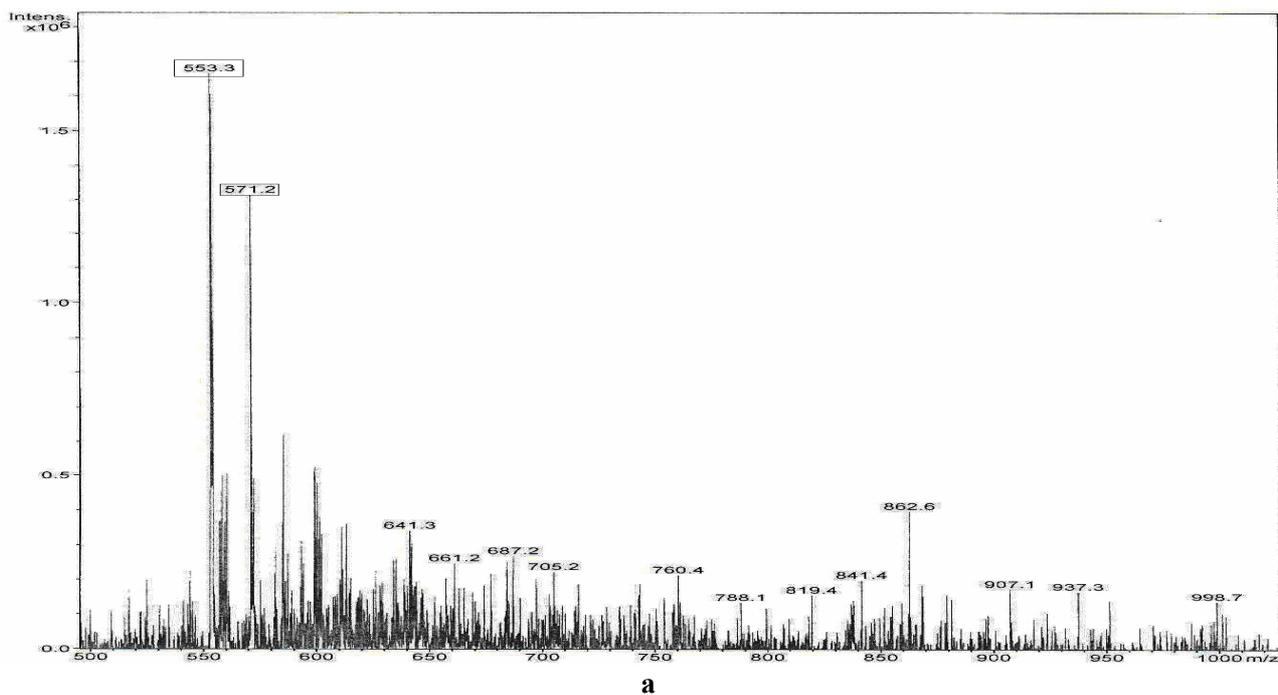
Fig. 5 (a and b) – MSD measurements (direct injection in MSD) of acetone-soluble fraction of polymer **III**.

EXPERIMENTAL

Materials: 1,4-Phenylenediamine and terephthaldehyde (Aldrich) are commercially products and were purified just before use by recrystallization from methanol. N-Hexyl 3,6-diformyl carbazole was synthesized by formylation of N-hexyl carbazole in presence of a high excess of $POCl_3/DMF$ mixture.[16] N- Hexyl 3,6-diamino carbazole was synthesized from N-hexylcarbazole by nitration with $Cu(NO_3)_2$ and reduction of dinitro derivative with $SnCl_2.2H_2O$.[12,16] All polycondensations were carried out in similar conditions using dried chloroform as solvent, at room temperature (7 hours) and at final 0.5 h reflux and absence of the catalyst. Polymers were precipitated in methanol and purified by reprecipitation.

Characterization: The FTIR spectra were recorded in KBr pellets on a DIGILAB-FTS 2000 spectrometer, while UV-Vis absorption spectra were obtained on a Specord M42 Carl Zeiss Jena spectrophotometer using 10 mm quartz cells. ^{1}H-NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz) as solutions in $CDCl_3$ and chemical shifts are reported in ppm and referenced to TMS as internal standard. The relative molecular weights were determined by gel permeation chromatography (GPC) using a PL-EMD instrument (England) and polystyrene standards for the calibration plot and N,N'-dimethylformamide as solvent. MS measurements were performed on Agilent 1100 Series LC/MSD Trap –XCT apparatus, by separation on C 18 column and MSD or direct injection in MSD of solution in acetone (1 μl), full scan 100-2200 m/z.

CONCLUSIONS

The solution polycondensation of N-hexyl 3,6-diformyl carbazole with 1,4-phenylenediamine and therephthaldehyde with N-hexyl 3,6-diaminocarbazole was studied to obtain soluble and high performance polyimines based on carbazole moiety. Some preliminary studies on the polymer structures using IR, ^{1}H-NMR, UV, GPC and TGA methods are presented. Polymers are soluble and amorphous materials with high thermal stability. The presence of linear and cyclic oligomers was evidenced by gel permeation chromatography and their quantity is higher when both partners have functional groups non-linear positioned.

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