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Synthesis and characterization of some polyazomethine conducting polymers and oligomers

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Abstract

Polyazomethine polymers were prepared from the polycondensation of terephthaldehye with different diamines, namely, benzidine, 2,3-diaminopyridine, 1,4-diaminoanthraquinone and 3,5 diamino-1,2,4-triazole. The electrical conductivities of the polymers were studied with doping with H_2SO_4 and 5% I_2 together with the undoped polymers. The crystallinity and morphology of the polymers were studied using XRD and scanning electron microscopy. A comparative study of the electrical conductivities of oligomers of polyazomethines and those of their corresponding polymers was performed.

Key words: polyazomethines, oligomers, conducting polymers, synthesis, characterization.

Introduction

The electrical conductivity of polymers will depend upon many factors among which is conjugation, crystallinity, linearity and doping [1]. Polyazomethine polymers have all these properties and more. Polyazomethines, as conducting polymers, seem potentially useful for electronic applications since they are environmentally stable with good mechanical and electrical properties [2]. The presence of the nitrogen atom in their backbone makes them environmentally stable [3]. Many studies have been devoted to the electrical properties of polymers since the discovery of metallic-conducting doped polyacetylene [4].

As a continuation of our interest in conducting polymers [5,6,7] we report in this paper the synthesis of some conducting polyazomethine polymers and oligomers.

Experimental

Materials

All the chemicals (Aldrich) were recrystallized before use. Terephthaldehyde [8] and benzidine [9] were prepared according to literature. Ethanol was distilled twice before use.

A. Synthesis of polyazomethines

All the reactions were carried out in refluxing ethanol for 6-10 hours. A general method for the synthesis of polyazomethine polymers was carried out by dissolving the

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terephthaldehyde (0.1 mole) in a minimum amount of absolute ethanol (~15ml) and added slowly to the diamine (0.1 mole) also in a minimum amount of ethanol (~15ml) and then refluxed under air for 6-10 hours depending on the diamine. The synthesized polymers were filtered, washed three times with water and once with dichloromethane then dried in air for 48 hours. All the melting points were higher than 300°C. The different polymers prepared are shown in Table-1 together with the starting materials.

B. Synthesis of oligomers

I - Oligomer 1: Benzidine (0.01 mole) was reacted with terephthaldehyde (0.03 mole) in refluxing ethanol (1 hr) to give oligomer 1.

$\mathrm{H_2N\text{-}ArAr\text{-}NH_2 + 3OHC\text{-}Ar\text{-}CHO \longrightarrow OHC\text{-}Ar\text{-}CH{=}N\text{-}ArAr\text{-}N{=}HC\text{-}ArCHO}$

Oligomer 1

II - Oligomer 2: The resulted oligomer 1 (0.01 mole) was further reacted with (0.03 mole) benzidine in refluxing ethanol (1 hr) to give oligomer 2.

$\mathrm{Oligomer\ 1 + 3H_2N\text{-}ArAr\text{-}NH_2 \longrightarrow H_2N\text{-}(\text{-}ArAr\text{-}N{=}CH\text{-}Ar\text{-}CH{=}N\text{-})_2ArAr\text{-}NH_2}$

Oligomer 2

III - Oligomer 3: Further reaction of oligomer 2 (0.01 mole) with p-chlorobenzaldehyde (0.03 mole) in refluxing ethanol (1 hr) was carried out to give oligomer 3.

$\mathrm{Oligomer\ 2 + 3OHC\text{-}Ar\text{-}Cl \longrightarrow Cl\text{-}(\text{-}Ar\text{-}CH{=}N\text{-}ArAr\text{-}N{=}CH\text{-})_3Ar\text{-}Cl}$

Oligomer 3

Polymer Charaterization

Infrared spectra were recorded using the KBr disc technique on a Perkin Elmer 1600 spectrophotometer. Wide-angle X-ray diffractograms were obtained for powder specimens at room temperature using a Rikagu XRD-BW 1729 diffractometer. The morphology of the polymers was examined using a Jeol JSM 840A Scanning Electron Microscope. The viscosities were determined on 0.2% (w/v) polymer solution in acetone at 30°C using a Cannon-Ubbelohde suspended level viscometer. The excitation emission spectra were measured using a Shimadza RF 510 spectrofluorophotometer. A solution of anthracene in benzene (~3.2×10^{-5} mol-dm^3) was used as a reference standard. The current was measured using a nanoammeter (2830 digital multimeter), a dc power supply (Leybold Heraeus) and a high impedance voltmeter.

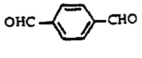
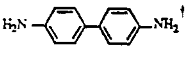
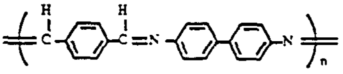
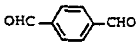
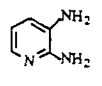
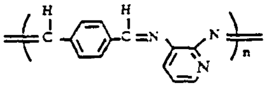
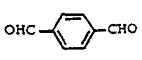
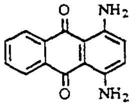
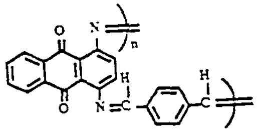
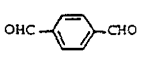
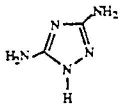
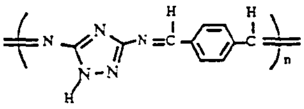
Doping was done by the addition of 5% I_2 (w/w) to the polymer or oligomer, mixing then pressing into a pellet. In case of conc. H_2SO_4 a drop was added to the polymer (~200mg), left to dry in an oven at 60°C overnight, then pressed under 10^4 Kgcm^{-2} pressure and subjected to measurements.

The solubilities of the polymers were determined using 0.2 g of the polymer in about 3 ml of solvent at room temperature and with heating when necessary.

Results and Discussion

The structures of the prepared polymers were established from elemental analyses which were found to be satisfactory for all the prepared polymers and oligomers. The IR spectra are included in Table-2 together with the % yield, inherent viscosity, and color of the polymers. The IR spectra of all the polymers showed the disappearance of the aldehyde

Table-1: The diamines and dicarboxaldehydes reacted and the polymers produced.

Polymer	dicarboxaldehyde	diamine	polymer
Ie			
Ig			
Ih			
Ii			

carbonyls and the diamines of the starting materials and the appearance of absorption bands absorption at 810-1160 cm^{-1}. The IR spectra of the polyazomethine polymers also included other characteristic absorption bands for the rest of the molecules such as the C=O of polymer Ih at 1700cm^{-1} and NH of polymer Ii at 3430 cm^{-1}.

The inherent viscosities of the polymers is 0.21 to 0.35. These small inherent viscosity values indicate short chain polyazomethines which is reflected on the properties of the polymers. Accordingly, the solubilities are much better than expected for long chain polymers, and the electrical conductivities of these short chain polymers are comparable to those of the prepared oligomers in the doped and undoped states as will be seen later.

The solubility characteristics of the synthesized polymers are shown in Table-3. A 10% (w/v) solution was taken as criterion for solubility [10]. The solubility behavior is very useful for the processing of these materials for technological applications [11]. The low solubility of polymer Ie is due to its rigid linear backbone. On the other hand, the relatively high solubilities of the polymers Ig and Ih arise from the kinked backbone structure and bulky lateral substituent, respectively. Polymer Ii is relatively linear and hence poorer solubility would be expected.

The excitation emission spectrum of polymer Ih is shown in Fig-1. Polymer Ih had an unsymmetrical emission spectrum with a maximum intensity at ~415 nm. It showed two excitation intensity maxima at 365 and 380 nm. All the measurements were taken in acetone as solvent with the emission spectra follow at the excitation maximum. The electronic absorption spectrum of polymer Ih showed a broad band structure expanded from 435 to 635 nm with a maximum at ~ 550 nm. This is an attempt to explore the optical

Table-2: The % yield, inherent viscosity, color and important IR spectral data of the polyazomethines.

Polymer	% Yield	Inh. Vis (η_{inh})	Color	IR cm^{-1}			
				C=N	C=C	C=C-H^a	C=O
Ie	89	-	yellowish green	1590	1610	1130 1025 810	-
Ig	59	0.35	brown	1580	1620	1120 1080	-
Ih	68	0.21	black	1570	1600	1160 1020 820	1700
Ii	73	0.31	yellow	1600	1600	1100 1010 840	-

a) CH out of plane deformation vibrations of para substituted phenyls.

and photochemistry properties of the polyazomethines. More detailed work on the optical properties of polyazomethines is in progress.

The X-ray diffractograms of polymers Ih and Ii before and after annealing at 50°C for 24 hours are shown in Fig-2. Polymers Ih and Ii show reflections of sharp peaks which indicate more crystalline structures usually not noticed in amorphous interfaces in the region $2\theta = 5° - 45°$ [10,12]. The X-ray differactograms of the polymers showed similar patterns before and after annealing. The crystallinity of these linear rigid polyazomethines is expected.

The morphologies of these polymers were examined by scanning electron microscopy and all the images of the polymers showed crystalline surfaces typical for linear polymers.

The electrical conductivity values of the undoped polymers and doped polymers (H_2SO_4 and I_2) are shown in Table-4. The polymers showed good conductivities after doping, well in the semiconducting region.

The electrical conductivity of polymer Ie together with oligomers 1 and 3 as a function of temperture was studied and the results are shown in Fig-3 ($\ln\sigma$ vs 1000/T). The dc conductivity of polymer Ie and the oligomers was found to increase upon heating of the samples in a similar behavior. This is mainly due to variation of carrier concentration with temperature as in the case of semiconductors [13].

The prepared oligomers of the polyzomethines were compared to their corresponding polymer Ie. Table-5 summarizes the physical properties of oligomers 1, 2, 3 and polymer Ie, namely % yield, color, melting points and electrical conductivities of both their doped and undoped states.

The structures of the prepared oligomers were confirmed by their elemental analyses data and their typical IR absorption bands. The IR spectra showed the disappearance of the

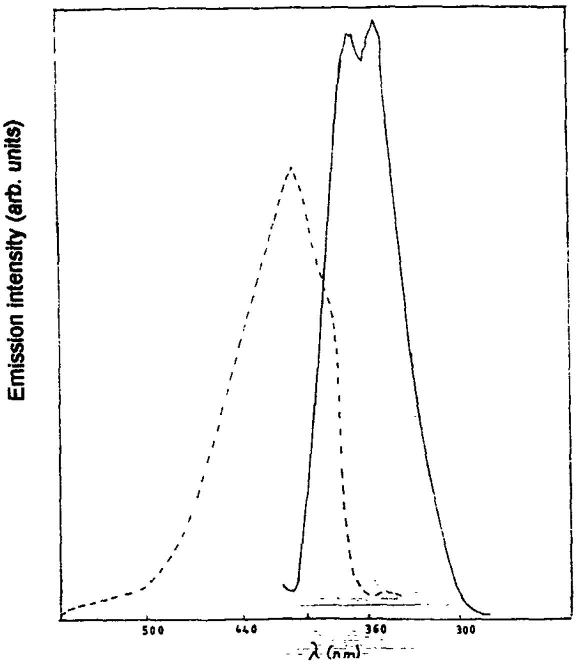


Fig-1: The excitation emission spectrum of polymer Ih.

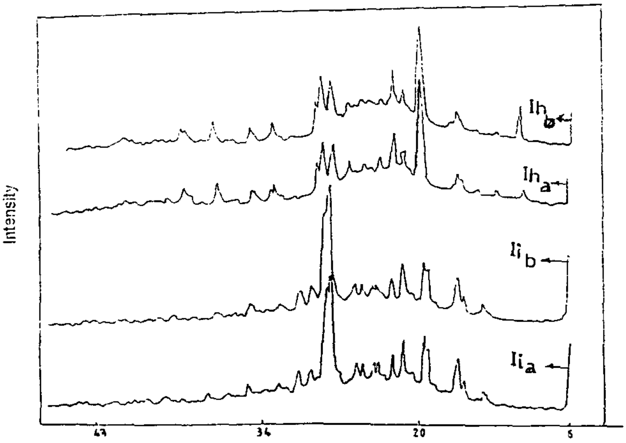


Fig-2: X-ray diffractograms of polymers Ih and Ii before (a) and after (b) annealing at 50°C for 24 hours.

absorption bands of the starting materials and the appearance of the absorption bands of the condensation products. All the three oligomers showed the absorption bands of C=N and C=C at 1580 to 1610 cm^{-1} and the out-of-plane bands of C=C-H at 800 to 1200 cm^{-1}. the IR spectra also showed other absorption bands for the rest of the molecules such as the aldehyde carbonyl of oligomer 1 at 1690 cm^{-1} and the NH_2 of oligomer 2 at 3450 cm^{-1}.

Similarity in the electrical conductivity values of the undoped oligomers and their corresponding polymer Ie was observed. The conductivity values ranged between 10^{-10}-10^{-12} S/cm.

In case of the doped materials (I_2 and H_2SO_4 doped), the conductivity values of both the oligomers and their Ie polymer fall in the range of 10^{-3}-10^{-5} S/cm.

The above observations allow us to conclude that the oligomers and their corresponding polyazomethine Ie had almost the same conductivity values. This may probably be due to the low molecular weight of the polymer as can be seen from its low inherent viscosity value. Our findings are in accordance with with Wudl [2] and coworkers who found that polyaniline oligomers with eight rings showed the same conductivity values as the long chain polymers.

Table-3: Solubility characteristics of the polyazomethines: (+): soluble at r.t., (+-); partially soluble at r.t., (+-H); partially soluble upon heating, (-); insoluble.

Polymer	Ie	Ig	Ih	Ii
Water	-	-	-	-
Acetone	+-H	+	+-H	+-H
DMF	-	+	+	-
Acetic acid	+-H	+	-	-
Ethanol	+-	-	-	-
Chloroform	+-H	-	+	-
Methanol	+-H	-	+	-
Benzene	+-H	-	-	-
Pet-ether 80-100	-	-	-	-
DMSO	+-	+	+-	+-
CH_2Cl_2	-	-	-	-
m-Cresol	-	+	+-	-

Table-4: The electrical properties of the polyazomethines prepared.

Polymer	Conductivity (S/cm)		
	Undoped	H_2SO_4 Doped	I_2 Doped
Ie	1.9 x10^{-11}	6.8 x 10^{-5}	7.1 x10^{-5}
Ig	5.5 x 10^{-11}	7.5 x 10^{-6}	3.2 x 10^{-5}
Ih	6.0 x 10^{-10}	2.1 x 10^{-3}	1.1 x 10^{-3}
Ii	1.3 x 10^{-11}	3.9 x 10^{-3}	1.3 x 10^{-3}

Table-5: The physical properties of oligomers 1, 2, and 3 compared to polymer Ie

ligomers	% yield	M.pt (°C)	color	Conductivity S/cm		
				undoped	H_2SO_4 doped	I_2 doped
1	63	108-110	grey	2.0x10^{-11}	6.0x10^{-4}	3.7x10^{-5}
2	97	248-250	dark green	2.7x10^{-10}	1.2x10^{-3}	6.8x10^{-4}
3	91	220-221	brown	4.2x10^{-12}	1.0x10^{-3}	1.7x10^{-3}
Ie	89	>300	yellowish green	1.9x10^{-11}	6.8x10^{-3}	7.1x10^{-3}

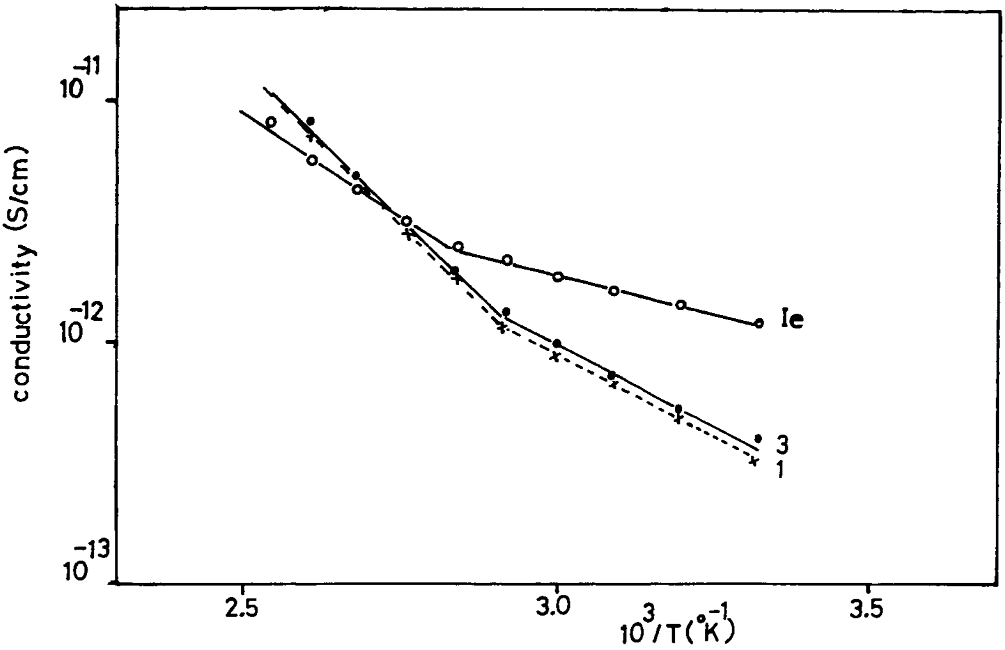


Fig-3: Electrical conductivity of polymer Ie and oligomers 1 and 3 vs. temperature

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