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SYNTHESIS AND PROPERTIES OF SOME SCHIFF-BASE POLYMERS CONTAINING SULFUR

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ABSTRACT

Condensation of 5,5'-methylene-bis-salicylaldehyde with thiocarbohydrazide, bis(4-aminophenyl) sulfone, 4,4'-diaminostilbene-2,2'-disulfonic acid or 3,5-diaminobenzenesulfonic acid gave the corresponding polymeric schiff-bases (1, 2, 3, or 4). Also, condensation of terephthalaldehyde with thiocarbohydrazide or bis(4-aminophenyl) sulfone produced the schiff base polymers (5 or 6). Finally, condensation of di(p-formylphenyl) terephthalate or di(p-acetylphenyl) terephthalate produced the polymers (7, 8). Structures of these polymers (1 - 8), their properties, viscosities measurements and the effect of various reaction conditions on the yield percent are studied. These variable conditions showed no effect on the molecular weight of the present schiff polymers.

INTRODUCTION

Polymers with a system of conjugated -C=C- and -C=N- bonds in their main chain have been drawing the attention of researchers more due to their importance in many aspects. Of interest among these polymers are polyazines and polymeric-schiff bases. Polyazines are obtained by the polycondensation reaction of hydrazine with a number of diketones. The polymeric schiff-bases are produced by polycondensation of diamines with various dicarbonyl compounds.

Polymeric schiff-bases have developed over the past decade into a fast growing field in applied and specific separations(1). They have also attracted attention because of their importance as catenation ligands, where the coordination polymers derived from polymeric schiff-bases have been extensively studied(2). Also, the thermal stabilities of wholly aromatic polymeric schiff-bases are comparable or even better than aromatic polyamides(3). In addition, some of them are of electrophysical interesting, especially those having semiconductor properties(4).

EXPERIMENTAL

All of the reagents and starting materials used in the present work are of reagent grade and are used without purification unless otherwise noted. Melting points are uncorrected and were determined on a Kofler melting point block. IR spectra were performed on a Pye Unicam SP 2000 spectrometer. The microanalyses were performed in the Chemistry Department, Faculty of Science, Cairo and/or Alexandria University.

Preparation of Schiff-Base Polymer (1):

To a solution of 2.56 g (0.01 mol) of 5,5'-methylene-bis-salicylaldehyde(5), in 25 mL THF and 30 mL glacial acetic acid, was added a warm solution of 1.06 g (0.01 mol) of thiocarbohydrazide(6) in 5 mL of glacial acetic acid. Warming the mixture on a water-bath, about 10 seconds at 90°C, a bright orange precipitate formed. After dilution with 200 mL methanol, the precipitate was filtered, washed with methanol and ether, dried in an oven at 110°C.

Preparation of Schiff-Base Polymer (2):

A solution of 2.48 g (0.01 mol) of bis(4-aminophenol) sulfone (Merk) in a mixture of 30 mL ethanol and 20 mL acetic acid was added to a solution of 2.56 g (0.01 mol) of 5,5'-methylene-bis-salicylaldehyde in 20 mL THF and 20 mL of glacial acetic acid. On heating the reaction mixture, in a water-bath at 90°C, an orange precipitate was formed within few seconds. The precipitate was filtered, washed with ethanol, ether and dried in an oven at 110°C.

Preparation of Schiff-Base Polymer (3):

3.70 g (0.01 mol) of 4,4'-diaminostilbene-2,2'-disulfonic acid (BDH), in 100 mL distilled water, was treated with equivalent amount of 2N NaOH till complete dissolution took place. The diamine sodium salt solution was then warmed and added slowly, with stirring, to 2.56 g (0.01 mol) of 5,5'-methylene-bis-salicylaldehyde in100 mL THF. After heating on water-bath for one hour at 90°C, an orange color was developed. On acidification, with dil. HCl, an orange precipitate formed. The product was filtered, washed with water, alcohol, ether and then dried in an oven at 110°C.

Preparation of Schiff-Base Polymer (4):

To a stirred solution of 2.56 g (0.01 mol) of 5,5'-methylene-bis-salicylaldehyde, in 100 mL THF, was added slowly a solution of 2.10 g (0.01 mol) of 1,3-phenylene diamine-4-sodium sulfonate (Aldrich), in 100 mL redistilled water. Upon heating in a water bath for an hour at 90°C, an orange coloration appeared. A yellow precipitate was formed on acidification with dilute HCl. The polymer was filtered, washed with redistilled water, then alcohol, ether and dried in an oven at 110°C.

Preparation of Schiff-Base Polymer (5):

A warm solution of 1.60 g (0.01 mol) of thiocarbohydrazide, in 50 mL mixture (50% v/v) of acetic acid and methanol, was added to a solution of 1.34 g (0.01 mol) of terephthalaldehyde (Aldrich) in a mixture of 50 mL methanol and 20 mL acetic acid. A yellow precipitate formed, after warming on water-bath for one hour at 90°C. Diluted with 100 mL methanol, filtered, washed with methanol, ether and then dried in an oven at 110°C.

Preparation of Schiff-Base Polymer (6):

It was prepared as the same procedure adopted for schiff-base polymer (5), using bis(4-aminophenyl) sulfone instead of thiocarbohydrazide.

Preparation of Schiff-Base Polymer (7) and (8):

To a solution of (0.01 mol) of di(p-formylphenyl) terephthalate or di(p-acetylphenyl) terephthalate in 100 mL chlorobenzene, added slowly with continuous shaking, 1.06 g (0.01 mol of thiocarbohydrazide, in 50 mL of acetic acid and ethanol (equal volumes). The reaction mixture refluxed for 24 h. A yellow precipitate was formed, cooled washed with ethanol and ether, dried in an oven at 110°C.

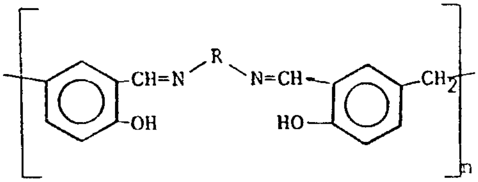
Preparation of di(p-formylphenyl) terephthalate (9) and di(p-acetylphenyl) terephthalate (10):

Terephthaloyl chloride (0.01 mol) was added to a solution of (0.02 mol) of p-hydroxybenzaldehyde (or p-hydroxyacetophenone) in 50 ml of dry pyridine. The mixture was refluxed for 30 minutes. The formed white precipitate was filtered and washed with petroleum ether and then with diethylether, dried in an oven at 110°C. The structures of the products are confirmed by elemental analysis and i.r. spectra (Table 1). Compound 9, m.p. 201-203°C, i.r. data, 1640 (-CHO), 1400 (-CHO), 1690 cm^{-1} (carbonyl ester). Compound 10, m.p. 210°C, i.r. data, 1690 (-CO-CH$_3$), 1740 cm^{-1} (carbonyl ester).

Viscosity measurements:

The viscosities of the polymer in a proper solvent (0.5 g in 100 mL solvent), were measured at 30 ± 0.01°C using Ubbelhode suspended level viscometer as modified by Ravikov$^{(7)}$. The flow time of pure solvents in the viscometers used throughout this work ranged from 80 to 120 sec. The reduced viscosity (η_{red}) was measured in DMF (polymer 1,2), 0.1 N NaOH (polymer 3, 4), and DMSO (polymer 5, 8).

POLYMER STRUCTURES



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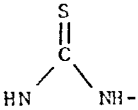

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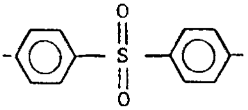

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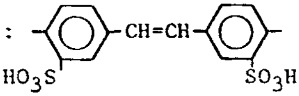

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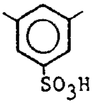

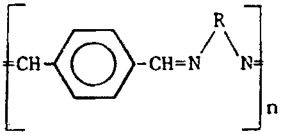

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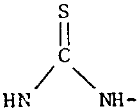

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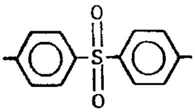

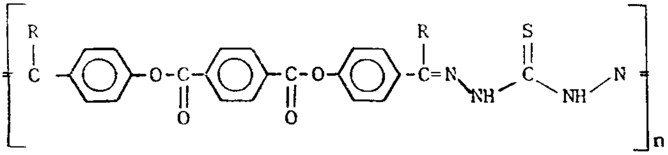

7 ; R : H

8 ; R : CH_3

Table (1) : Physical Properties and Elemental Analysis of Schiff-base Polymers (1-8) and Dicarbonyl Compounds (9-10).

Cpd. No.	Chemical Formula	M.Wt.	Yield %	η_{red}	% C	% H	% N
					(Calc./Found)		
(1)	$(C_{16}H_{14}N_4SO_2)_n + \frac{1}{2}H_2O$	335	96	0.241	57.31	4.48	16.71
					56.89	4.20	15.78
(2)	$(C_{27}H_{20}N_2SO_4)_n + \frac{1}{2}H_2O$	477	94	0.122	67.92	4.40	5.87
					67.51	4.27	5.88
(3)	$(C_{29}H_{22}N_2S_2O_8)_n + \frac{1}{2}H_2O$	599	89	0.019	58.09	3.84	4.67
					57.51	4.28	4.54
(4)	$(C_{21}H_{16}N_2SO_5)_n$	408	92	0.040	61.76	3.92	6.86
					61.92	4.10	5.95
(5)	$(C_9H_8N_4SO)_n + \frac{1}{2}H_2O$	213	98	0.200	50.70	4.23	26.29
					51.07	3.86	26.74
(6)	$(C_{25}H_{20}N_4SO_4)_n + \frac{1}{2}H_2O$	481	75	Insol.	62.37	4.37	11.64
					62.08	4.38	11.82
(7)	$(C_{20}H_{14}N_2SO_2)_n$	346	96	Insol.	69.36	4.07	8.09
					68.68	4.00	7.90
(8)	$(C_{22}H_{16}N_4SO_4)_n$	432	93	0.200	61.11	3.70	12.96
					60.78	3.52	12.66
(9)	$C_{22}H_{14}O_6$	374	89	-----	70.59	3.74	-----
					70.45	3.87	-----
(10)	$C_{24}H_{18}O_6$	402	92	-----	71.64	4.40	-----
					71.83	4.24	-----

RESULTS AND DISCUSSION

In the present work, some new polymeric schiff-bases containing sulfur have been synthesized. Their characteristics, viscosity measurements and their structures will be discussed. Condensation of 5,5'-methylene-bis-salicylaldehyde with thiocarbohydrazide, bis(4-aminophenyl) sulfone, 4,4'-diaminostilbene-2,2'-disulfonic acid or 3,5-diaminobenzenesulfonic acid gave the corresponding polymeric schiff-bases (1, 2, 3 or 4), respectively. Also, condensation of terephthalaldehyde with thiocarbohydrazide yielded polymeric schiff-base (5), while its condensation with bis(4-aminophenyl) sulfone gave the schiff-base polymer (6). Finally, condensation of di(p-formylphenyl) terephthalate or di(p-acetylphenyl) terephthalate with thiocarbohydrazide produced the polymers (7) or (8).

Table (2) : IR-Spectral data (in cm^{-1}) of the polymers (1-8):

Polymer No.	C=N	C-O phenolic	C=S	SO_2	SO_3H	Carbonyl end group
1	1610	1280	1500 1160			1640
2	1585	1275		1150 1320		1640
3	1550	1280			1345 1140	1635
4	1600	1280			1230 1150	1670
5	1595	1510 1135				1720
6	1602			1125 1300		1687
7	1600	1500 1170				1700
8	1605	1510 1175				1710

To study the effect of various reaction conditions on the percentage yield, polymerization reactions were carried out at different temperatures (-10 to 50°C), in different solvents (THF, MeOH, EtOH, chlorobenzene and DMF), and at different times of reaction, neither the temperature nor the solvent has affected the percent yield. Also, the time of condensation showed no effect. Following the reduced viscosities of all the present polymers (1 - 8), leads to the conclusion that, all the previously described variable conditions have no effect on the molecular weight of these polymers(8).

The reduced viscosities of the present polymers showed low values (Table 1). These low viscosity values are attributed to chain propagation being inhibited by the poor solubility of the polymer as it is being formed. The much lower viscosity values of polymers (3) and (4) (which may be oligomers) could be understood, since their polymerizations are carried out in alkaline medium. This alkali may consume a part of the used dialdehyde in a Cannizzaro side reaction, which also affects the stoichiometry of the reaction. Moreover, the viscosities of the polymeric schiff-bases (1) and (2) were measured by GPC and light scattering. The schiff-base polymers (1) and (2) were run in the GPC, based on polystyrene standards. Both polymers were eluted at longer time than the smallest polystyrene standard (M-3000). Using light scattering technique gave a weight average molecular weight of 11,000 and 8,900 for the polymers (1) and (2), respectively. All molecular weight measurements were made in N-methylpyrrolidone.

The structures of the present polymers (1-8) were confirmed by elemental analysis and i.r. spectroscopy. The elemental analyses found are in good agreement with the calculated values for the repeating units present in each polymer (Table 1).

The infrared spectra of the present schiff-base polymers exhibited their characteristic features. The most common bands(9) are tabulated in Table (2). Although many data are available in the literature concerning the IR-spectra of imines, less is known about i.r. absorption by polymeric azomethines. In the present work, the (C=N) stretching was observed around 1600 cm^{-1}. This low frequency, for the azomethine group, may attributed to its conjugation with an aromatic ring(10), and/or its hydrogen bonding to an adjacent o-hydroxy group(11). The appearance of a weak band around 1650 cm^{-1} indicates that the end groups of these polymers (1-8) are carbonyl groups.

Beside the typical i.r., bands (Table 2), each of the present polymers showed other bands characteristic of its own structure. Schiff-base polymer (3) exhibited an olefinic (C=C) stretching vibration band at 1600 cm^{-1}, and two bands are 635 and 1035 cm^{-1}, due to (C-H) olefinic bonding vibrations. The polymeric compounds (7) and (8) showed the characteristic vibration bands of the ester structure at 1225-1195 cm^{-1} [(C-C(C=O)-O and O-C-C], and around 1740 cm^{-1} (carbonyl ester).

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