

Design, Synthesis, Characterization and Modification of Novel Aromatic Compounds with Poly Vinyl Alcohol

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Summary: New aromatic compounds were prepared by reacting 5,5'-methylene di-anthranilic acid with 4,4'-(diazene-1,2-diyl) dibenzoyl chloride by the well-known classical methods. To prepare compounds to contain an amide, ester, and azo groups as a bonding bridge between them. The synthesized was characterized by CHN, FT-IR, ¹HNMR, and ¹³CNMR spectra. Then, they were reacted with polyvinyl alcohol PVA polymer using cold-warm esterification to prepare new graft polymers. The structures of the composites were determined by FT-IR. Graft polymerization of PVA with new aromatic compounds was a way to prepare important polymeric materials with original physicochemical properties for use in new industrial applications. By testing aromatic derivatives the swelling results of the newly prepared graft polymers were very good, ranging from 3-665%, with a life span of a quarter of an hour to three days. While DSC analysis showed good temperatures in the range of 23.4-289.2°C for the prepared graft polymers.

Key words: 5,5'-methylenebis(2-aminobenzoic acid), 4,4'-(diazene-1,2-diyl)dibenzoyl chloride, polyvinyl alcohol, swelling and DSC.

Introduction

Aromatic compounds are the backbone for preparing most of the important pharmaceutical and industrial compounds, especially if they are azo, Schiff, and esterification compounds, which is characterized by their biological activity in addition to their wide industrial applications due to the presence they contain many effective functional groups [1-5]. When grafting these prepared compounds with polymers, which polymers today play an important role in the industry, it was found that they have many industrial applications and efficacy. Polyvinyl alcohol PVA, for example, is one of the most important polymeric materials because of its high solubility in water and other solvents [6-11]. Where it was added as an emulsifier or adhesive and later in some pharmaceutical applications as a drug carrier reacting a suspended active hydroxyl group -OH with various reagents and various aromatic compounds, to form new polymers with new surfactant properties. Polyvinyl alcohol PVA has high hydrophobicity, one of the most important physicochemical properties of the polyvinyl alcohol film is that it is possible to prepare hydrophilic filter membranes, in addition to the possibility of preparing nano-filtration membranes [12-16]. Its high-water content through the swelling process gave vinyl alcohol polymers important properties in the medical industries, such as lenses, adhesives, and some biological applications. It is possible to obtain polymers with strong chemical properties and thus increase the scope of their applications through some modifications [17-19]. Attracting researchers' attention to polymers containing different functional groups (carboxylate, ketone,

aldehyde, etc.), which are promising for the development of medical and biological materials [20-21]. The purpose of this study is to prepare new aromatic compounds containing azo bridge and then react with polyvinyl alcohol (PVA) to prepare new graft polymers and then study the physical properties of the prepared polymers. The structures of the various synthesized compounds were assigned on the As a result, we are trying to find the best compounds and complete the research to industrial application.

Experimental

Materials and methods

In this work all chemicals used and their suppliers are used as received without further purification. Anthranilic acid, formalin and ethyl acetate from Aldrich. p-nitrobenzoic acid from Riedel-Dehaen 99%. Glucose from pharmaceutical drug Samara PDS 99%. dimethylformamide (DMF), dimethyl sulfoxide (DMSO) 99%, Pyridine, petroleum ether (60-80) and sodium hydroxide from BDH. All compound synthesized are determined melting point by open capillary tube via hot-stage, to confirmed presence of functional groups in all compounds characterized by FTIR spectroscopy use KBr disc in the SHIMADAZU-FT-IR Spectroscopy from the BPC-Analysis Center. The ¹HNMR spectra were calculated in ppm(μ) and using DMSO as solvent and TMS(Tetramethyl silane) as internal standard, recorded on nuclear magnetic resonance Bruker BioSpin GmbH spectrophotometer model Ultra shield 100 MHz.

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Table-1: Spectral data of prepared compounds and graft polymer [A-C5].

Comp.	C H N. Analysis			-CH Arom.	IR ν cm ⁻¹			1HNMR	C13 NMR δ (ppm)		
	found/calculate	C	H		C=O carbo,	N=N	Other		H-Arom.	C-Arom.	CO2H
A	62.5	3.5	10.2	3090	1712	1543	OH 3431-2933	OH 11.5	110-142	158	168
	62.4	3.4	10.1		1686		NH 8.7	NH 8.7			
							NH 3232	CH 7.1-8.6			
A1	65.3	3.1	10.7	3064	1740	1552	/	CH-6.5-8.7	119-145	152	162
	65.2	3.0	10.6	3010							
B1	53.4	3.3	4.8	3055	1776	/	NH 3215	NH 11.2	149-125	167	/
	53.7	3.3	4.6				C-S1090	CH 7.1-8.4			
B2	55.1	4.3	4.5	3065	1687	/	3210NH,	NH 11.4	127-133	167	/
	54.9	4.1	4.4				2983 CH	CH 7.2-7.8			
							Alph.				
B3	58.8	3.5	8.1	3063	1662	/	C=N1604	CH 6.6-8.8	120-132	166	/
	58.8	3.4	8.0				2982CH	CH Alph 2.5-3.9			
							Alph.				
B4	61.0	4.3	7.5	3066	1680	/	C=N1606	CH 7.2-8.1	120-135	167	/
	60.8	4.3	7.4				2983CH	CH Alph. 2.5-4			
							Alph.				
C1	/	/	/	3100	1722	/	CH Alph.				
							2980				
							3200 NH				
C2	/	/	/	3064	1716	/	3392 NH				
							2978CH				
C3	/	/	/	3026	1676	/	NH 3255				
C4	/	/	/	3085	1672	/	2989CH				
C5	/	/	/	3105	1707	/	2997 CH				

Synthesis of 5,5'-methylenedianthranilic acid

We prepared 5,5'-methylene di anthranilic acid compounds according to the Pardip method [22]. As well as the compound azo benzoic acid, which was prepared by Zakaria gives good yield of benzoic acid [23].

Synthesis of 5,5'-methylenedianthranilic acid derivatives: -

Synthesis of 5,5'-methylenebis(2-(4-(4-chlorocarbonyl) phenyl) diazenyl) benzamido) benzoic acid [A]:-

(0.572 gm, 0.001 mol) 5,5'-methylenedianthranilic acid was added in 100ml of round bottom with 4,4'-(diazene -1,2-diyl) dibenzoic acid (0.307gm, 0.002mol) containing magnetic bar and dissolve in 50ml of DMSO. The reaction mixture was stirred for 6 hrs., during which the reaction process is monitored by TLC using ethanol: ethyl acetate [4:6]. Then the mixture is cooled, filtered, and re-crystallized by DMF, (0.0685 gm, yield 57%, m.p. 320°C), scheme (2).

Synthesis of 4,4'-(4,4'-(6,6'-methylenebis(4-oxo-4H-benzo[d][1,3]oxazine-6,2-diyl))bis(4,1-phenylene))bis(diazene-2,1-diyl)dibenzoyl chloride[A1] [24]

To a clear solution of 5,5'-methylene bis, (2-(4-((4-(Chlorocarbonyl) phenyl) diazenyl) benzamide) benzoic acid)] (0.826 gm, 0.001 mol) in DMSO (50ml), dry pyridine was added. Then, an excess of acetic anhydride was added to the reaction mixture. The reaction is followed by TLC for 5 hrs., using ethanol: ethyl acetate [4:6]. The mixture was left to cool, and then re-filtered and crystallized by chloroform, (0.44gm, yield 90%, m.p. 286°C), scheme (2).

Synthesis of 5,5'-methylenedianthranilic acid derivatives [B1-B4]

(0.572gm, 0.001 mol) of 5,5'-methylenedianthranilic acid was added in 100ml of round bottom flask with one of benzene sulphonyl chloride or 4-methyl benzene sulphonyl chloride or formaldehyde or acetaldehyde (0.002mol), containing magnetic bar and dissolve in 50ml of DMSO fitted with thermometer. The reaction mixtures was stirred for 6hrs, during which the reaction process is monitored by TLC using ethanol: ethyl acetate [4:6]. Then the mixture was cooled, filtered and re-crystallized by DMF, (0.68gm, yield 77%, m.p. 210 °C., 0.55gm, yield 67%, m.p. 298 °C. 0.7gm, yield 80%, m.p. 235 °C and 0.39gm, yield 65%, m.p. 270 °C) respectively of compounds [B1,B2, B3 and B4], as shown in Table (1), scheme (3).

Table-2: Some physicochemical properties of prepared graft polymers.

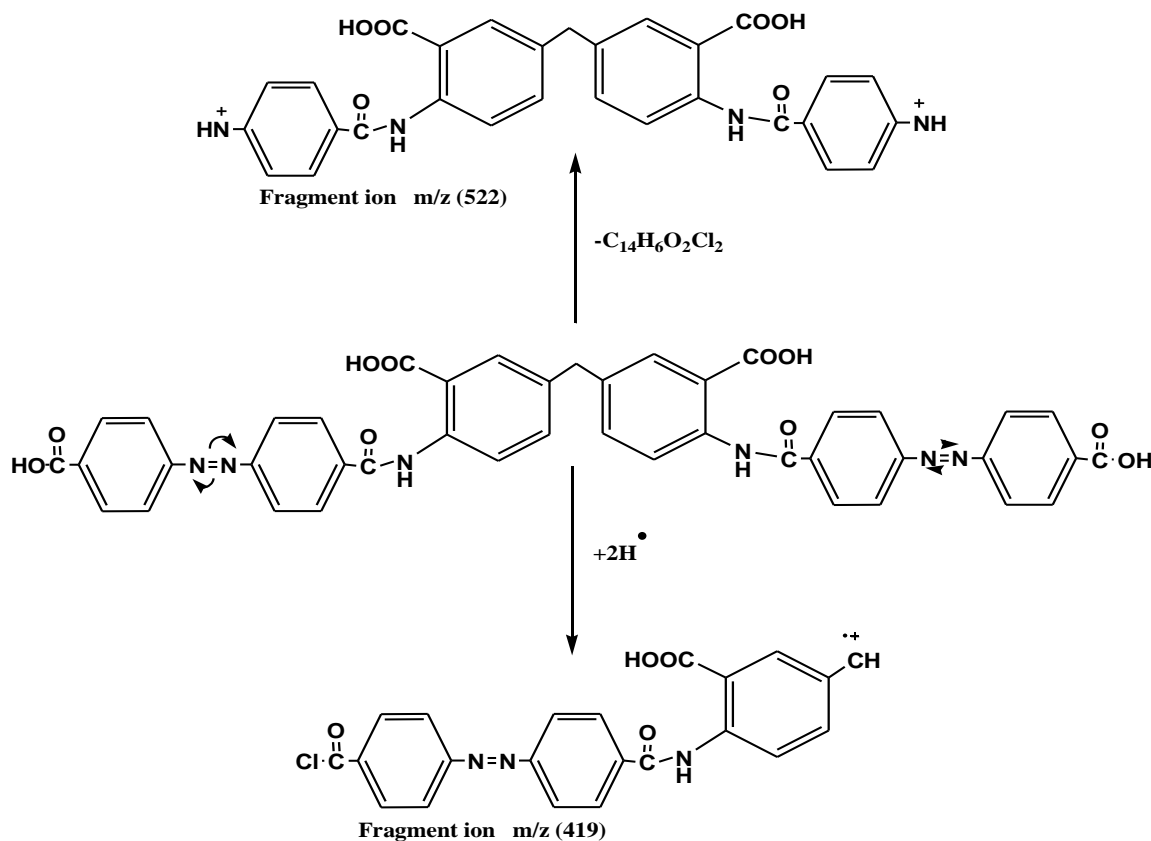
Comp. No.	Glass Transition T _g °C	Crystallization State T _c °C	Melting State T _m °C	Decomposition Temperature T _D °C	Solubility*		
					DMSO	DMF	H ₂ O
C1	66.8	146.3	172.4	>1000	+++	+	-
C2	58.6	193.3	284.6	>1000	++	++	-
C3	23.4	210.5	221.5	>1000	++	++	-
C4	67.4	180.5	289.2	>1000	++	+	-
C5	95.3	155.4	241.1	>1000	+++	+	-

(-): Insoluble less, (+): Weakly (less), (++) : Moderately soluble, (+++) : Highly soluble (good and above)*

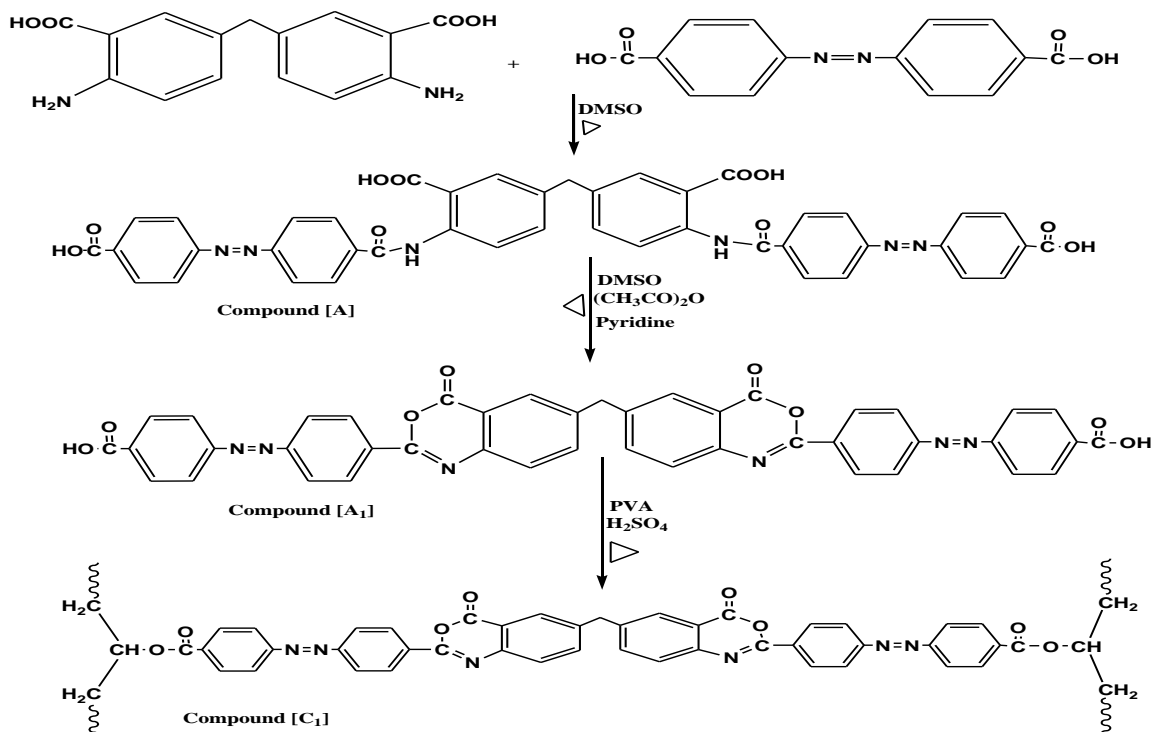
Synthesis of New graft polymers [C1-C5][25]

(2 gm) PVA was added to a round flask and dissolved in 100 ml of distilled water with continuous stirring and keeping the reaction temperature below 50°C until the reaction mixture was homogeneous, then 3-5 drops of H₂SO₄ were gradually added to it over 1 hour. Then, the mixture was left to cool for ½ hour. After that, (0.790 gm, 0.002mol) of compound [B1] was added. The reaction was heated again for 3 hrs., and another 3-5 drops of H₂SO₄ was added to it gradually and with

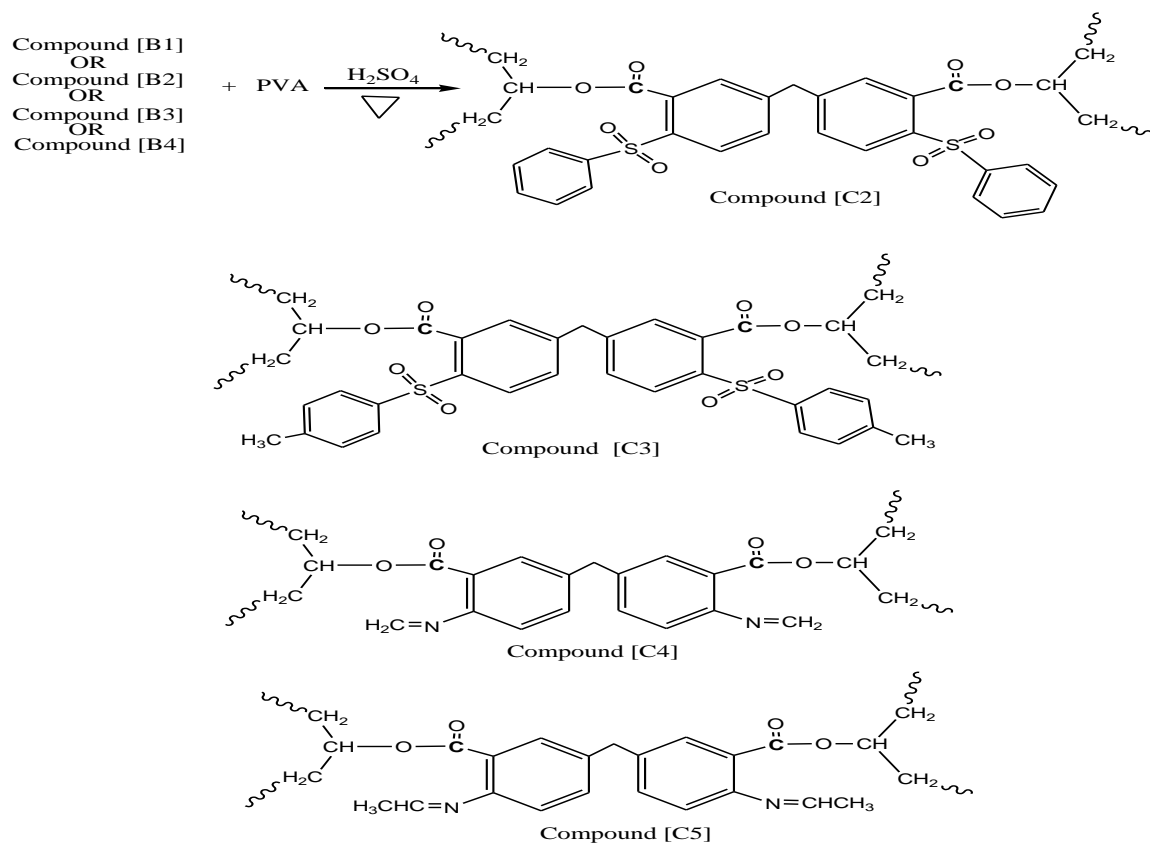
continuous stirring and maintaining the temperature below 50°C. After changing the color of the reaction and its homogeneity, it was left to dry at laboratory temperature for a whole day. Then, the product was re-washed with distilled water, to get rid of the remnants of non-reactive substances, left to dry, and then kept in a dark place to produce [C2]. The experiment was repeated using the same polymer (PVA) with compound [B2, B3 and B4] to prepared compounds [C3, C4 and C5], as shown in table (2), scheme (3 and 4).



Scheme-1: Suggestion fragment of compound [A].



Scheme-2: Synthesis of compounds [A-A1] and [C1].



Scheme-3: Synthesis of compounds [B1, B2, B3 and B4].

Graft polymer swelling [26-28]

The swelling experiment of the graft polymer was carried out at a laboratory temperature in distilled water, using samples of the prepared polymer with a range of 0.13-0.15gm. The percentage of swelling (water absorption of the prepared polymer samples against time and reaching the equilibrium state), was measured using the following equation:

$$\text{Swelling \% } (\Delta M) = \frac{M_t - M_0}{M_0} \times 100 \quad 1$$

where m_0 and m_t are the masses of dry and wet samples.

Results and Discussion

The all of the synthesized compounds [A-C5] were recrystallization by ethanol and DMF, which determined spectral data FTIR and CHN-analysis. In addition to some compounds characterized by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra [29-30]. All the newly synthesized compounds were in full agreement with the proposed structures, especially analysis by CHN, agreement of calculated/ found Table (1).

FT-IR of compounds [A-A1] showed a stretching absorption of (-CH) aromatic at 3090, 3010 cm^{-1} for aromatic molecule, (C=O) 1712, 1740 cm^{-1} , azo group (N=N) 1543, 1552 cm^{-1} respectively, and esoteric group (C-O-C) at 1089 cm^{-1} . While FTIR of compounds [B1-B4] showed a stretching absorption of (-CH) aromatic at 3055, 3065, 3065, and 3066 cm^{-1} , (C=O) 1776, 1687, 1662 and 1680 cm^{-1} , graft polymer was composed [C1] through ester of the azo bridge showed a stretching absorption of (-CH) aromatic at 3100 cm^{-1} for aromatic molecule, (C=O) 1722 cm^{-1} , azo group (N=N) 1552 cm^{-1} , 2980 cm^{-1} for aliphatic molecule, 3200 cm^{-1} for NH group. While [C2-C3] with amide groups showed a stretching absorption of (-CH) aromatic at 3064 and 3026 cm^{-1} , and (C=O) 1716, 1676 cm^{-1} , NH-group showed at 3210 and 3225 cm^{-1} , respectively. But [C4-C5] showed a stretching absorption of (-CH) aromatic at 3085 and 3105 cm^{-1} , (C=O) 1672, 1707 cm^{-1} , 2989, 2997 cm^{-1} for aliphatic molecule, respectively, Scheme-2, Table-1. $^1\text{H-NMR}$ spectral analysis of compounds [A] showed hydroxyl and amine protons signal (OH, NH) at δ (11.5, 8.7) ppm, (-CH) aromatic (22H) protons signals at δ (7.1-8.6) ppm but for compound [A1] notice disappear the hydroxyl and amine protons signal and appear the -CH aromatic (22H) protons signals at δ (6.5-8.7) ppm. While $^1\text{H-NMR}$ spectral analysis of compounds [B1], showed

amine protons signal (NH) at δ (11.2) ppm, (-CH) aromatic (16H) protons signals at δ (7.1-8.6) ppm, (-CH) aliphatic (2H) protons signals at δ (3.9) ppm. $^1\text{H-NMR}$ spectral analysis of compounds [B2] showed amine protons signal (NH) at δ (11.4) ppm, (-CH) aromatic (14H) protons signals at δ (7.2-7.3) ppm, (-CH) aliphatic (2H) protons signals at δ (3.5) ppm. $^1\text{H-NMR}$ spectral analysis of compounds [B3] showed (-CH) aromatic (6H) protons signals at δ (6.6-8.8) ppm, (-CH) aliphatic (2H) protons signals at δ (2.5) ppm. While $^1\text{H-NMR}$ spectral analysis of compounds [B4] showed (-CH) aromatic (6H) protons signals at δ (7.2-8.1) ppm, (-CH) aliphatic (2H) protons signals at δ (3.5) ppm, table (1). In addition to the $^{13}\text{C-NMR}$ spectrum of compounds [A] was noted that the carbonyl group at δ 158, carbonyl amide group at δ 168, and C-aromatic at δ 110-142 ppm. Compounds [A1] appeared carbonyl group at δ 152, the carbonyl amide group at δ 162, and C-aromatic at δ 119-145 ppm. While the $^{13}\text{C-NMR}$ spectrum of compounds [B1] was noted in the carbonyl group at δ 167, and C-aromatic at δ 125-149ppm. Compounds [B2] have appeared carbonyl group at δ 167 and C-aromatic at δ 127-133ppm. Compounds [B3] showed a carbonyl group at δ 166, and C-aromatic at δ 120-132ppm. Compounds [B4] appeared carbonyl group at δ 167 and C-aromatic at δ 120-135ppm, table (1).

While the mass spectra of compound [A] showed $(M+H)^{+2}$ and showed fragmented ions m/z (519, 100%) and (422, 80%), respectively, probably obtained from molecular ion decomposition with charge was considered to be localized at azo-nitrogen atoms of the synthesized molecule of symmetrical [A]. As in the following fragments:

Thermal analysis or heat flow versus the change in temperature or time, it is used in the analysis of polymers, especially those involved in the preparation of medicines and foodstuffs in terms of food analysis and preservation and the effect of temperatures during storage, transportation, and consumption [31]. It is useful in determining physical and chemical properties of components that affect Taste, appearance, and texture. After this characteristic was measured for industrial polymers and plastics [27], we found that the prepared new graft polymers have a T_g between 23.4-289.2 $^{\circ}\text{C}$ by measuring the DSC, it was good T_g especially compound C5. All this information is in Table-2 and Fig. 1.

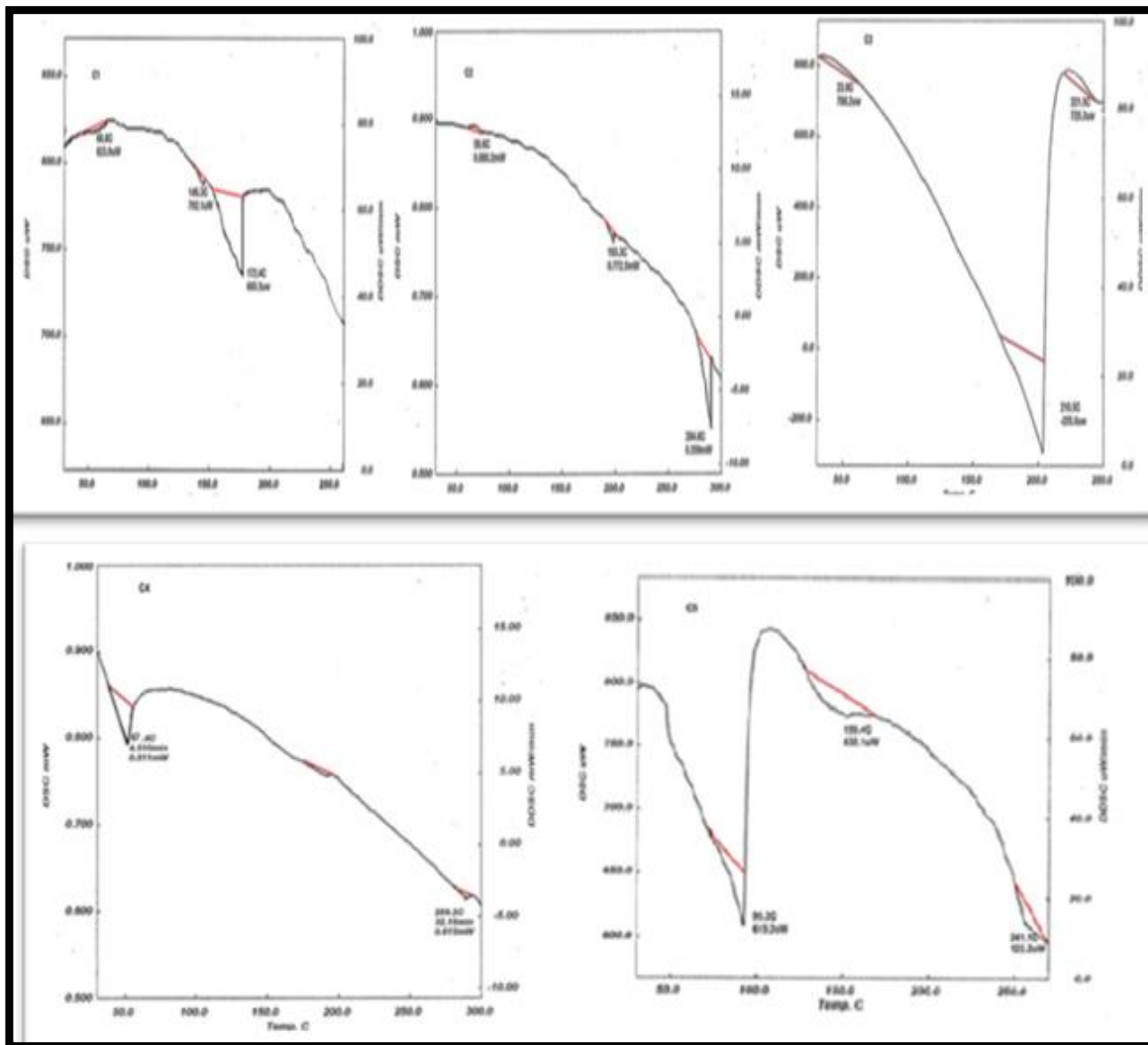
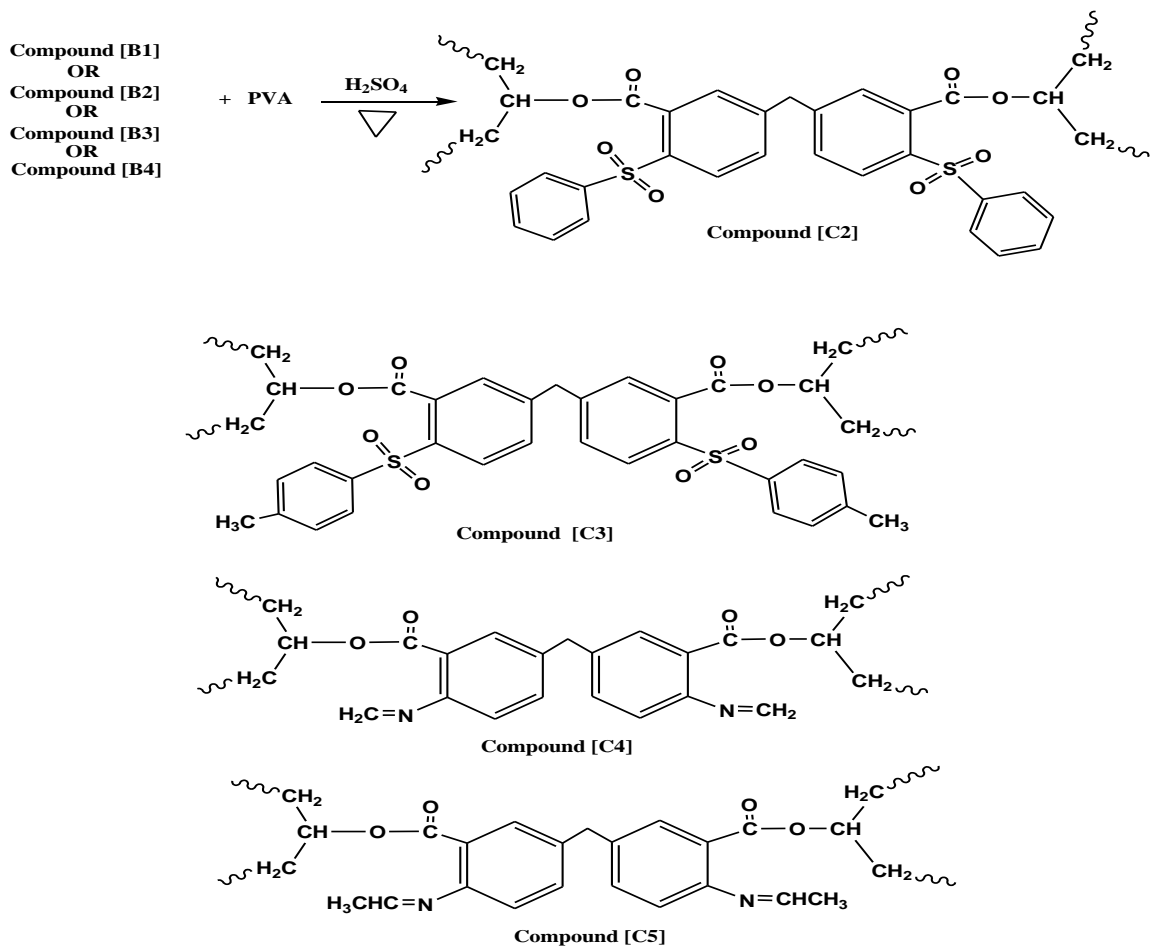


Fig. 1: DSC Curves of graft polymers [C1, C2, C3, C4 and C5] in 10°C / min.

Swelling experiments (hydrogel) Fig (2), were carried out for the prepared and dry polymers using distilled water at laboratory temperature (25-30 °C), and with a molecular weight close to all polymers. We noted that all the graft polymers were swelled with water in different percentages and at a rate of (3-685%), due to

the difference in the chemical composition of the prepared polymer, and the relative relationship between hydrophilic or hydrophobic polymers [32]. It was a good hydrophilic graft polymer specially the compounds [C3 and C5].



Scheme-4: Synthesis of compounds [C1, C2, C3 and C4].

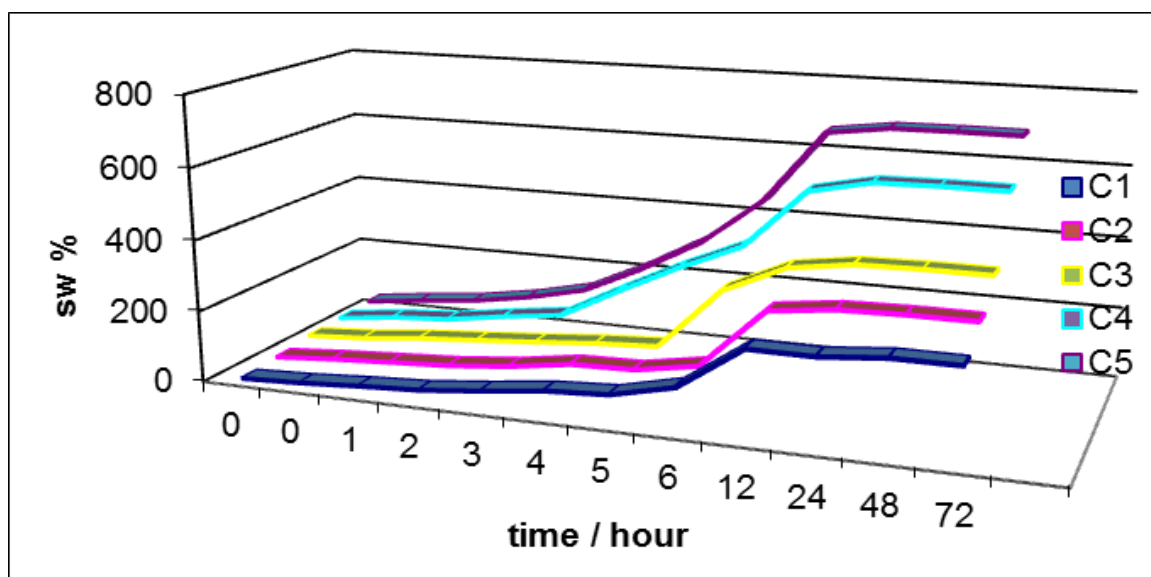


Fig. 2: Swelling of new graft polymers [C1, C2, C3, C4 and C5].

Conclusion

In summary, new aromatic compounds [A-A1 and B1-B4] containing multiple active groups such as azo, ester, and amide were prepared by the classical methods and reacted by the esterification method with polyvinyl alcohol (PVA). The prepared new graft polymers [C1, C2, C3, C4, and C5] showed good running stability, good DSC values, and excellent swelling and solubility in some common solvents.

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