



Synthesis, Characterization of *p*-Nitrophenyl azo- β -Naphthyl-(4'-Azobenzoic acid)-4-benzoate and its PVA-Grafting Polymer

DHEFAF HASHIM BADRI

Department of Chemistry, College of Education for Pure Sciences/Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq

Corresponding author: Tel: +964 7700298592; E-mail: dhefaf_alqudsy@yahoo.com

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An aromatic ester containing two azo groups namely *p*-nitro phenyl azo- β -naphthyl-(4'-azobenzoic acid)-4-benzoate was synthesized by esterification of 4,4'-azo dibenzoic acid with *p*-nitro phenyl azo- β -naphthol. Synthesized ester was characterized by CHN-elemental analysis, FTIR, ^1H NMR and ^{13}C NMR. A modified poly(vinyl alcohol) PVA was obtained by grafting 10 g of PVA-polymer *via* partial esterification with (2, 3, 4 g) *p*-nitro phenyl azo-1-naphthyl-4-azobenzoic acid)-4-azo benzoate. Grafting behaviour of PVA-polymer was studied by physical measurements (solubility, swelling), thermal properties (DSC) and tensile strength.

Keywords: 4,4'-Azo dibenzoic acid, *p*-Nitro phenyl azo- β -naphthol, Esterification.

INTRODUCTION

Poly(vinyl alcohol) (PVA) is one of the most important polymers due to its chemical resistance, good thermal stability, film forming ability and biodegradability. It is used in surgical devices and soft lenses [1]. It is a water hydrophilic and soluble polymer and can be used for absorbing water and swollen while its cross-linking with many dicarboxylic acids lead to increasing diffusion properties [2].

Grafting is a modification of conventional polymers allows to imparting a variety of functional groups to polymer [3] so it is one of the promising methods of modification [4]. Grafting copolymerization has generated interest among researches because few co-monomer molecules change significantly a number of the characteristic of original natural polymer [5].

This work involve the synthesis of *p*-nitro phenyl azo- β -naphthyl-(4'-azobenzoic acid)-4-benzoate by esterification reaction of 4,4'-azo dibenzoic acid and *p*-nitro-phenyl azo- β -naphthol and its PVA grafting polymerization *via* esterification reaction process and to study its physical parameter.

EXPERIMENTAL

Poly(vinyl alcohol) (72000 g/mol) (Fluka, 97 %), was used without purification. *p*-Nitro benzoic acid, azo compounds with its copolymer and other solvents were recorded on (Shimadzu, FTIR. 8400s) in the range (4000-400) cm^{-1} using KBr pellets. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) measurements were performed with a spotlight 400 Perkin Elemer, CHN

analysis was recorded on Microestimation technique Euro EA 3000 Single.

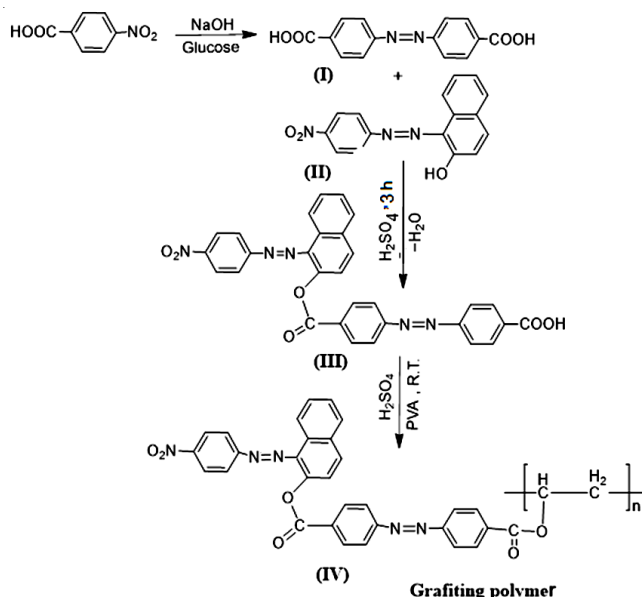
Synthesis of 4,4'-azodibenzoic acid (I): 4,4'-Azodibenzoic acid was prepared by condensation of *p*-nitrobenzoic acid, reduction with glucose, then an oxidation give the compounds 4,4'-azodibenzoic acid [6].

Synthesis of *p*-nitrophenyl azo- β -naphthol (II): *p*-Nitrophenyl azo- β -naphthol was synthesized by coupling reaction of *p*-nitro phenyl diazonium chloride with β -naphthol [7].

Synthesis of *p*-nitro phenyl azo- β -naphthyl-(4'-azobenzoic acid)-4-benzoate (III): A solution of (0.27 g; 10^{-3} mol) of 4,4'-azo dibenzoic acid was dissolved in 5 mL conc. sulphuric acid was added drop by drop for 30 min to a stirred solution of *p*-nitro phenyl azo- β -naphthol in 5 mL DMSO at room temperature. Then the reaction mixture was heated for 3 h at 60 °C. Cool precipitated esters was formed, filtered and washed with DMSO and then with water several times, until a drop of washed water was neutral. The precipitated ester azobenzoic acid was dried to give 83 % yield, m.p. above 300 °C. stretching absorption bands of OH group at 3270-2985 cm^{-1} , CH-aliphatic and aromatic bands at 3074, 2885 cm^{-1} respectively, C=O band at 1680 cm^{-1} , N=N band at 1504 cm^{-1} and NO₂ band at 1599, 1385 cm^{-1} . Anal. calcd. (%) for C₃₀H₁₉N₅O₆ (545.51): C, 66.05; H, 3.51; N, 12.84; O, 17.60 Found: C, 66.22; H, 3.48; N, 12.56; O, 17.77. ^1H NMR (400 MHz, DMSO-*d*₆, δ ppm): 11.85 (s, 1H, C_{COOH}), 8.91-7.82 (m, 12H, H_{abcdgik}), 7.82-7.52 (s, 1H, H_f), 7.52-7.22 (d, 2H, H_j), 7.22-7.07 (d, 2H, H_h), 7.07-6.78 (s, 1H, H_e). ^{13}C NMR (100 MHz, DMSO-*d*₆, δ ppm): 166.72

(C_{COOH}), 163.10 (C_{CO₂Ar}), 157.12 (C₄), 154.34 (C₁₄), 148.23 (C₁₇), 147.14 (C₁₃), 136.33 (C_{1,8}), 130.50 (C₂), 129.62 (C_{5,9}), 128.31 (C₁₀), 127.10 (C₁₂), 123.50 (C₃), 121.62 (C₁₅), 118.51 (C₇).

Synthesis of *p*-nitro phenyl azo- β -naphthyl-(4'-azobenzoic acid)-4-benzoate containing PVA-grafting polymer (IV): In 20 mL beaker containing (0.1 g) of PVA dissolved in 50 mL DMSO, a solution of 2 g *p*-nitro phenyl- β -naphthyl-(4'-azobenzoic acid)-4-benzoate in 1 mL conc. H₂SO₄ (36 N), was added drop wise for 5 min with stirring at room temperature. The reaction mixture was stirred for another 10 min then added to pretidish and leaved for two days then the formed filter washed with cold water until free from acid, dried at 80 °C. The experiment was repeated with 0.1 g of PVA with 3 and 4 g of compound **III** to form three percentages of PVA samples (**1**, **2** and **3**). **Scheme-I** shows the synthetic route of compounds.



Scheme-I: Synthetic route for compounds synthesis

RESULTS AND DISCUSSION

Ester (III) and polymer (IV) Synthesis: 4,4'-Azobenzene-4-carboxylic acid (**I**) synthesized by oxidative of *p*-nitrobenzoic acid. *p*-Nitrophenyl azo- β -naphthol (**II**) was synthesized by coupling reaction of *p*-nitro phenyl diazonium chloride with β -naphthol [6,7].

Di azobenzoic acid was esterified with phenolic group of *p*-nitrophenyl azo- β -naphthol in presence of small amount of H₂SO₄ in DMSO to give *p*-nitro phenyl azo- β -naphthyl-(4'-azobenzoic acid)-4-benzoate (**III**) as a diazo benzoate ester. Diazobenzoate ester was characterized by CHN, FTIR, ¹H NMR and ¹³C NMR analysis. FTIR spectrum showed the stretching absorption bands of OH group at 3270-2985 cm⁻¹ as abroad band, CH-aliphatic and aromatic bands at 3074, 2885 cm⁻¹ respectively, C=O band at 1680 cm⁻¹, N=N bond at 1504 cm⁻¹ and NO₂ band at 1599, 1385 cm⁻¹.

Fig. 1 showed ¹H NMR spectrum of (**III**) which exhibited the small singlet broad peak with higher field 11.85 (s, 1H, C_{COOH}) of carboxylic proton which is hardly observed because of replacement hydrogen atoms of (COOH) by deuterium of DMSO solvent. The following two doublet peaks (a, b) due to

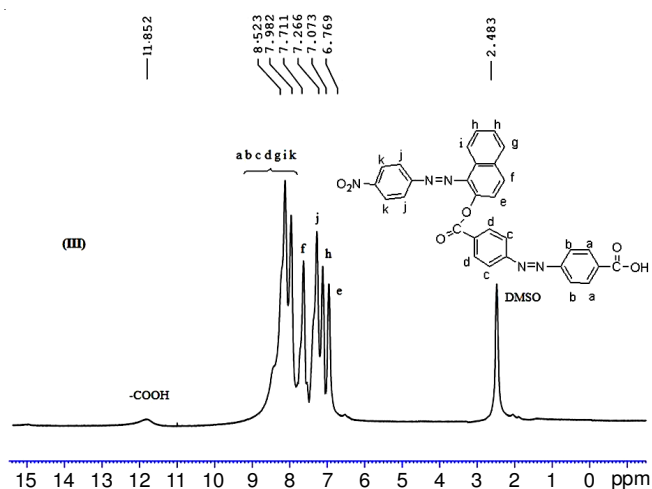


Fig. 1. ¹H NMR spectrum of (**III**)

aromatic hydrogens (a, b) near carboxylic group which extend the resonance effect the high field. Also the multi peaks of other aromatic hydrogens appeared in lower field.

¹³C NMR of dibenzoate ester showed two strong peaks of 2 and 3 aromatic carbons at 123.50 and 130.50 ppm, respectively and carbonyl ester carbon (CO₂Ar) at 163.10 ppm and carboxyl carbon (CO₂H) at 166.72 ppm (Fig. 2).

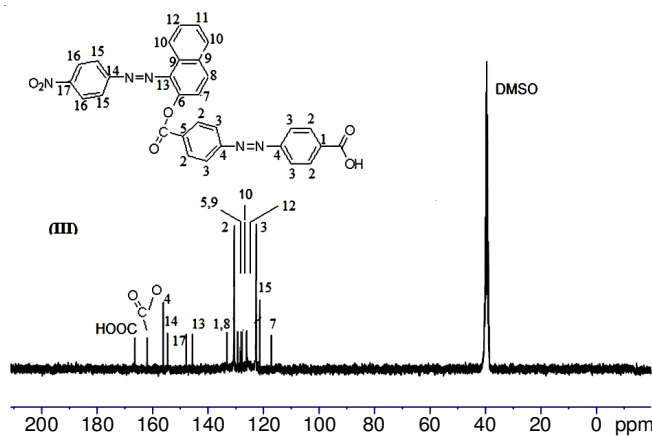


Fig. 2. ¹³C NMR spectrum of (**III**)

Properties of compound (IV)

Solubility: 0.2 g (M1) of synthesized polymer **IV** under investigation was dissolved in different solvents at 25 °C with continuous shaking for 12 h and left to stand overnight. The solution was then filtrated through pre weighed filter paper No. 41 and then the filter paper was re-weighed after a complete drying. The difference in weight gives the mass of the dissolved sample (M2). The degree of solubility (S %) can be calculating from the following relation [8,9]. The synthesized of *p*-nitro phenyl azo- β -naphthyl-(4'-azobenzoic acid)-4-benzoate containing PVA-grafting polymer derivatives were soluble in organic solvents such as DMF, DMSO, but they were all weak soluble in THF and pyridine and insoluble in ethanol. *etc.* While the modified PVA as different percentage were observed lower solubility than the pure PVA at the same conditions and that could be copolymer leads to decrease the number of inter molecules hydrogen bonds of the graft polymers.

TABLE-1
SOLUBILITY OF COMPOUND (IV) IN DIFFERENT SOLVENTS

Polymer code	Solubility in solvents ^b						
	(IV) η_{inh}^a (dL/g)	DMSO	DMF	NMP	DMAc	Pyridine	THF
(1)	0.62	++	++	++	++	+	+
(2)	0.57	++	++	++	++	+	+
(3)	0.54	++	++	++	++	+	+

^aMeasured at a concentration of 10^{-5} M in DMSO; ^bSolubility was tested with 10 % (w/v) of stirred solvent; DMSO = Dimethyl sulfoxide; DMF = N,N-dimethylformamide; NMP = N-methyl-2-pyrrolidone; DMAc = N,N-dimethylacetamide; THF = tetrahydrofuran; ++ High soluble at room temperature; +Low soluble at room temperature

$$S (\%) = M_2/M_1 \times 100 \quad (1)$$

Grafting polymer swelling: Swelling of grafting polymer was carried out in water at 25 °C using film samples with an average mass in the range of 0.1-0.15 g. The sample mass-to-water volume ratio was 1-30. The samples were removed from water at the predetermined time intervals, wiped gently with filter paper and weighed using an analytical balance. The sample mass change resulting from the water uptake expressed in percent was calculated according to the formula:

$$m = (m_t - m_0)/m_0 \times 100 \quad (2)$$

where (m_0 and m_t) are the masses of dry and wet samples, respectively [10].

It is found that the grafting polymer benzoate ester lose the swelling when the small percentage of 2 g of compound **III** than 4 g of compound **III**. The experiments of swelling were carried out at room temperature (25 °C). The samples were weighed at different time intervals until the hydrated weight was constant. Absorbency was calculated as grams of water per gram of dry polymer. In the second procedure a polymer sample that had been weighed accurately was immersed in distilled water at room temperature and left until equilibrium was attained Fig. 3. All the grafting polymers obtained in the study swelled in distilled water. The amount of absorbed water was dependent on the material composition (Table-2). The most hydrophobic polymers based on poly(vinyl alcohol) and benzoate ester absorbed (156-345 % at 24 h). The same increase of the PVA hydrogels obtained by freezing-thawing processes at -20 °C/ 20 °C has been evidenced by other researchers corresponding to the relative swelling decrease [9].

Differential scanning calorimeter DSC of compound IV: Thermal behaviours of modified *p*-nitro phenyl azo- β -naphthyl-(4'-azobenzoic acid)-4-benzoate containing PVA-

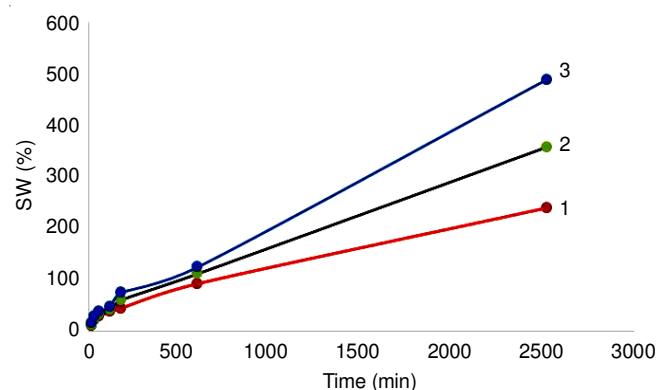


Fig. 3. Swelling behaviours as a function of time for grafting polymers (1), (2) and (3) in 25 °C

TABLE-2
SOME PROPERTIES OF COMPOUND IV

Sample No.	Tensile strength (MPa)	m.p. (°C)	Swelling degree (%)
(1)	7.62	130	156
(2)	10.72	171	300
(3)	12.75	192	345

grafting polymer with different percentage were studied using differential scanning calorimeter (DSC-60 Shimadzu) to identify whether the modification leads to produce cross linked or/and grafted structures. Each 10 mg sample was weighed into an aluminum crimped pan which gave an air tight seal and the reference was empty pan. The instrument was calibrated using indium of known melting point and heat of fusion and the scanning rate of 10 °C/min.

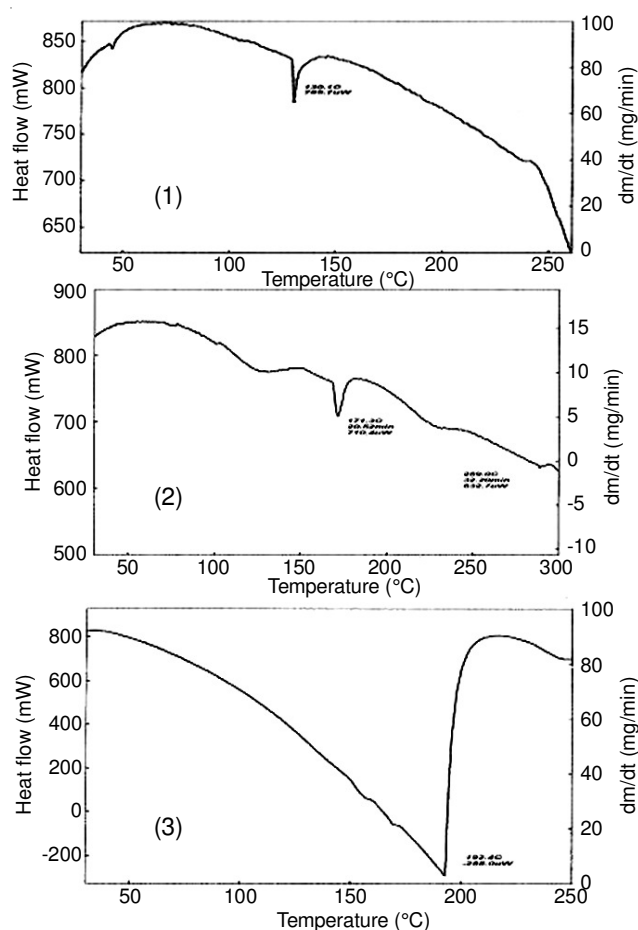


Fig. 4. DSC curves of *p*-nitro phenyl azo- β -naphthyl-(4'-azobenzoic acid)-4-benzoate containing PVA-grafting polymerization (1), (2) and (3) of 10 °C/min

Differential scanning calorimeter (DSC) was used to study the thermal properties and kinetic parameters involved in the cross linking processes so conversional kinetic analysis was applied to non-isothermal data to determine the dependence of activation energy on the degree of conversion [11]. DSC parameter of pure PVA-film showed its melt at 70 °C, but upon grafting PVA with diazobenzoate ester (**III**) in a ratio of 10 g PVA to 2, 3 and 4 g of diazobenzoate ester (**III**) respectably showed a melting range of (130, 171 and 197) °C as shown in Fig. 4 and Table-2.

Tensile strength: Tensile strength is important for a material that is going to be stretched or under tension. Therefore, fiber have need good tensile strength to improve the tensile of a polymer sample. We take the sample which is stretched by a machine such as an in stron, then using Zewigle machine and continue to increase the amount of force on the sample until it breaks. The stress needed to break the sample represents the tensile strength of the material. Since tensile stress is the force placed on the sample divided by the cross-sectional area of the sample, tensile stress and tensile strength as well as both measured I unit of fore divided by units of area and it is usually N/m² [8]. The reinforcing order can be written as follows:

Grafting polymer 10 g PVA: 2 g (III) (1) < Grafting polymer 10 g PVA: 3 g (III) (2) < (3-Grafting polymer 10 g PVA: 4 g (III) (3) Table-2.

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