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Modification of Poly Ethylene Glycol with 4, 4-Azo Di Benzoic Acid and Study of Its Physical Properties

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ABSTRACT

Polyethylene glycol 20000 was modified by copolymerization with 4, 4-Azo di benzoic acid, using cold-warm esterfication. The modified copolymer has been characterized by Fourier transform infrared spectrophotometer (FT-IR) which showed characteristic vibrational bands of OH, CO and N=N groups. The modified copolymer was subjected to differential scanning colorimeter (DSC), conductivity and swelling measurements. The obtained results of the thermal behavior (DSC) for the different percentage of prepared copolymers were (I=10% PEG +10% 4, 4-Azo di benzoic acid)= 54.2°C, as well as (II=20%) = 68.6°C, (III=30%) = 81.5°C, (IV=40%) = 93.3°C and (V=50%) = 120°C. This means that perfect results when the polyethylene glycol 50% mixed with 50% of 4, 4-Azo di benzoic acid. While the conductivity of all copolymer in an aqueous phase with varying chain lengths of PEG reacted with 4, 4-Azo di benzoic acid, in different percentage were (I) = 75.6, (II) = 151.8, (III) = 165.3, (IV) = 226 and (V) = 277 Λ_m(S.cm^2.mol^{-1}). In ethanol, the copolymers were observed to have electrolyte behaviors. The solubility of the prepared copolymer was tested in different solvents at 25°C. It is highly soluble in DMSO and DMF and insoluble in other solvents. The experiment of measuring the degree of swelling under room temperature, in equal periods of time, showed good water uptake and required ~ 12 hours for reaching the equilibrium for the different percentage of prepared copolymers.

Keyword: modification of polyethylene glycol 20000, 4, 4-Azo di benzoic acid, DSC, Conductivity, Swelling

1. INTRODUCTION

Poly (ethylene glycol) (PEG) is a linear polymer formed by the polymerization of ethylene oxide. PEG, usually indicates the polyether, of molecular weight less than 20000 is known to be inexpensive, thermally stable, recoverable, biologically compatible and non-toxic (Harris, 1992 & Harris, 1997). Furthermore, PEG and its mono methyl ethers have low vapor pressure, nonflammable, present simple workup procedures and can be recycled. For these reasons PEG is considered to be an environmentally benign alternative to chemical volatile solvents and a highly practical medium for organic reactions. PEG is most commonly employed as support for various transformations (PEG 2000-20000) (Juntao, et al. 2007& Mathmai, 2008), as a biologically acceptable polymer used extensively in drug delivery and bio conjugates as tools for diagnostics (Harris, 1992. & Rao, 1997. & Ying Shang, et al. 2008). But it can also be employed as an efficient medium for phase transfer catalysts.

Its use as solvent in organic reactions is relatively recent and it is usually used in low molecular weights (< 2000) because it is either liquid at room temperature or has a low melting point (Campbell, 1993. & Almousway, 2002 & Dickerson, et al. 2002). Although it is less popular, PEG is commercially available and is much cheaper than ionic liquids. Unlike the latter, its properties cannot be easily tuned. One of the major drawbacks in its use in organic reactions, which also applies to ionic liquids, is the inconvenience of using organic solvents to extract the products, even though it can also be used in both cases (Fontana, et al. 1995. & Talhavini, et al. 2000).

Probably due to the higher popularity of other alternative solvents, especially ionic liquids, there are only a few examples in the literature of using PEG as solvent in organic reactions, which will be disclosed in this review. To the best of our knowledge this is the first review describing the use of PEG as solvent in organic reactions. And for this reason the influence of relative humidity (RH) on aging of AZO/PEG blends was also considered (Vieilla, et al, 2001. & Khajeh, et al, 2006).

Azo compounds have a great biological activity as well as industrial importance because of their mutagenic and carcinogenic effects (Patai, 1975). They are capable of oxidizing many compounds bearing the functional groups R-N=N-R' (Azo-dyes), in which R and R' can be either aryl or alkyl groups. These compounds are widely used and discarded in worker collections. Additionally, azo-dyes can cause biological alteration (Houk, 1992. & Chung, 1992).

2. MATERIAL AND METHODS

All chemicals were obtained from specially Poly (ethylene glycol) with a molecular weight of 20000 g/mol (Fluka), and were used without purification. Infrared spectra of the azo compounds and its copolymer were recorded on (shimadzu, FTIR.8400s) in the range (4000-400) cm^{-1} using KBr pellets. Molar conductance of the copolymer was determined in ethanol (10^{-3}) at room temperature using (Philips PW-Digital Conduct meter).

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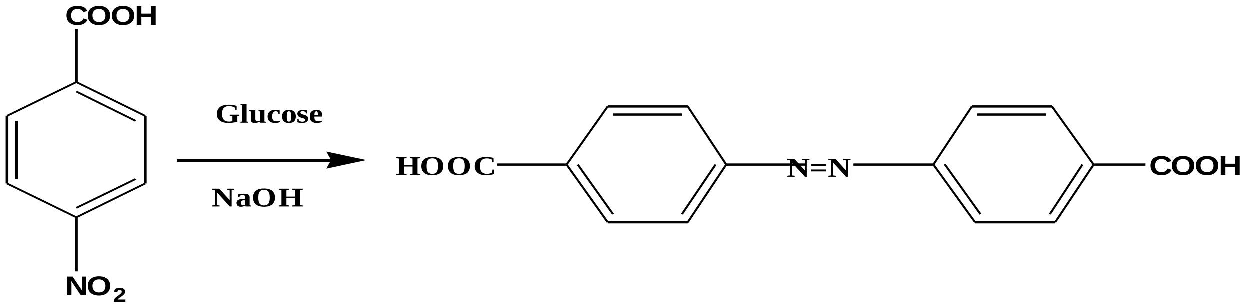
3. SYNTHESIS METHOD OF COPOLYMER AND SCHEME

3.1 *Synthesis of copolymers PEG- CO - AZO*

Synthesis of copolymer PEG (Mwt = 20000) with 4, 4-Azodibenzoic acid (Mwt = 270), was initiated from the starting material P-Nitro benzoic acid (I), (Khalil, at el. 2007). As shown in scheme (1).

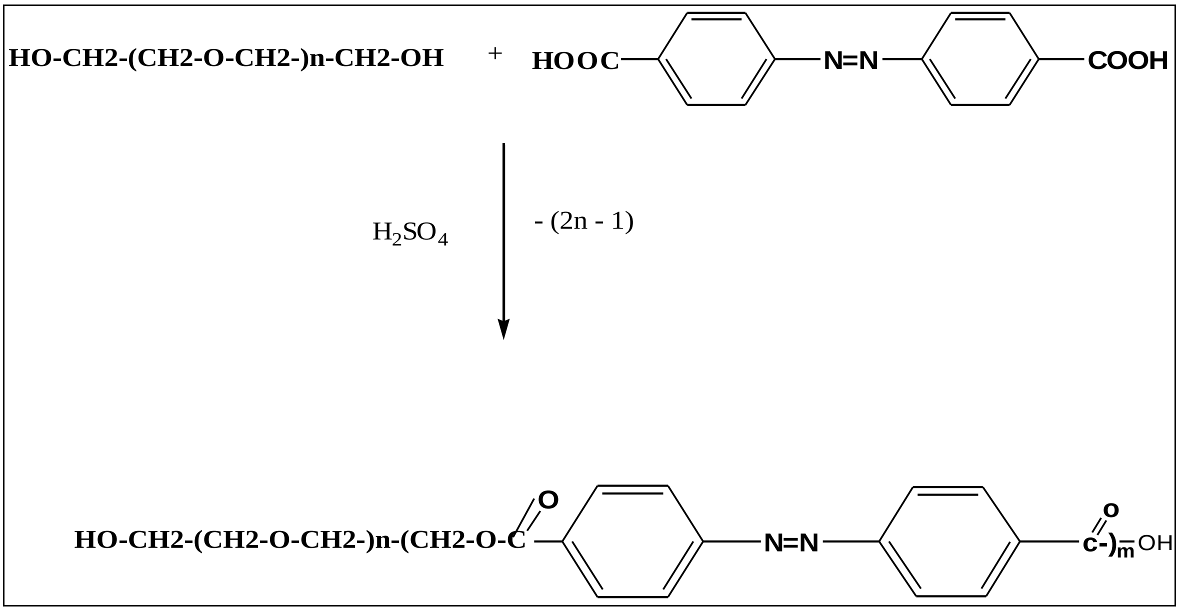


Scheme-1: Showed synthesis of 4, 4-Azodibenzoic acid (I).

To synthesis the copolymer; 10gm (0.1590mmol) of poly (ethylene glycol) were dissolve in distilled water and the solution was then introduced into a 250 ml two necked round bottom flask contains magnetic bar and fitted with a thermometer. The solution was then stirred and heated to reach 50-60ºC, and 2-3 drops of concentrated H_2SO_4 with continuous stirring for 2 hours. The reaction mixture was then transferred as soon as possible to a water- ice bath at 10ºC with horizontal shaking for 30 min. and then 2.16 gm of AZO (0.008mol) were added. Another 2-3 drops of concentrated H_2SO_4 were added and the reaction mixture was refluxed for 2 hours at 40-50◦C, A light wood color shown (see Table-1 and scheme-2). The solution was then poured on a glass mould and left to dry slowly at room temperature in a dark place for 2 days. The dried sample was then washed with distilled water to remove the unreacted materials and re-dried in an oven at 30ºC for 2 hours and stored in a dry and dark glass box. The experiment was repeated with 20%, 30%, 40% and 50%.of poly (ethylene glycol) and azo compound, see Table-1.

Table-1: The percentage of polyethylene reacts with 4, 4-Azodibenzoic acid

Sample No.	PEG	4,4-Azodibenzoic acid	Yield	Color
I	10%	2.16	62	Light Wood
II	20%	4.32	68	Wood
III	30%	6.48	71	Light orange
IV	40%	8.64	75	0range
V	50%	10.80	80	Reddish orange



Scheme-2: Synthesis of co polymer *PEG - CO-* 4, 4-Azodibenzoic acid (II).

3.2 *DSC Analysis*

Thermal behaviors of the modified PEG-AZO and its modified compounds 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 ºC /min.

3.3 *Solubility*

0.2 gm (M1) of each compound under investigation was dissolved in different solvents (see Table 2) at 25ºC with continuous shaking for 12 hours 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 calculate from the following relation (Finch, 1973) :

$$S\ \% = M2 / M1 \times 100 \quad \ldots\ldots\ldots\ldots (1)$$

3.4 *Copolymer Swelling*

Swelling of copolymer was carried out in water at 25◦C using film samples with an average mass in the range of 0.17-0.130gm. 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:

$$\Delta m = (m_t - m_0) / m_0 * 100 \quad \ldots\ldots\ldots\ldots (2)$$

Where m_0 and m_t are the masses of dry and wet samples, respectively. (Katazyna, et al. 2002. & Jatuphorn, et al. 2007).

4. RESULT & DISCUSSION

Linear PEG (Mwt=20000) was modified with 4, 4-azodibenzoic acid at different percentage, used the different between the original polymer (a) and modified polymer (b). The FT-IR spectra of the PEG alone and of the modified polymer were as seen in fig. (1a, 1b) respectively. The FT-IR spectrum fig(1a) shows the characteristic important strong peak of the hydroxyl group (OH) at 3400 cm^{-1}, and also the peak of methylene group (CH) of PEG near 2980 cm^{-1}. There is an absorption maximum at 3412cm^{-1} for the (OH) group of polyethylene glycol modified. In fig (2a) The strong peaks observed at 3324 cm^{-1} is the characteristic of the hydroxyl group (OH) of PEG, and the peak at 1647 cm^{-1} is the characteristic peak of carbonyl group (C=O) of the produced ester. On the other hand, the peak of group (N=N) at 1591 cm^{-1} has been depleted when PEG is in excess. The (C-O) sing stretching band at 1016, 1026 cm^{-1}.

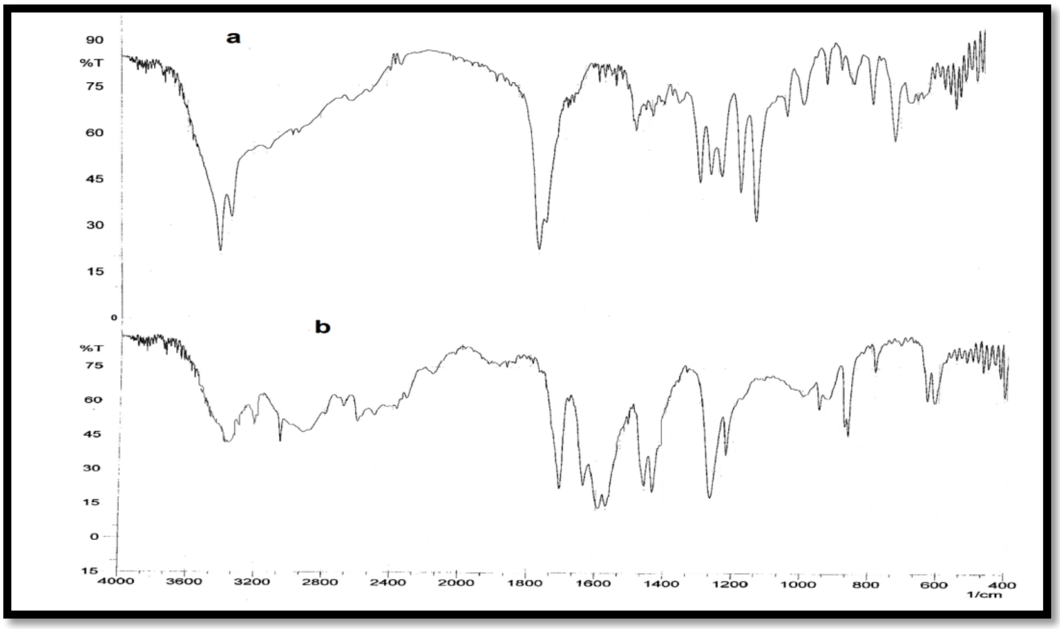


Fig-1: FTIR Spectra of copolymers (a), poly ethylene glycol alone, (b). Of co polymer *PEG - CO-* 4, 4-Azodibenzoic acid

Differential scanning colorimetric (DSC) was used to characterization the percent crystalline in the physically cross linked samples using a scan of 10°C / min. Law endothermic peaks were observed for all samples (fig.2). We find that melting temperature increases as the azo unit increased (fig.2), we showed the thermal behavior DSC for the different percentage of new copolymers were (I=10%)= 54.2°C, (II=20%) = 68.6°C, (III=30%) = 81.5°C, (IV=40%) = 93.3°C and (V=50%) = 120°C. that is mean is the perfect result when we mixed 50% of polyethylene glycol and 50% of 4,4-azo di benzoic acid. While the theoretical heat of 138.6 J/g for 100% crystalline sample of PEG (Peppas, et al. 1982 & Wenlong, et al. 2010).

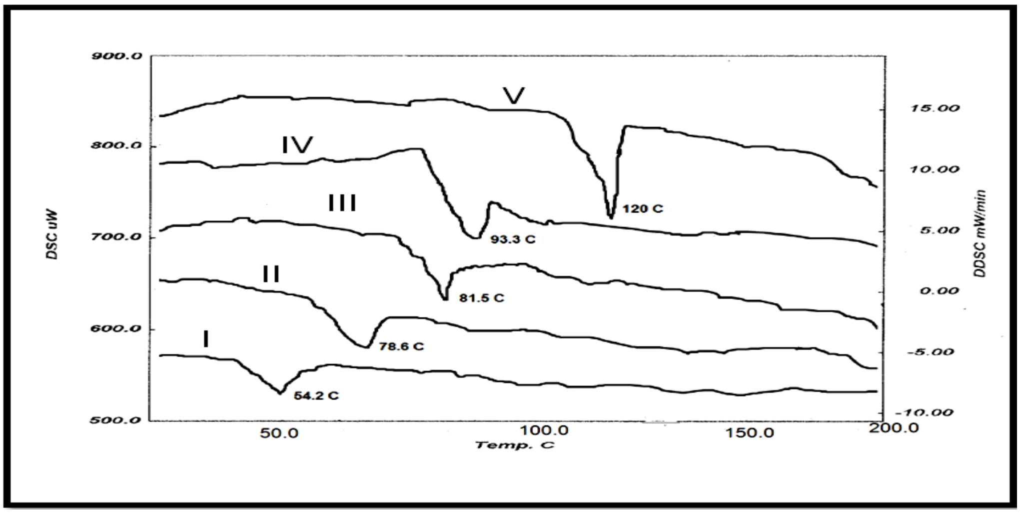


Fig-2: DSC Curves of new copolymers (I), (II), (III), (IV) and (V) of 10°C / min.

The dynamic swelling behavior is shown in fig (3), where it can be noted that all of the copolymers rapidly reach their equilibrium (in ~ 12 h). It was found that all copolymers obtained in this study swelled in water in room temperature at 25◦C. the amount of absorbed water was dependent on the number of ethylene glycol units and the azo units in the polymer chain, dependent on the molecular weight of PEG and 4,4-azo di benzoic acid used in the synthesis of copolymer. The amount of water absorbed has increased with time, and the maximum degree of swelling decreased from (73.4%) for 10% of copolymer of (I), to (65.4%) for copolymer (II), to (48%) for copolymer (III), to (46%) for copolymer (IV) and to (45%) for copolymer (V). in addition The molecular weight distribution is an important characteristic of PEG because it affects many of its properties including crystallite ability, adhesion, mechanical strength, and diffusivity (Christie, et al. 2000 & Yafeng, et al. 2011).

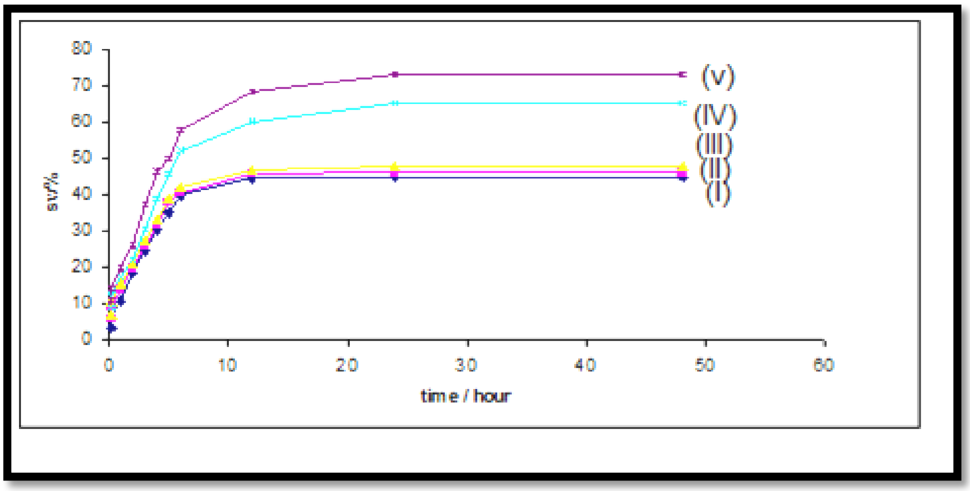


Fig-3: Swelling behaviors as a function of time for copolymers (I), (II), (III), (IV), and (V).

The solubility of the synthesis copolymers was tested in different solvent at room temperature with concentrations of approximately (1% W/V). It was found that the new copolymers soluble in a parotic polar solvents such as Di methyl sluphoxide (DMSO), Di methyl formaldehyde (DMF), Di methyl actamide (DMAC), and less solvent like pyridine, xylene, but in soluble in common organic solvents such as alcohol, chloroform, acetone, toluene and benzene (table-2).

Table-2: Solubility of copolymers in different solvents at 25◦C.

Sample No.	DMSO	DMF	DMAC	Pyridine	Xylene	Hexanol	Chloroform	Acetone	Toluene	Benzene
I	V.S	V.S	V.S	W	N.S	N.S	N.S	N.S	N.S	N.S
II	V.S	V.S	V.S	W	N.S	N.S	N.S	N.S	N.S	N.S
III	S	S	S	W	N.S	N.S	N.S	N.S	N.S	N.S
IV	S	S	S	W	N.S	N.S	N.S	N.S	N.S	N.S
V	S	S	S	W	N.S	N.S	N.S	N.S	N.S	N.S

-V.S= very strong when the percentage reached >80%, S= strong when reached 70%,
W= slightly soluble weak when reached 50% and N.S = not soluble when less than 50%.

The conductivity measurement in ethanol 10^{-3} M at 25◦C indicates of the copolymer as different percentage was electrolyte behavior (Gearg, 1971). It is recorded (I) = 75.6, (II) = 151.8, (III) = 165.3, (IV) = 226 and (V) = 277 in Λ_m ($S.cm^2.mol^{-1}$) in ethanol. Organic semiconductors have been the subject of intense scientific investigation for the past 50 years. Due to often weak bonding between organic molecules in the solid state, they share many of the properties of both semiconductors and insulators. Applications of these materials include chemical, physical and biological sensors, electric, electronic, and photonic devices (Bohwon, et al. 2004. & Amanda, 2009).

5. CONCLUSIONS

From the above observation, we can suggest that the existence of PEG molecules on the copolymers modified composite membrane, which is the results that the hydroxyl group of PEG modified, is not only physically adsorbed on the membrane but also chemically bound by forming covalent bond with polymer molecules on the composite layer particles. Therefore, PEG is working as hydrophilic stabilizer in our system. Thermal behavior of the synthesis copolymers was studied by DSC, It is showed good thermal resistance and high melting temperature and the melting temperature increased as the number of azo units in the chain are in creased. It is possible to swell there polymers with water and they would have some degree of wet ability.

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