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Some characteristics of poly(vinyl alcohol) with azido aromatic groups

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Poly(vinyl alcohol), a hydrophilic and low cost polymer seems be a good candidate in making supports with different functionalities. Chemical modification of this polymer can be obtained by polymer-analogue reactions. Applications of modified poly(vinyl alcohol) have been proposed in coatings, biomedical or photoresist field, due to its desirable properties, low toxicity and biocompatibility. In this paper we report some characteristics of poly(vinyl alcohol) with pendant azido aromatic groups. The azido substituent makes this polymer potentially useful as membrane.

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Keywords: Poly(vinyl alcohol), Azido group, Photosensitive polymer, UV irradiation

1. Introduction

Poly(vinyl alcohol) has gained a great attention because of its many desirable characteristics as well as its applications. It is a non-toxic, non-carcinogenic, biocompatible, biodegradable, non-expensive and the largest volume water-soluble polymer produced today (on the order of several hundred kton/yr). Poly(vinyl alcohol) (PVA) have been widely used in the field of biomaterials, biosensors, electrochemical sensors, membranes with selective permittivity, viscous medium for controlling the crystallization process of salts, drug delivery or catalytic systems in medical, cosmetic, and packaging materials. It could be also matrix for metal ions or salts in ecological composites and filter which cut out ultraviolet and infrared radiation. Poly(vinyl alcohol) has a simple chemical structure with pendant polar hydroxyl groups along its macromolecular chain, that permit the physical interactions (by H bonding or by van der Waals dipole-ion or dipole-dipole interactions) and complexing reactions. The –OH groups which are mainly in 1,3-diol structure can also react with different organic or inorganic substances. Multi-functional compounds can be used to obtain three-dimensional PVA networks by crosslinking. Poly(vinyl alcohol) must be crosslinked in order to be useful for many applications, especially in the medicine and pharmaceutical field. Poly(vinyl alcohol) can be crosslinked through the use of difunctional crosslinking agents, electron-beam or γ-irradiation [1-7] .

The incorporation of pendant substituents along the polymer main chain of poly(vinyl alcohol) by esterification is one of the various attempts tested in order to obtain new polymers which may be tailored to the demanding requirements of specific applications. It is well known that aromatic azides have attract much attention because of versatile transformations of the azide functional group. Nitrene intermediates, in triplet or singlet state, that appear in their decomposition under thermal or photochemical conditions, confer to these compounds a high reactivity and many applications such as polymerization initiators, crosslinking agents, labels for biomolecules, precursors of electrically conducting polymers and other componds, analytical reagents [8]. Based on the special properties of poly(vinyl alcohol) and azides we introduced azide groups in side-chain of poly(vinyl alcohol) structure to form novel polymers.

We hope that the introduction of azido groups may make poly(vinyl alcohol) photosensitive and cross-linkable.

The PVA containing the azidobenzoyl side chain was characterized by spectral and thermal methods and its photosensitive properties were investigated herein.

2. Experimental

A poly(vinyl alcohol) powder with a high degree of hydrolysis (about 98 %) was used for synthesis of the poly(vinyl alcohol) modified with azidobenzoyl groups that consists in three steps, namely reaction of diazonium salt of p-aminobenzoic acid with sodium azide, treatment of the resulting compound with thionyl chloride and preparation of polymer.

The thin film samples were deposited onto glass substrates. The precursor solution was prepared by dissolving the polymer in dioxane. Infrared spectra spectra were recorded on a VERTEX 70 FT-IR spectrometer in the reflectance mode. The scanning wave number ranged from 4 000 to 550 cm^{-1} with a scan resolution of 4 cm^{-1}. UV-VIS absorption spectra were acquired on a SPECORD M42 Carl Zeiss Jena spectrophotometer. The samples were irradiated with a 350 W medium-pressure mercury arc lamp. The glass transition temperatures were determined with a METTLER DSC 112E differential scanning calorimeter at a heating rate of 10^{o}C/min. Thermogravimetric analysis (TGA) was performed on a

MOM Derivatograph in air atmosphere at a heating rate of 10°C/min.

3. Results and discussion

The most common way to esterify polymers containing -OH groups with acid chlorides uses a homogeneous medium by solution in appropriate solvent. In the case of poly(vinyl alcohol) the solvent must be very polar such as N-methyl pyrrolidone or dimethylsulfoxide. Since only a partial esterification was desired, the remained hydroxylic groups can interact with the solvent making their complete elimination difficult and therefore giving a low yield of pure product. The synthesis of the target polymer was achieved through the use of the Schotten-Bauman method since water is a good solvent for poly(vinyl alcohol). The reaction was carried out with a slight excess of acid chloride. The direction for preparation of modified poly(vinyl alcohol) give a satisfactory yield and purity, but careful attention to details is necessary. The degrees of hydrolysis and polymerization of poly(vinyl alcohol) affect its solubility in water. It is known that polymers with high degrees of hydrolysis have low solubility in water. The presence of residual acetate groups affects the polymer crystallization and weaken the intra- and intermolecular hydrogen bonding [5]

The solubility of poly(vinyl alcohol) in water is mainly due to hydrogen bonding between -OH groups of the polymer and molecules of water and it is important for polymer modification steps. The strong intermolecular association by hydrogen bonds can be destroyed by dilution. Because poly(vinyl alcohol) is a semicrystalline polymer, their macromolecules are not molecularly dispersed at room temperature, even at high dilution and the solutions contain microgel particles (in low concentrations) consisting of paracrystalline and amorphous domains. The former are prone to grow on standing and stronger association by hydrogen bonds appear in altered solutions that is connected with an increase in size and amount of paracrystalline domains. Aging phenomena are a consequence of an increase in the cross-linking density with time. On the other hand it is well known that water is one of the active factors that influence the polymers' aging [9,10]. The structure of solutions, in particular after aging, can be visualized as a physical network where paracrystalline domains act as multifunctional physical cross-linking units. The microgels are difficult to remove even by repeating filtration and they could be responsible for problems in polymer analogue reaction. Thus, heating to 353-373 K destroys hydrogen bonds with a concomitant increase of the role of hydrophobic interactions, both intramolecular and intermolecular.

On the other hand the azido group is very photosensitive. The photochemistry of arylazides is somewhat complicated and not totally understood [11].

The nitrene radicals generated upon irradiation, by loss of nitrogen from azides are unstable and very reactive at room temperature and they can perform recombination reaction which lead to the formation of azoaromatic compounds.

$$ArN_3 \xrightarrow{h\nu \text{ or } \Delta} ArN: + N_2$$

$$Ar{-}N: + Ar{-}N: \longrightarrow Ar{-}N{=}N{-}Ar$$

or insertion reactions into all kinds of C-H and X-H bonds.

Also, nitrenes can react with oxygen and lead to formation of nitro type compounds:

$$Ar{-}N: + O_2 \longrightarrow RNO_2$$

The crosslinking of the PVA may be achieved due to the presence of -OH and azido group incorporated in their structure by insertion and/or recombination reactions. Therefore both the intermediate with azido group (azide and its chloride) and target polymer must protect to light.

The infrared and elemental analysis indicated that azido groups were successfully introduced into the poly(vinyl alcohol) structure [3] . For the IR absorption spectrum of poly(vinyl alcohol) there is a broad and strong absorption peak at about 3470 cm^{-1}, representing the stretching vibration of OH with strong hydrogen bonding. Other characteristic vibration bands are observed at 2940, 2910, 2660, 1446, 1430, 850 and 835 cm^{-1}, attributed to $-CH_2-$ units and at 2840, 2660 1326 and 1235 cm^{-1} associated with –CH– units.

The stretching vibration bands of unsaturated bonds C=O and C=C which are present in the tail–head of the polymer appeared at 1610 and 1570 cm^{-1} for all the samples under investigation. The IR spectrum of the modified polymer presented in Figure 1 have absorption bands which reflect the presence of functional group, N_3 at 2125cm^{-1} and CO(O) linkage at 1712 cm^{-1}, respectively and exhibit also a diminution of the OH stretching band.

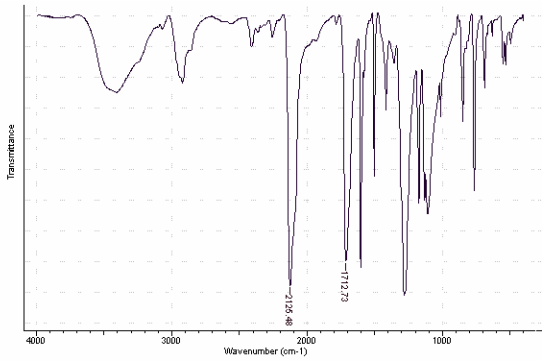

Fig. 1. FT IR spectrum of the modified poly(vinyl alcohol).

UV spectroscopy is the most sensitive technique for monitoring this photoactivated tranformation in the structure of the polymer**.** The optical absorption measurements for poly(vinyl alcohol) evidenced bands in the UV region (see Figure 2) at 223, 282 and 327 nm assigned to $n \rightarrow \pi^*$ transition, due to the presence of the C=O group and $\pi \rightarrow \pi^*$ transition, respectively which arise

from unsaturated bonds, C=O and/or C=C, which are present in the tail–head of the polymer.

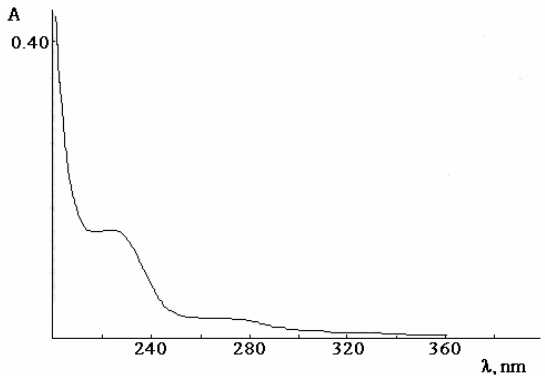

Fig. 2. UV absorption spectrum of the poly(vinyl alcohol).

To demonstrate the photosensitivity of modified poly(vinyl alcohol) due to the presence of azido group in pendant units dioxane solution of polymer was irradiated.

The behavior of the polymer under UV light irradiation was monitored by UV spectroscopy in the range of 200 to 500 nm. Dilute solution of polymer in dioxane was exposed to 280 nm light.

The successive changes in the absorption spectra of the polymer are characterized by decreasing of absorption band at 280 nm and the presence of two isosbestic points which appear at about 250 and 300 nm, respectively as is shown in Fig. 3. The decrease in the absorption peak at 280 nm suggests the decomposition of the azido group.

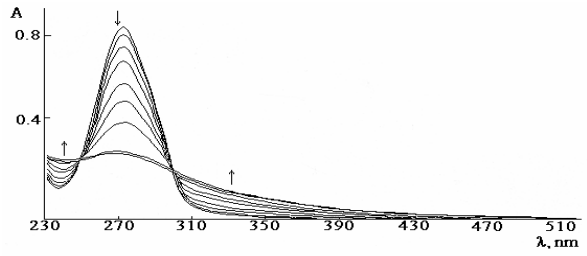

Fig. 3. Electronic absorption spectra following 280 nm irradiation of the modified poly(vinyl alcohol) in dioxane solution; irradiation times: 0, 10, 30, 60, 120, 180, 300, 1320, 2160 s.

The presence of the two isosbestic points indicates the fact that only one transformation is involved in this photoreaction in the system when modified poly(vinyl alcohol) is irradiated with light of wavelenghts filtered at 280 nm.

The disappearance of the isosbestic points on continued irradiation has been assigned to other photoreaction, taking into account highly reactivity of azido species. At the same time a new broad absorption band appears in the longer wavelenght region at around 400 nm and this fact is presumed to be due to the formation of azo bonds by reaction of nitrene radicals. Consequently, the changes in the absorbance are caused by photodecomposition of azido groups and crosslinking reactions.

The kinetics of the photochemical behaviour of modified poly(vinyl alcohol) was studied plotting $\ln(A_0-A_\infty)/(A_t-A_\infty)$ versus time, where A_0, A_∞ and A_t are the absorbances before irradiation, after irradiation for infinite time and during irradiation at different time intervals respectively.

The analysis of UV spectra indicated that the photodecomposition of azido group in pendant units of modified poly(vinyl alcohol) follows a kinetic relation for first-order reaction accrding to the formula:

$$\ln\frac{A_o - A_\infty}{A_t - A_\infty} = kt$$

where k is the rate constant.

Curves of $\ln (A_o-A_\infty)/(A_t-A_\infty)$ versus irradiation time were linear as depicted in Fig. 4.

A rate constant value of 4.69×10^{-3} s^{-1} was found for the photolysis reaction of modified poly(vinyl alcohol).

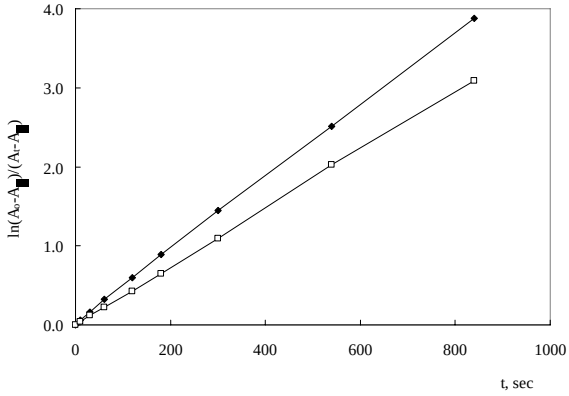

Fig. 4. Kinetics of the photochemical behaviour of modified poly(vinyl alcohol) (■) and p-azidobenzoic acid.

The rate of photochemical process is higher in the case of the polymer than in that of pure azide (see Fig. 4). It is probable that this behavior reflect the electron-withdrawing effect of the carbonyl group from carboxyl part of side-chain and the hydrogen bonding interaction between two molecules of p-azidobenzoic acid.

The changes in the UV spectrum of the film of modified poly(vinyl alcohol) on irradiation are similar to those observed in dioxane solution.

The occurrence of crosslinking reaction was followed by the increase of insolubility of the polymer films (casting from 2% solution in dioxane) in usual organic solvents.

Poly(vinyl alcohol) is characterized by high interconnecting of hydrogen bonding which contributes to its glass transition. PVA exhibits an endotherm at 70 °C corresponding to the glass transition temperature, T_g. The introduction of functional group as side chain breaks this bonding and diminished the T_g value, but on the other hand the rigidity of pendant group limit the chain mobility and this may contribute to the increasing of T_g value. As

can seen in Fig. 5 the T_g value of polymer under study is 75 ^oC.

Compared with the neat poly(vinyl alcohol) (T_m = 225 °C) the melting temperature of modified poly(vinyl alcohol) is lower (T_m = 192 °C).

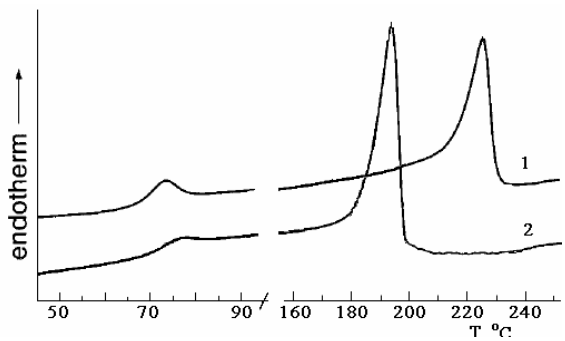

Fig. 5. DSC curves for poly(vinyl alcohol) (1) and modified poly(vinyl alcohol) (2)Thermal gravimetric analysis (TGA) of pure poly(vinyl alcohol) and modified polymer evidenced that the weight loss (of 53 %) due to the decomposition of PVA is nearly the same until the temperature of about 275 °C. In the case of modified poly(vinyl alcohol) major weight losses are observed at 190 ^oC which may be correspondent to the structural decomposition of the polymers when the weight loss increase at about 61 % in comparison with pure poly(vinyl alcohol).

In conclusion, poly(vinyl alcohol) with pendant p-azidobenzoyl side chain was obtained by polymer analogues reaction. The azido group photosensitivity was confirmed by UV spectroscopy. The changes in the absorption spectra of the polymer are characterized by decreasing of absorption band at 280 nm and the presence of two isosbestic points. This behavior is associated with photoactivated tranformation in the structure of the polymer, namely, decomposition of azido group and crosslinking reaction, which lead predominantly to azo linkages.

Acknowledgements

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