

¹H NMR Study of Polyvinylalcohol Irradiated by Ultra-violet

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Abstract: The effect of Ultra-violet light on the structure and motion of the polyvinyl alcohol (PVA) chains was studied by ¹H NMR, spin-lattice relaxation and IR spectroscopy. The results indicated that with the increase of irradiation time, the intensity of the polymer hydroxyl proton peaks decreased and finally vanished, which suggested the self-condensation between the hydroxyl groups proceeded. No methyl proton peaks appeared in the spectra after irradiation shows that there is no cleavage of polymer chain. The longer the irradiation time is, the wider the proton peak of the residual water of the solvent is and it shifted toward low field. This result implies that the hydrogen bonds formed between the polymer and the residual water. The absorption peak of hydroxyl group of the polymer moves toward the lower wave number in the IR spectrum that showed the existence of the hydrogen bonds between the PVA macromolecules.

Keywords: PVA, UV, relaxation, hydrogen bond.

Polymers may be aged by many physical and chemical factors¹⁻⁴. Reduction of their molecular weights, the change of colors, and worse the mechanics properties are all the signs of their aging. Ultra-violet light (UV) is a higher energy source, it can cause stronger effect on the aging of the polymer. We studied the motion of polyvinyl alcohol (PVA) chains after irradiated of UV with a wavelength of 310 nm, the formation of hydrogen bonds between hydroxyl groups and the residual water in the solvent DMSO by ¹H NMR spectra, spin-lattice relation time (T₁) measurements and infrared (IR) spectrometry.

Experimental

PVA (DP=1750±50) is a commercial product of the Chemical Plant of Beijing East City. It was irradiated in a box with a lamp of 365 nm in distance of 10 cm, which type is UV-A of the lamps' plant of Tianjin. The irradiation time varies from 1 to 5 hours.

The irradiation polymers were then dissolved in dimethyl sulfoxide (DMSO) at a concentration of 5g/L. NMR experiments were performed on a Varian Inova 400 NMR spectrometer at 30°C at a proton frequency of 399.74 MHz. Spin-lattice relaxation times were measured by the inversion recovery method, with an errorless than 5%. IR spectra were recorded with potassium bromide pellets on Bruker Equinox 55 IR spectrometer.

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Results and Discussion

Figure 1 shows that the ^1H NMR spectra of PVA before and after irradiation by UV at 365 nm at different time.

Figure 1 ^1H NMR spectra of PVA before and after irradiation by UV light

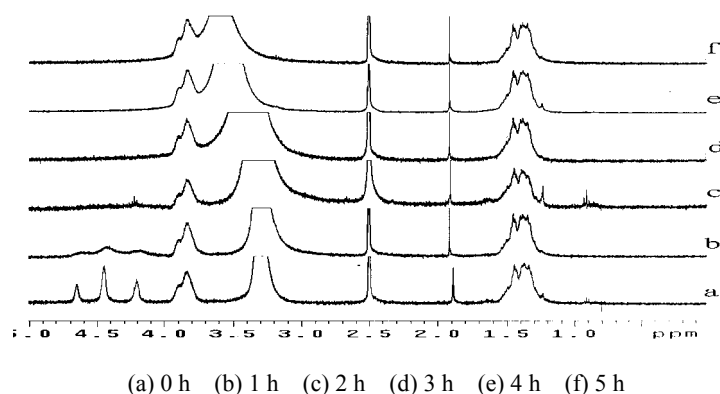
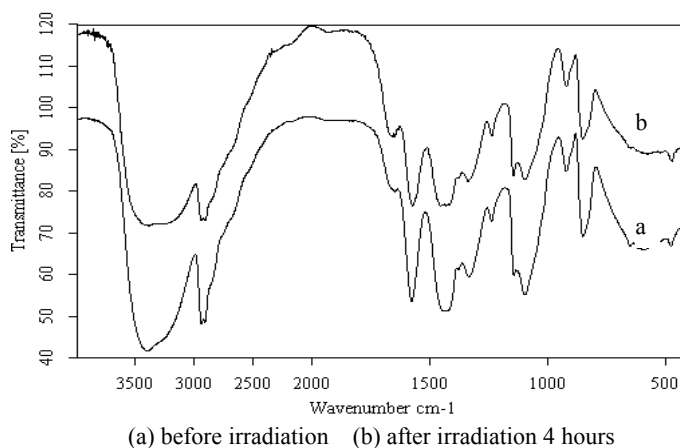


Table 1 The spin-lattice relaxation times (T_1) of PVA at various irradiation time

Irradiation time (h)	Spin-lattice relaxation times (s)	
	CH	CH ₂
0	0.57	0.36
1	0.62	0.35
2	0.59	0.35
3	0.69	0.35
4	0.70	0.36
5	0.77	0.36

Peaks at δ 1.33-1.45, 3.84 and 3.30 ppm are the proton of CH₂, CH and the residual water protons, respectively. The group of peaks at δ 4.19-4.64 ppm is the resonance of the OH group of the polymer originating from the “head-tail” sequence structure⁵ of the PVA main chain. The peak at δ 2.50 ppm belongs to the proton of the solvent DMSO. It is obvious that the OH proton peak of the polymer becomes wider and featureless as the duration of irradiation increases, and finally vanishes. Meanwhile, the water proton peak is widened simultaneously, and shifts to the high field, while those of the CH₂ and CH remain unchanged. These results suggest that the amount of hydroxyl groups in the polymer decreased, probably owing to the self-condensation, forming the ether bonds. These oxygen atoms bearing lone pair electrons, which can form hydrogen bonds with water molecules, resulting the shift of the water proton peak towards low field in ^1H NMR. Meanwhile, the widening of this peak further indicates that the motion of the water protons is seriously restricted by the bonding with the soft-solid like polymer.

Table 1 shows the variation of the spin-lattice relaxation times (T_1) of the CH and CH₂ protons with the increase of irradiation time. T_1 of CH₂ remains unchanged, while that of CH₁ connected with the hydroxyl group increases monotonously.

Figure 2 IR spectra of PVA

As shown in **Table 1**, T_1 of CH_2 remains almost unchanged, while that of CH , connected with the hydroxyl group, increases monotonously. This indicates the existence of OH groups in the PVA chain which connect with CH group. These OH groups can not form hydrogen bond between themselves, but it can form hydrogen bond with water molecule. So the movement of CH group is somehow inhibited and the relaxation times T_1 increase. In contrast, CH_2 group cannot be affected by the hydrogen bond of OH group. So the relaxation times did not change obviously.

Figure 2 shows that the IR spectra before and after UV irradiation, the stronger peaks of IR adsorption at wave number of 3400 cm^{-1} indicated the formation of the intermolecular hydrogen bond. Usually the peaks of hydroxyl group are at 3600 cm^{-1} .

In conclusion, for PVA, before and after irradiation by UV, the formation of hydrogen bond between hydroxyl group and water proton and their exchange not only make the peak of water proton moves to lower field, but also effect the movement of CH group.

Acknowledgments

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