PHOTOCROSSLINKING OF WATER-SOLUBLE POLYMERS BEARING A PENDANT CYCLOHEXENONE MOIETY

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We have reported that the reaction of poly(vinyl alcohol) (PVA) with methyl vinyl ketone under basic conditions gives water-soluble polymers which have a pendant α,β -unsaturated carbonyl group (a cyclohexenone moiety) [1] and their films become insoluble in water very effectively when irradiated with UV light [2]. It was deduced that the insolubilization was caused by the photodimerization of pendant α,β -unsaturated groups and that the aggregation and segment motion of the pendant groups induced the highly-efficient photodimerization. The amount of α,β -unsaturated carbonyl groups in the polymers, however, was one-tenth of pendant saturated carbonyl groups and it was difficult to differentiate the aggregation and segment motion of α,β -unsaturated carbonyl groups from those of saturated carbonyl groups. Thus, in order to get the information of photochemical behavior of pendant α,β -unsaturated carbonyl groups, the PVA which has a small amount of a pendant α,β -unsaturated carbonyl group (a cyclohexenone moiety) only was required. In this article, we report the preparation of PVA which has only pendant α,β -unsaturated carbonyl groups (PCPVA-R) and its photochemical behavior.

The route of polymer preparation was shown in Scheme I. The introduction of pendant α,β -unsaturated carbonyl groups into PVA was carried out as follows: (1) the reaction of hydroxyl groups in (4) with (3) in the presence of DCC and (2) partial hydrolysis of (5) under basic conditions.

Figure 1 shows the IR spectra of (4), (5), and (6). Absorption bands at 3330, 1715, and 1655 cm^{-1} were assigned to hydroxyl, ester carbonyl, and α,β -unsaturated carbonyl groups, respectively. Since the absorption band at

LDA: lithium diisopropylamide, DCC: dicyclohexyl carbodiimide

Scheme I

Figure 1. IR spectra of polymers: (4), (5), and (6).

Figure 2. Emission spectra of aqueous solutions of ANS: (1)water, (2)PVA, (3)PCPVA-R2, and (4)PCPVA-R1. [polymer]=1.0 g/l, [ANS]=0.18g/l, λ_{ex} : 380nm at 30 °C

Figure 3. Changes in UV spectra of a PCPVA-R1 film irradiated at 254nm.

Figure 4. Relationship between irradiation temperatures and quantum yields of disappearance of pendant α,β -unsaturated carbonyl groups in PCPVA-R1.

1240 cm^{-1} assigned to acetoxy groups in (6) was very weak, it is deduced that almost all of the acetoxy groups in (6) were removed and that a small amount of pendant α,β -unsaturated carbonyl groups remained in (6). Two kinds of PCPVA-Rs (No 1 and No 2) were prepared and contents of α,β -unsaturated carbonyl groups in them, which were determined from their UV spectra, were 3.36 and 0.09 mol%, respectively.

Figure 2 shows the emission spectra of ammonium N-phenyl-1-aminonaphthalene-8-sulfonate [ANS] solutions containing polymers. In Fig. 2, emission intensities increased in the following order: PVA < PCPVA-R2 < PCPVA-R1, which suggests that the introduction of α,β -unsaturated carbonyl groups in PVA increased the hydrophobic properties of polymers and that pendant α,β -unsaturated carbonyl groups aggregated with each other by hydrophobic interaction with increasing contents of α,β -unsaturated carbonyl groups.

Figure 3 shows UV spectral changes of a PCPVA-R1 film irradiated at 254nm. The absorbance around 237nm decreased with irradiation time. The plots of $1/\text{Abs.}$ against irradiation time gave a linear relationship, suggesting that the photoreaction proceeds in the second order of the concentration of pendant α,β -unsaturated carbonyl groups. In the IR spectrum, the absorbance at 1656 cm^{-1} (α,β -unsaturated carbonyl groups) decreased with UV irradiation, and the absorbance at 1714 cm^{-1} (saturated carbonyl groups) increased simultaneously. These results support that the pendant α,β -unsaturated carbonyl groups disappeared by their photodimerization upon UV irradiation.

In order to estimate the effect of temperature on photoreactivities of pendant α,β -unsaturated carbonyl groups, we measured quantum yields of disappearance of α,β -unsaturated carbonyl groups (Fig. 5). The quantum yields increased with irradiation temperatures. This result indicates that the segment motion of pendant α,β -unsaturated carbonyl groups in the polymer matrix also plays an important role in their photodimerization. The activation energy calculated from Fig. 5 was 15.5 kJ/mol. Further details are under investigation.

References

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