Promotion of Thermal Dehydration of Poly(vinyl alcohol) Film by Diphenyliodonium Salt

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Thermal dehydration of a poly(vinyl alcohol) (PVA) film was greatly promoted by diphenyliodonium trifluoromethane-sulfonate, which is known as a thermally stable photo acid generator. The oxidation of thermally generated PVA radicals by the salt is considered to lead to the dehydration. Liquid-nitrogen trapping of volatile products during the heating largely accelerated the dehydration for the salt-free film but not for the salt-containing film.

Previously we reported on the promotion effect of γ-ray ir-radiation on the conjugated double bond formation in the ther-mal degradation of poly(vinyl alcohol) (PVA), poly(vinyl chlo-ride), and polyacrylonitrile.[1–3] In the present study it was found that the thermal dehydration of PVA films is greatly promoted in the presence of diphenyliodonium trifluoromethanesulfonate ($Ph_2I^+Tf^-$). Diaryliodonium salts are known as photo acid gen-erators used in the fields of UV-curing coating and microelec-tronic photolithography as well as triarylsulfonium salts.[4] They are photosensitive but thermally stable at least below the melt-ing points. In the photolysis and radiolysis of diaryliodonium salts in 2-propanol solutions, a chain reaction has been reported to be initiated through the oxidation of 1-hydroxy-1-methyl-ethyl radicals by the salts.[5–8] On this basis the oxidation of the thermally generated PVA radicals by $Ph_2I^+Tf^-$ is consid-ered to contribute to the promotion of the dehydration of PVA.

PVA (Wako Chemicals; completely hydrolyzed; average degree of polymerization, 400–600) was dissolved in distilled water without further purification. Self-supported films were prepared from the aqueous solution of PVA (3 wt%) by the so-lution casting method. The weight of the 4 cm square film was 96 mg, corresponding to a thickness of 60 μm by taking the den-sity of the film as unity. The salt-containing film was prepared by dissolving $Ph_2I^+Tf^-$ (Midori Kagaku; mp, 178–179 °C; 5 wt% to PVA) in the aqueous solution. The salt was used be-cause of the solubility in water. The films were sealed under vacuum in a Pyrex glass tube having a branch. While the sample was heated in an electric furnace, the branch was cooled with liquid nitrogen to trap volatile products, largely consisting of water, unless otherwise noted. The salt-containing samples were carefully shielded from UV light during the sample preparation and the heating. Absorption spectra of the heated films were measured by using Shimadzu UV-3100PC scanning spectro-photometer.

Figure 1 shows the absorption spectra of the salt-free films heated at 150 °C. It has been well established that the thermal coloration of PVA films is due to the formation of the conju-gated double bonds consisting of polyene and polyenone units, -(CH=CH)$_n$- and -(CH=CH)$_n$-CO-, respectively.[9–11] It can be seen that the liquid-nitrogen trapping of the volatile products largely accelerates the dehydration as previously reported.[1,2]

Figure 2 shows the absorption spectra of the salt-containing

film heated for 2 h at 150 °C with and without the liquid-nitro-gen trapping of the volatile products together with that of the original film. The absorption of the original film below ca. 300 nm is due to the salt. It is shown that the dehydration is greatly promoted by the salt and that the effect of the liquid ni-trogen trapping of the volatile products is negligible in contrast to the case of the salt-free film.

The absorption of the salt-containing PVA film after the heat treatment is too large to follow the conjugate double bond formation quantitatively, and the samples were submitted to ele-
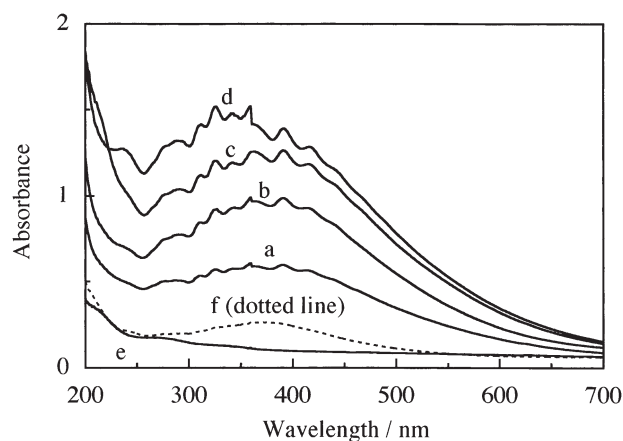

Figure 1. Absorption spectra of the salt-free PVA films heated for (a) 1, (b) 2, (c) 3, and (d) 4 h at 150 °C and (e) of the original PVA film: the dotted line (f) shows the ab-sorption spectrum of the sample heated for 4 h at 150 °C without the liquid-nitrogen trapping of the volatile products.
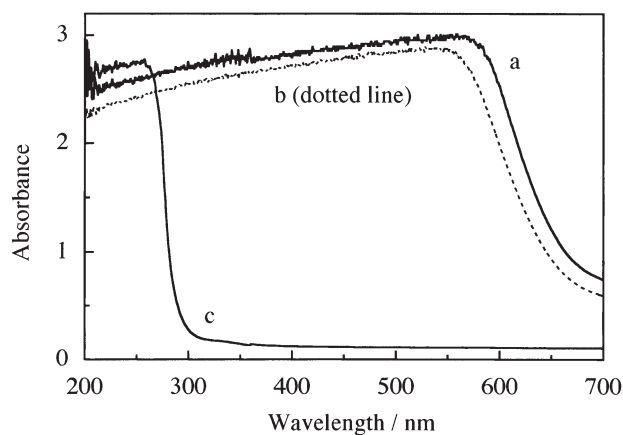

Figure 2. Absorption spectra of the salt-containing PVA films heated for 2 h at 150 °C (a) with and (b, dotted line) without liquid-nitrogen trapping of the volatile products, and (c) of the original film.

Table 1. Elemental analysis results for the salt-free and salt-containing PVA films heated for 2 h at 150, 160, and 170 °C

Temp.	Salt-free film			Salt-containing film		
	C/%	H/%	Conv/%[a]	C/%	H/%	Conv./%[a]
150 °C	53.97	9.03	≈0	59.85	8.45	12.7
160 °C	54.64	9.01	≈0	63.55	8.54	23.2
170 °C	54.06	9.00	≈0	68.50	8.33	36.2

[a]Dehydration yields calculated from the oxygen contents by assuming the zero oxygen content as the 100% yield.

mental analysis. The results of the elemental analysis of the salt-free and salt-containing films heated for 2 h are presented in Table 1. The dehydration yields presented in Table 1 were calculated from the oxygen contents, obtained from the carbon and hydrogen contents, by assuming the zero oxygen content as the 100% yield. These are the minimum yields of the conjugated double bond formation, because the formation of polyenone units was neglected. The carbon contents of the salt-containing films are apparently higher than those of the salt-free films, and increases with increasing temperature. It is also shown that the salt-containing films have low hydrogen contents compared with the salt-free films. The carbon and hydrogen contents of the salt-free films are close to the theoretical values of PVA, 54.53 and 9.15%, respectively. The elemental analysis results are evidence for the efficient promotion effect of the salt on the dehydration. The calculated dehydration yield for the salt-containing film reaches to 36.2% by the heat treatment for 2 h at 150 °C, indicating that the dehydration is a chain reaction as well as the decomposition of the salt. On the other hand, the yields for the salt-free film are close to zero, although the films are colored by the heat treatment. This can be attributed to the high extinction coefficient of the conjugated double bonds. The low yields of the conjugated double bond formation of the salt-free film may be responsible for the absence of the spectral shift to longer wavelengths with the heating time up to 4 h (Figure 1).

The following reactions are tentatively proposed for the dehydration in the presence and absence of the salts. The thermally generated PVA radicals, α-hydroxyalkyl radicals, are oxidized by the salt, similarly to the case of the photolysis and radiolysis of the salt in 2-propanol,[5–8] leading to the dehydration by cationic chain reactions as shown in Scheme 1. For the salt-free system, the effect of the liquid-nitrogen trapping of the volatile products suggests that the dehydration proceeds through the equilibrium reaction shown in Scheme 2.

In the previous study, we reported on the effect of the γ-ray irradiation on the thermal dehydration of PVA films.[1,2] The promotion of the γ-ray irradiation is very limited compared with that of $Ph_2I^+Tf^-$ in the present study. We proposed a reaction mechanism including the neutralization of the radiolytically produced cations with the electron for the thermal dehydration under the γ-ray irradiation.[2] The dehydration is due mainly to radical reactions because of the neutralization. On the other hand, the thermal dehydration in the presence of $Ph_2I^+Tf^-$ proceeds through the cationic chain reactions in the presence of
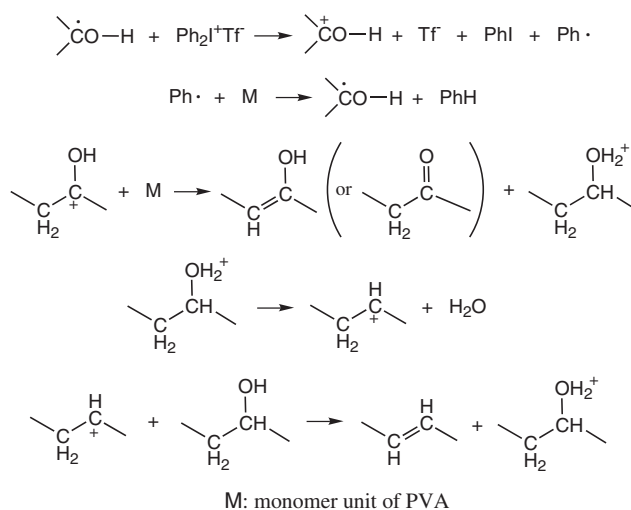
Scheme 1.
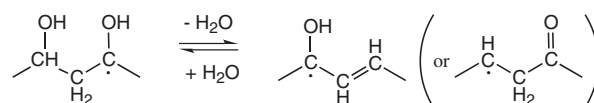
Scheme 2.

Tf^- as a counter anion.

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