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Thermal Dehydration of a Poly(vinyl alcohol) Film Promoted by Diphenyliodonium Trifluoromethanesulfonate: Absorption Spectra and Elemental Analysis Results

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The thermal dehydration of poly(vinyl alcohol) (PVA) films containing diphenyliodonium trifluoromethanesulfonate ($Ph_2I^+Tf^-$) was investigated in the temperature range of 150 to 190 °C by absorption spectroscopy and elemental analysis. The dehydration was greatly promoted in the presence of $Ph_2I^+Tf^-$, which is known to be a thermally stable photoacid generator. The oxidation of thermally generated PVA radicals, α-hydroxyalkyl type radicals, by $Ph_2I^+Tf^-$ is considered to lead to the dehydration by cationic reactions. The dehydration yield, calculated from the elemental analysis results, became highest at 170 °C. A lowering of the dehydration yields at the higher temperatures, 180 and 190 °C, has been attributed to an elimination of the volatile H^+Tf^- from the films, resulting in the disappearance of the cationic intermediates participating in the dehydration.

Diaryliodonium salts are known to be photoacid generators used in the fields of UV-curing coating and microelectronic photolithography as well as triarylsulfonium salts.[1] They are photosensitive, but thermally stable at least below the melting points. In the photolysis and radiolysis of diaryliodonium salts in 2-propanol solutions, a chain reaction is known to occur through the oxidation of 1-hydroxy-1-methylethyl radicals by the salts.[2–6] In the preceding communication we reported that the thermal dehydration of poly(vinyl alcohol) (PVA) films is greatly promoted in the presence of diphenyliodonium trifluoromethanesulfonate ($Ph_2I^+Tf^-$).[7] The result has been interpreted in terms of the oxidation of the thermally generated PVA radicals, α-hydroxyalkyl type radicals, by $Ph_2I^+Tf^-$, leading to the dehydration by cationic reactions. We have also reported on the promotion effect of PVA on the radiation-induced acid generation of $Ph_2I^+Tf^-$ in aqueous solutions, where the radiolytically produced PVA radicals are oxidized by the salt.[8] In this paper, the detailed results of absorption spectroscopy and elemental analysis of the PVA films heated in the temperature range of 150 to 190 °C are presented to reveal the promotion effect of the salt on the thermal dehydration.

It has been well established that the heat treatment of PVA films results in coloration arising from the formation of conjugated double bonds consisting of polyene and polyenone units, $-(CH{=}CH)_n-$ and $-(CH{=}CH)_n-CO-$, respectively.[9–11] For example, the conjugated double-bond units formed in the PVA films heated up to 175 °C under a nitrogen flow have been assigned to be $-(CH{=}CH)_n-$, $n = 2–14$ and $-(CH{=}CH)_n-CO-$, $n = 1–7$ by an analysis of the absorption spectra in the range of 200 to 700 nm.[10] In the present study, PVA films were heated under vacuum in a sealed ampule having a branch to trap volatile products, largely consisting of water, by cooling with liquid nitrogen. The effect of liquid-nitrogen cooling of the branch on the dehydration yield is described.

Experimental

PVA (Wako Chemicals; completely hydrolyzed; average degree of polymerization, 400–600) was used without further purification. Self-supported PVA films were prepared from an aqueous solution of PVA (3 wt %) by the solution casting method. The weight of 4 cm square film was 96 mg, corresponding to a thickness of 60 μm, by taking the density of the film as unity. The salt-containing PVA film was prepared by dissolving $Ph_2I^+Tf^-$ (Midori Kagaku; mp, 178–179 °C) in the aqueous solution. The concentration of $Ph_2I^+Tf^-$ was 5 wt % to PVA. The films were sealed under vacuum ($<10^{-5}$ Torr) in a Pyrex glass ampule having a branch. The sample was heated in an electric furnace with or without liquid-nitrogen cooling of the branch. The preparation and the heat treatment of the salt-containing samples were carried out under careful shielding from UV light. The absorption spectra of the heated films were measured by using a Shimadzu UV-3100PC scanning spectrophotometer.

Results and Discussion

Figure 1 shows the absorption spectra of the salt-free and salt-containing PVA films heated for 2 h at 150 °C with and without liquid-nitrogen cooling of the branch. The coloration caused by the dehydration, resulting in the formation of the conjugated double bonds, is greatly promoted in the presence of the salt. It is also shown that the dehydration is appreciably accelerated by liquid-nitrogen cooling of the branch for the salt-free PVA film, but scarcely for the salt-containing one. Virtually, the shapes of the absorption spectra of the salt-free PVA film are similar to those reported in the literature.[10]

Elongation of the heating time and a rise in the temperature were examined for the salt-free PVA film. Figure 2 shows the dependence of the absorbance at 370 nm on the heating time at 150 °C with and without liquid-nitrogen cooling of the

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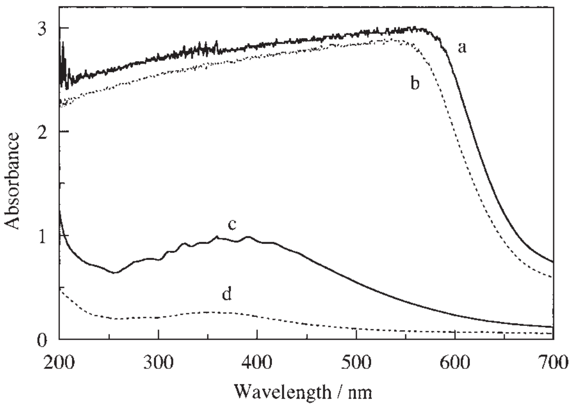


Fig. 1. Absorption spectra of the PVA films heated for 2 h at 150 °C: a (solid line), the salt-containing film heated with liquid-nitrogen cooling of the branch; b (dotted line), the salt-containing film heated without liquid-nitrogen cooling of the branch; c (solid line), the salt-free film heated with liquid-nitrogen cooling of the branch; and d (dotted line), the salt-free film heated without liquid-nitrogen cooling of the branch.

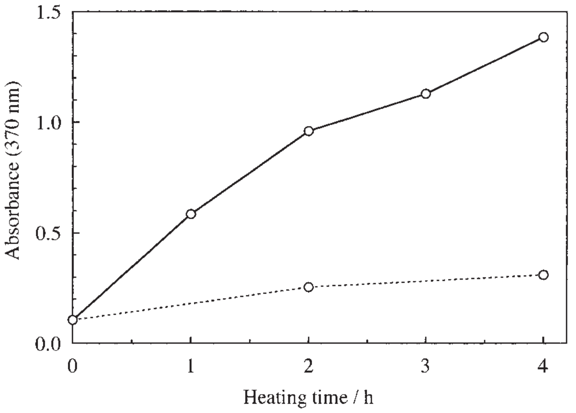


Fig. 2. Time dependence of the absorbance at 370 nm of the salt-free PVA films heated at 150 °C: the solid line, heated with liquid-nitrogen cooling of the branch; and the dotted line, heated without liquid-nitrogen cooling of the branch.

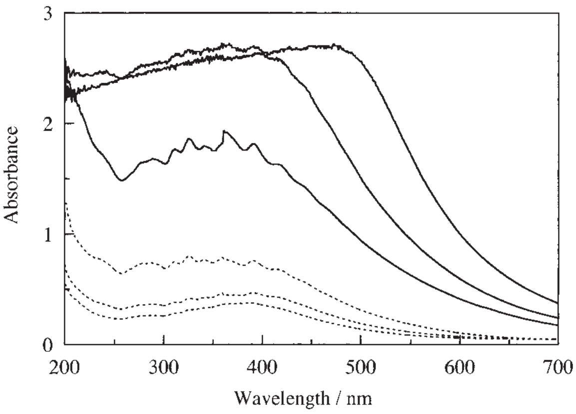


Fig. 3. Absorption spectra of the salt-free PVA films heated for 2 h: the solid lines, heated with liquid-nitrogen cooling of the branch; and the dotted lines, heated without liquid-nitrogen cooling of the branch. The heating temperatures are 160, 170, and 180 °C from the bottom to the top, respectively.

Table 1. Elemental Analysis Results for the Salt-Free and Salt-Containing PVA Films Heated for 2 h with Liquid-Nitrogen Cooling of the Branch

Temp./°C	Salt-free film			Salt-containing film		
	C/%	H/%	conv./%[a]	C/%	H/%	conv./%[a]
150	53.97	9.03	~0	59.85	8.45	12.7
160	54.64	9.01	~0	63.55	8.54	23.2
170	54.06	9.00	~0	68.50	8.33	36.2
180	55.64	9.27	3.4	67.48	8.54	34.0
190	58.38	9.15	10.6	66.53	8.39	30.9

a) Dehydration yields calculated from the oxygen contents by assuming zero oxygen content as the 100% yield; the oxygen contents were determined from the carbon and hydrogen contents.

branch. For both cases, the rate of the dehydration decreases with the heating time. Especially, without liquid-nitrogen cooling of the branch, the enhanced coloration, like that of the salt-containing PVA film (Fig. 1, curve b), does not seem to be attained by further elongation of the heating time. Figure 3 shows the absorption spectra of the salt-free PVA films heated for 2 h at 160, 170, and 180 °C. The appreciable acceleration of the dehydration by liquid-nitrogen cooling of the branch can be seen even at the high temperatures. The absorbance below 500 nm goes up to the range of 2 to 3 when heated at 180 °C with liquid-nitrogen cooling of the branch, similarly to the case of the salt-containing PVA film heated at 150 °C (Fig. 1, curve a). However, when heated without liquid-nitrogen cooling of the branch, the absorbance of the salt-free PVA films is much lower than that of the salt-containing one heated at 150 °C (Fig. 1, curve b). These results suggest that the dehydration mechanism differs between the salt-free and salt-containing PVA films. The appreciable acceleration of the dehydration by liquid-nitrogen cooling of the branch suggests that the thermal dehydration of the salt-free PVA film proceeds through an equilibrium process.

The absorbance of these samples is too large to follow the dehydration quantitatively, and the samples were submitted to elemental analysis. The results of the elemental analysis for the salt-free and salt-containing PVA films heated for 2 h at different heating temperatures are presented in Table 1. The heat treatment of these samples was carried out with liquid-nitrogen cooling of the branch. The carbon content is a measure of the extent of the dehydration of PVA. The carbon contents of the salt-containing PVA films are higher than those of the salt-free ones, demonstrating the promotion effect of the salt on the thermal dehydration. The carbon content of the salt-containing PVA film becomes highest at 170 °C, and then decreases at the higher temperatures, 180 and 190 °C. On the other hand, the carbon content of the salt-free PVA film is close to the theoretical value of PVA, 54.53%, at 170 °C and below, and increases at the higher temperatures, 180 and 190 °C, in contrast to the case of the salt-containing PVA film. The temperature dependence of the carbon contents again demonstrates that the dehydration mechanisms of the salt-free and salt-containing PVA films differ from one another. The hydrogen contents of the salt-containing PVA films are lower than those of the salt-free ones. This is also an evidence for the efficient promotion effect of the salt on the dehydration. The hydrogen contents of the salt-free PVA films are the same level as the theoretical PVA value, 9.15%, in the whole range of the temperature. The temperature dependence of the hydrogen content is not clear, in contrast to the carbon content, for both the salt-containing and salt-free PVA films. This is probably due to the small change in magnitude caused by the change in temperature.

The dehydration yields were calculated from the oxygen contents, determined from the carbon and hydrogen contents, by assuming the zero oxygen content as the 100% dehydration yield; the data are presented in Table 1. These are the minimum yields, because the formation of the polyenone units is neglected. The dehydration yield of the salt-free PVA film was calculated to be zero at 170 °C and below, although the absorption spectra of the samples (Figs. 1 and 3) show that conjugated double bonds are formed to some extent. Such a difference of the results between the absorption spectra and the elemental analysis can be attributed to the high extinction coefficients of the conjugated double bonds as well as to an error of the elemental analysis, ±3%.

As is shown in Table 1, the dehydration yield of the salt-containing PVA film becomes highest at 170 °C, and then decreases at the higher temperatures, 180 and 190 °C. In order to reveal the temperature dependence of the dehydration yield, the absorption spectra of the samples heated for 2 h at 170 and 180 °C with and without liquid-nitrogen cooling of the branch are compared in Fig. 4. The wavelength range of the absorption spectra is above 500 nm, since the absorbance below 500 nm is quite high with little difference among the samples. In accordance with the results of the elemental analysis, the absorbance of the samples heated at 180 °C is smaller than that of the samples heated at 170 °C. Furthermore, it can be seen that the absorbance of the sample heated at 180 °C is decreased by liquid-nitrogen cooling of the branch, in contrast to the case of the sample heated at 170 °C. These results are interpreted in terms of the disappearance of the dehydration-promoting species in the sample heated at the higher temperature, 180 °C. It is reasonable to consider that the disappearance of the dehydration promoting species is caused by removal of the volatile H^+Tf^-, which is enhanced by liquid-nitrogen cooling of the branch.

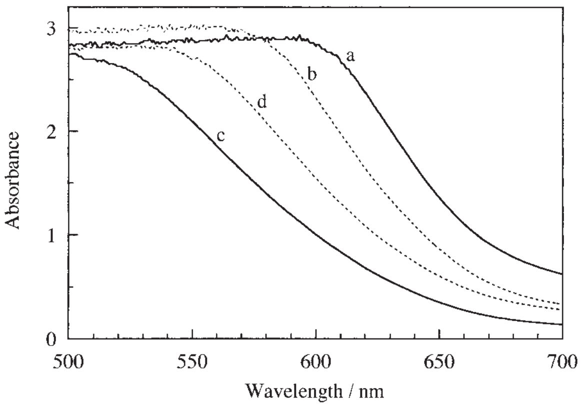


Fig. 4. Absorption spectra of the salt-containing PVA film heated for 2 h: a (solid line), heated at 170 °C with liquid-nitrogen cooling of the branch; b (dotted line), heated at 170 °C without liquid-nitrogen cooling of the branch; c (solid line), heated at 180 °C with liquid-nitrogen cooling of the branch; and d (dotted line), heated at 180 °C without liquid-nitrogen cooling of the branch.

The elemental analysis was also carried out for the salt-containing PVA film heated without liquid-nitrogen cooling of the branch. The carbon and hydrogen contents of the sample heated for 2 h at 150 °C were 55.49 and 8.63%, respectively. They are rather close to the theoretical PVA values; the calculated value of the dehydration yield is 0.7%. On the other hand, the absorption spectra (Fig. 1) indicate that the extents of the dehydration of the salt-containing PVA films heated with and without liquid-nitrogen cooling of the branch are comparable. The results mean that the low carbon content of the salt-containing PVA film heated without liquid-nitrogen cooling of the branch is due to the remains of the produced water in the sample, but not to the low dehydration yield. That is to say, it can be said that the produced water remains in the sample when heated without liquid-nitrogen cooling of the branch, and that the dehydration of the salt-containing PVA film is hardly suppressed by the produced water remaining in the sample. This result is in contrast to the case of the salt-free PVA film, where the dehydration is extremely suppressed when the sample is heated without cooling of the branch. These elemental analysis and absorption spectral results support the difference in the dehydration mechanism between the salt-containing and salt-free PVA films, as described above. It is shown that the elemental analysis results are valid as a measure of the dehydration only for the samples heated with liquid-nitrogen cooling of the branch.

Among the heating conditions examined in the present study, the highest dehydration yield was attained for the salt-containing PVA film heated at 170 °C with liquid-nitrogen cooling of the branch. Figure 5 shows the heating-time dependence of the dehydration yield, calculated from the elemental analysis results, under the above heat treatment conditions. The dehydration yield attained by the 6-h heating is 54.9%; the mole number of the eliminated water is 111-times larger than that of the added salt, indicating the occurrence of efficient chain reactions. A saturation of the dehydration yield observed at around 6 h may be attributed to a decrease in the content of unreacted PVA

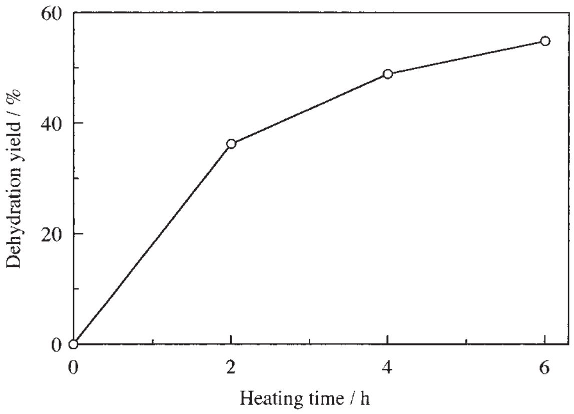
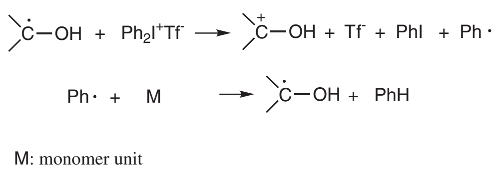
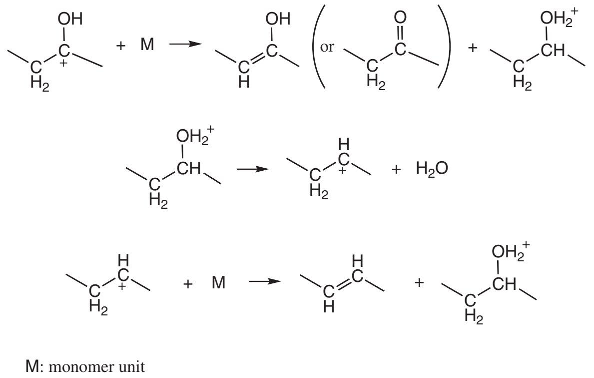


Fig. 5. Time-dependence of the dehydration yield, calculated from the elemental analysis results, for salt-containing PVA film heated at 170 °C with liquid-nitrogen cooling of the branch.



Scheme 1.

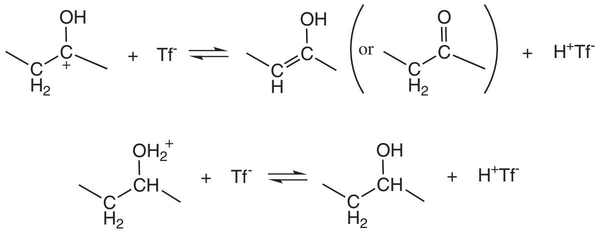


Scheme 2.

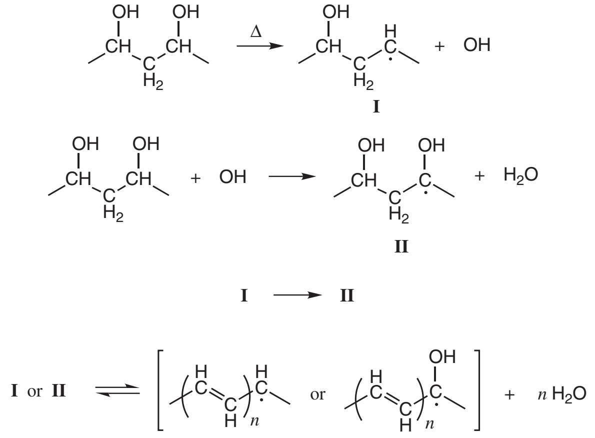
monomer units as a proton acceptor, as shown below.

The following reaction mechanism can be proposed for the dehydration in the presence of the salts. Since the salt is thermally stable, the thermally generated PVA radicals, α-hydroxyalkyl radicals, are considered to initiate the dehydration by the reaction with the salt. As shown in Scheme 1, the α-hydroxyalkyl type radicals are oxidized by the salt to initiate the chain reaction, similar to the case of the photolysis and radiolysis of the salt in 2-propanol solutions.[2–6] The dehydration is considered to proceed through the cationic chain reaction shown in Scheme 2, where the PVA monomer units act as a proton acceptor. The produced water remaining in the sample hardly suppresses the dehydration by the cationic reaction. When heated at the high temperatures, 180 and 190 °C, the release of H^+Tf^- from the cationic intermediates disturbs the cationic chain reaction, as shown in Scheme 3. The elimination of H^+Tf^- from the sample is enhanced by liquid-nitrogen cooling of the branch at the high temperatures, resulting in a decrease in the dehydration yield.

For the salt-free PVA film, liquid-nitrogen cooling of the branch appreciably accelerates the dehydration by removal of the produced water, even at the high temperatures, in contrast to the case of the salt-containing PVA film. This means that the thermal dehydration of the salt-free PVA film proceeds through an equilibrium reaction. It has been reported that the thermal decomposition of PVA occurs in two stages.[12–14] The first stage, occurring at lower temperatures of around 200 °C and below, is mainly dehydration, whereas the evolution of aromatic compounds dominates in the higher temperature second stage above 300 °C.[12,13] The dehydration in the first stage is a chain reaction, so-called unzipping, initiated by the scission of the C–OH bond. We consider that the α-hydroxyalkyl type radicals, oxidized by $Ph_2I^+Tf^-$ in the case of the salt-containing PVA film, are produced through tertiary hydrogen abstraction reactions of the initially produced radicals, OH and the γ-hydroxyalkyl type radicals. Both of the α- and γ-hydroxyalkyl type radicals may initiate the dehydration reaction. The shape of the absorption spectra of the salt-free PVA film was hardly affected by the heat treatment time and temperature (Figs. 1 and 3 and Ref. 7); only the absorption intensity increased along with an increase in the heating time and temperature. This means that the dehydration is a chain reaction with the kinetic chain lengths of the propagation step corresponding to the formation of $-(CH{=}CH)_n-$, $n = 2$–14 and $-(CH{=}CH)_n-CO-$, $n = 1$–7.[10] Thus, the formation of the polyenes by the dehydration can be represented by Scheme 4. It has been reported that the polyenones are formed through the C–C bond scission.[12] The shape of the absorption spectra of the salt-free PVA film was not affected by liquid-nitrogen cooling of the branch (Figs. 1 and 3). It is reasonable to consider that the rate of removal of the produced water promoted by liquid-nitrogen cooling of the branch is too slow to affect the kinetic chain lengths of the propagation step of the dehydration. The chain-transfer step of the dehydration may be an intramolecular or intermolecular transfer of the tertiary H atoms from the PVA monomer units to the radicals (**I** and **II** in Scheme 4).



Scheme 3.



Scheme 4.

In the previous study, we reported on the promotion effect of γ-ray irradiation on the thermal dehydration of PVA films.[15,16] The promotion effect of γ-ray irradiation was very limited compared with that of $Ph_2I^+Tf^-$ in the present study. We proposed a reaction mechanism including neutralization of the radiolytically produced cations with the electron for the thermal dehydration under γ-ray irradiation.[15] The dehydration is due mainly to the radical reactions because of 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 Tf^- as a counter anion.

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