Enhanced Degradation of Cellulose Acetate Films in the Copresence of Triphenylsulfonium Salt and Benzophenone

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ABSTRACT: To investigate whether benzophenone (BP) enhances triphenylsulfonium salt (TPS) degradation of cellulose acetate (CA) during photoirradiation, CA (degree of substitution = 2.45) films containing TPS and BP were prepared, and their degradative behavior was examined under simulated solar exposure. The irradiation-evoked generation of acetic acid from the films was greater in the copresence of TPS and BP than in the sole presence of TPS. This result indicates that the TPS was activated by BP to produce Brønsted acid, which induced the deacetylation of CA effectively. As a possible mechanism for this activation of TPS, we postulated that the TPS oxidized free-radical species induced by the photoreaction of BP, which was followed by the generation of Brønsted acid. The activation of TPS by BP did not appear to significantly accelerate the main-chain cleavage of CA because size exclusion chromatography data did not reveal any decrease in the molecular weight of CA. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3157–3164, 2008

Key words: biodegradable; degradation; polysaccharides

INTRODUCTION

Cellulose acetate (CA; Fig. 1) is a biodegradable polymer. The biodegradability of CA has been shown by several research groups to be inversely correlated with the degree of substitution. Low degrees of substitution are associated with higher biodegradabilities.[1–6]

Acid catalysts, such as hydrochloric acid, orthophosphoric acid, and sulfuric acid, lead to the deacetylation of CA by hydrolysis.[7–10] Yamashita and Endo[8] investigated the biodegradability of CA films containing phosphoric acid as an acid catalyst and demonstrated that the addition of the acid was effective in accelerating the biodegradation of CA in soil.

In our previous study,[11] the degradative behavior of CA films containing a triphenylsulfonium salt (TPS), which is a typical photoacid generator, was investigated under simulated solar exposure. Generation of acetic acid from the CA films and decrease in molecular weight of CA were observed after photoirradiation. We also found that increased concentrations of the photoacid generator led to higher degradation of the CA films. These results suggest that the photoinduced acid acted as a catalyst, which resulted in the main-chain cleavage and deacetylation of CA by hydrolysis. If the deacetylation of CA proceeds by solar irradiation, biodegradability in an ambient environment may be improved.

Aromatic hydrocarbons and ketones, such as anthracene, perylene, and benzophenone (BP), are suggested to induce acid generation from onium salts (e.g., TPS's and diphenyliodonium salts) by an indirect activation process.[12–15] If this indirect activation system works in CA films, it may accelerate the degradation of the films containing onium salts during photoirradiation. In this study, we examined whether BP, which is miscible with CA and an effective additive for the photodegradation of CA itself,[16] enhanced the degradation of CA films containing a TPS under simulated solar exposure.

EXPERIMENTAL

Materials

CA (degree of substitution = 2.45), triphenylsulfonium trifluoromethanesulfonate (also known as TPS; Fig. 2), and BP (Fig. 2) were purchased from Acros Organics (Geel, Belgium), Wako Pure Chemical Industries (Osaka, Japan), and Sigma-Aldrich (St. Louis, MO), respectively. These materials were used without further purification.
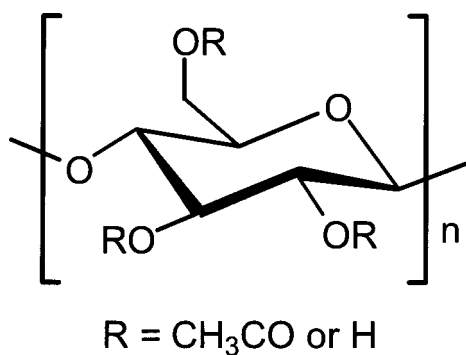
Figure 1 Molecular structure of CA.

Preparation of the CA films

CA films containing 10, 20, and 40 mg/g TPS and/or 5, 10, 20, 40 mg/g BP were prepared as follows by casting. An acetone solution (1 mL) containing 5% CA (w/v) and TPS and/or BP was spread on a glass Petri dish (inner diameter = 32.6 mm), and the acetone was evaporated under an ambient atmosphere. Then, the films were dried *in vacuo*, punched into circles (diameter = 25 mm), and stored at 22°C and 60% relative humidity for at least 1 week. The thickness of the films was measured with a micrometer, and films 40 ± 5 μm thick were selected for further investigation.

Photoirradiation

The CA films were placed in glass vials (20 mL, 23 × 75 mm), and the vials were sealed with aluminum caps attached by a polytetrafluoroethylene/silicon septum. The vials were then exposed to light from a 1.5-kW xenon arc lamp in a fadometer (TS-2, Suga Test Instruments, Tokyo). In accordance with the instructions in the fadometer users' manual, a cutoff value of 275 nm was used to generate a solar light spectrum. The intensity of illumination at the sample vials was 107 W/m^2 (integrated from 300 to 700 nm). During the irradiation, the temperature in the instrument was kept at 35°C by air cooling.

Measurements

The ultraviolet–visible (UV–vis) spectra of the CA films were collected with a UV–vis spectrophotometer (UV-1700, Shimadzu, Kyoto, Japan).

The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the degraded CA were estimated by size exclusion chromatography (SEC) by means of an HLC-8220GPC system (TOSOH, Tokyo) equipped with a differential refractive-index detector and four consecutive TSK$_{gel}$ columns (α-M, α-4000, α-3000, and α-2500) produced by TOSOH. The system was operated at 40°C and at

a flow rate of 1.0 mL/min with *N,N*-dimethylformamide containing 0.01*M* lithium bromide as an eluent. Polystyrene standards were used for calibration.

Acetic acid generated from the CA films was extracted by the shaking of the vial for 30 min with 3 mL of an ethanol solution containing anethole as an internal standard. The extract was analyzed by means of a gas chromatograph (Agilent 6890 series, Agilent Technologies, Nagoya, DE) equipped with a flame ionization detector. Helium gas was used as a mobile phase, and a DB-WAX column (inner diameter = 0.53 mm, film thickness = 1.0 μm, length = 15.0 m; Agilent Technologies) was used as a solid immobile phase. The temperatures of the injector and the detector were set at 250°C. The oven temperature program had an initial temperature of 160°C for 0 min and was programmed to reach 220°C at a rate of 20°C/min; it was then held for 2 min. The injection volume was 1 μL, and the split ratio at the injector was 1:10. The ratio of the decreased acetyl group was calculated from the initial film weight, the initial degree of substitution of CA (2.45), and the generated acetic acid evaluated by this method.

RESULTS AND DISCUSSION

UV absorption of the CA films

To investigate the effect of the copresence of TPS and BP on CA degradation, CA films containing different amounts of these compounds were prepared. Figure 3 depicts the UV–vis absorption spectra of the CA films containing TPS and BP. The CA film containing 20 mg/g TPS showed a lower transmittance than the film without any additives under 290 nm, and 0% transmittance was reached at about 250 nm. In the case of the film with 20 mg/g BP, a peak of the absorbance was observed at 337 nm, and 0% transmittance was reached at about 280 nm. The transmittance of the film containing both TPS and BP was similar to the film with BP. No significant peak shift of the absorbance at 337 nm was detected by the addition of TPS into the CA film containing BP.
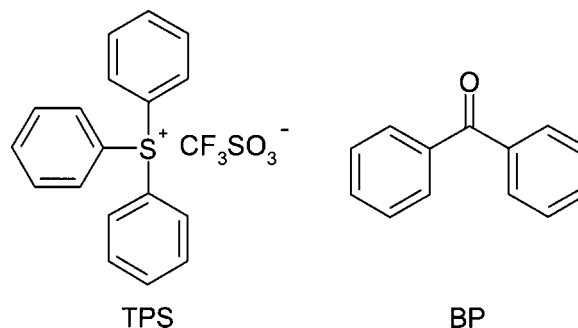

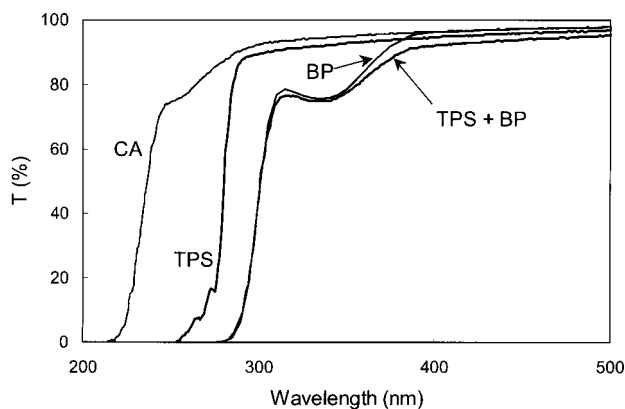**Figure 2** Molecular structures of TPS and BP.

Figure 3 UV–vis spectra of CA films containing TPS and BP. The concentrations of additives were as follows: [TPS] = 20 mg/g, [BP] = 20 mg/g, and TPS + BP: [TPS] = 20 mg/g and [BP] = 20 mg/g.

Generation of acetic acid from CA

In a previous article, we reported that acetic acid was liberated from CA films containing TPS by photoirradiation, and the photoacid generated from TPS by the irradiation acted as a catalyst, which led to the deacetylation of CA by hydrolysis.[11] In this study, the acetic acid liberated from the CA films by irradiation was determined by gas chromatography. The ratio of the liberated acetyl group was calculated from the initial film weight, the initial degree of substitution of CA (2.45), and the generated acetic acid. Figure 4 shows the ratio of the acetic acid liberated from the CA films containing 20 mg/g TPS and different amounts of BP against the irradiation time. In the case of the film with 20 mg/g TPS (without BP), the acetic acid accumulated during photoirradiation and the decreased acetyl groups reached 14.8% after 14 days of irradiation. The acetic acid generation increased with increasing concentration of BP. The film containing 20 mg/g TPS and 40 mg/g BP produced over three times the level of acetic acid than the film with 20 mg/g TPS (without BP) after 4 days. Acetic acid was also released from the films in the presence of BP alone, and the generated acetic acid increased with increasing BP concentration, as reported previously.[16] However, no acetic acid was detected from the film with 5 mg/g BP, and the decreased acetyl groups from the films with 20 and 40 mg/g BP were only 1.1 and 1.6%, respectively, even after 14 days. The liberation of acetic acid due to the existence of BP could not account for the increase in the acetic acid generation in the copresence of BP and TPS mentioned previously. Therefore, these results suggest that BP enhanced the photoacid generation from TPS in CA films, and then, the photoacid acted as a catalyst for hydrolysis, which led to the accelerated deacetylation of CA.

Figure 5 shows the effect of 10 mg/g BP on the deacetylation of CA films with different amount of TPS. Over the range of concentrations investigated (10–40 mg/g TPS), an enhanced acetic acid generation was observed with increasing TPS. The enhancement due to the existence of BP, however, declined with increasing concentration of TPS. Although the enhancement by 10 mg/g BP was approximately seven times after 7 days of irradiation of the film with 10 mg/g TPS [Fig. 5(A)], only 1.9 and 1.4 times enhancements were observed in the films with 20 and 40 mg/g TPS, respectively [Fig. 5(B,C)]. From these results, the suitable weight ratio of TPS and BP in the feed appeared to be one of the critical factors in determining the enhancement of CA deacetylation.

Main-chain cleavage of CA

The photoirradiation-evoked decrease in the molecular weight of the CA films containing TPS were observed. We postulated that the photoacid led to the main-chain scission of CA by hydrolysis.[11] The molecular weights of the CA films during the photoirradiation were estimated by SEC with polystyrene standards. Figure 6(A) shows the change in M_n of the films containing 20 mg/g TPS and different amounts of BP during irradiation. M_n of the film with 20 mg/g TPS decreased from about 50,000 to 18,500 after 14 days of irradiation, whereas no significant change was observed in the film without any additives. M_n further decreased with increasing concentrations of BP. After 14 days, the M_n values of the films were about 9300, 4700, 3300, and 2500 for the films with 20 mg/g TPS and 5, 10, 20, and 40 mg/g BP, respectively. However, M_n also decreased significantly in the presence of BP alone, as shown
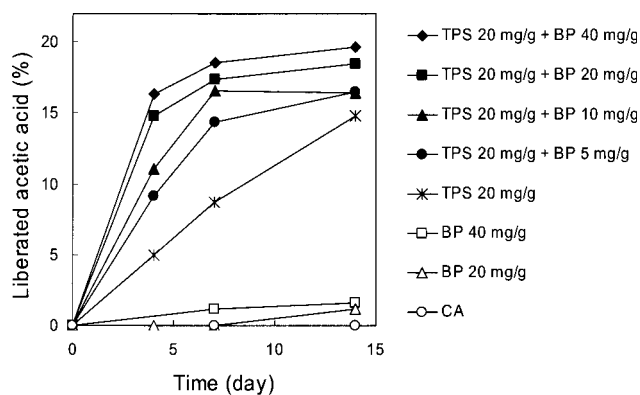

Figure 4 Accumulation of acetic acid liberated from CA films containing 20 mg/g TPS and different amounts of BP during photoirradiation. Acetic acid was quantified by gas chromatography, and the acetic acid liberation (%) was calculated from the generated acetic acid, the initial film weight, and the initial degree of substitution of CA (2.45).
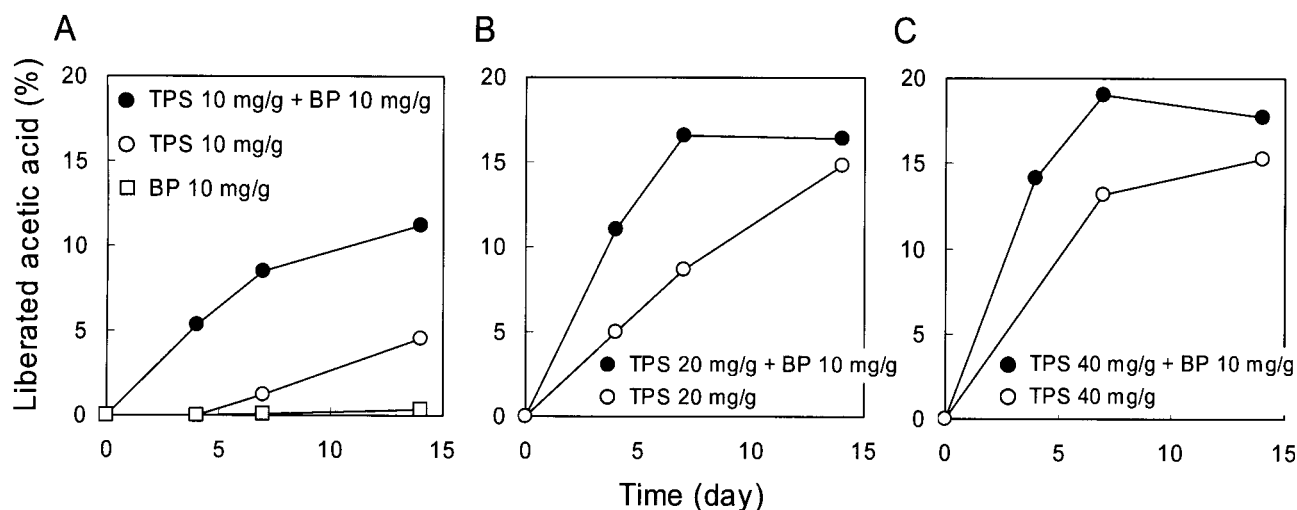
Figure 5 Accumulation of acetic acid liberated from CA films containing different amount of TPS with and without 10 mg/g BP during photoirradiation. The concentrations of TPS were as follows: (A) 10, (B) 20, and (C) 40 mg/g. Acetic acid was quantified by gas chromatography, and the acetic acid liberation (%) was calculated from the measured acetic acid, the initial film weight, and the initial degree of substitution of CA (2.45).

in Figure 6(B). The M_n values of the films after 14 days were about 27,000, 24,200, 15,900, and 6400 for the films with 5, 10, 20, and 40 mg/g BP, respectively, which may have accounted for the remarkable

Figure 6 Change in the molecular weight of CA films containing (A) TPS and BP and (B) BP during photoirradiation. M_n was determined by SEC on the basis of polystyrene standards (eluent: N, N-dimethylformamide containing 0.01M lithium bromide).

decrease in the M_n values of the films with both TPS and BP.

To further investigate the degradation mechanism of the specimens, the SEC traces of the CA films were compared (Fig. 7). In the case of the films with BP (without TPS), the peak of the SEC signal shifted to a lower molecular weight range with broader molecular weight distributions with increasing irradiation time, whereas little change in the peak onset time was observed, even for 14 days of irradiation [Fig. 7(A)]. If the degradation proceeded homogeneously, this observation may have suggested that the main-chain scission occurred at random positions of CA molecules in the presence of BP. Note that the cleavage at specific positions in the molecules, especially at the end position, may have led to relatively constant molecular weight distributions of the polymer during the degradation. In contrast to the films with BP, a progressive decrease in the molecular weight, with relatively unimodal SEC traces, were observed in the films with TPS (without BP) [Fig. 7(B)]. This result suggests that cleavage of the CA molecules at the end positions, so-called zipper-type degradation, was dominant. As described in Figure 7(C), the SEC traces of the film containing both TPS and BP appeared to share characteristics of the two different types shown in Figure 7(A,B). Notably, there were some delays in the peak onset time, and the peaks became broader after irradiation. Therefore, the random scission by BP and the zipper-type degradation induced by TPS appeared to occur simultaneously in the films containing both additives.
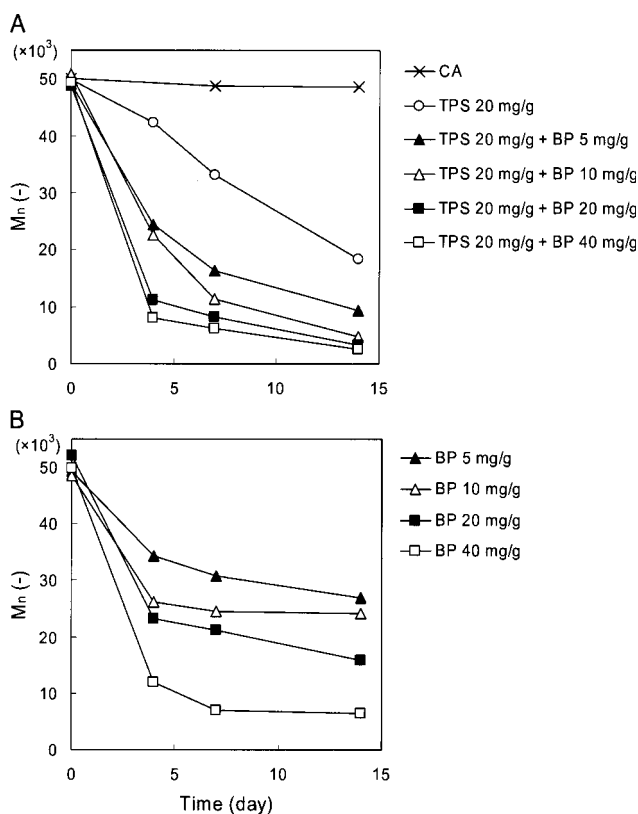
Figure 8 shows the relationship between M_n and the molecular weight distribution (M_w/M_n) of the specimens during photoirradiation. The M_w/M_n values of the films with BP increased significantly from

about 2.3 to 7.0 with decreasing M_n by irradiation. In contrast, the M_w/M_n values of the films with TPS increased only slightly to about 3.1, despite the M_n of both kinds of film reaching the same level (ca. 7000). The relationships between the M_n and M_w/M_n values of the films containing both BP and TPS was the middle of that seen in the films containing either BP or TPS alone. This observation may support the hypothesis that both of the mechanisms for main-chain scission by BP and by TPS proceeded simultaneously in the copresence of these compounds.

Mechanistic consideration of the degradation of CA

The photoirradiation of TPS's leads to the generation of Brønsted acid via the heterolytical or homolytical rupture of Ph—S bonds.[12,17] The acid could then act as a catalyst for hydrolysis and lead to the degradation of CA, as shown in Scheme 1.

The presence of BP in the films also led to decreases in the molecular weight of CA after light exposure (Fig. 6). Merlin and Fouassier[18,19] reported the generation of free radicals by the UV irradiation of cellulosic materials, including CA with BP. They assumed that both glycosidic scission and hydrogen abstraction occurred. A BP molecule is generally considered to be raised to the triplet state, via an excited singlet state, by light absorption. The molecule then abstracts hydrogen from a substrate, which leads to the oxidative degradation of the sub-
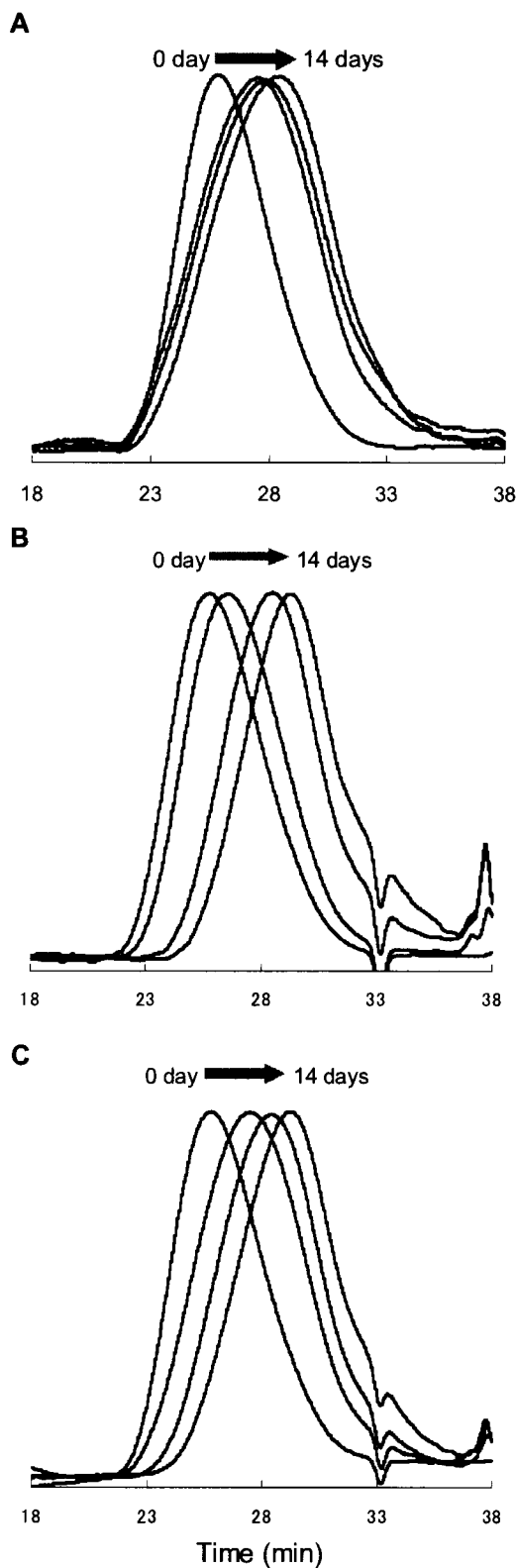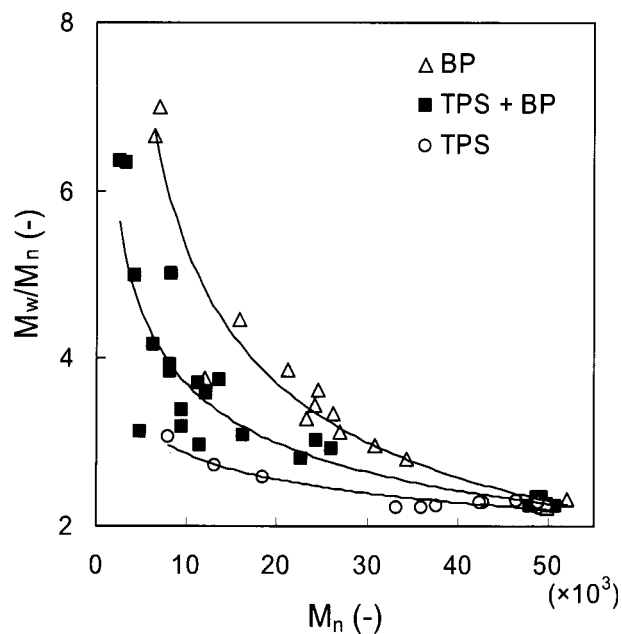

Figure 7 Examples of SEC traces of CA films with TPS and BP during photoirradiation: (A) [BP] = 20 mg/g, (B) [TPS] = 40 mg/g, and (C) [TPS] = 20 mg/g and [BP] = 10 mg/g.
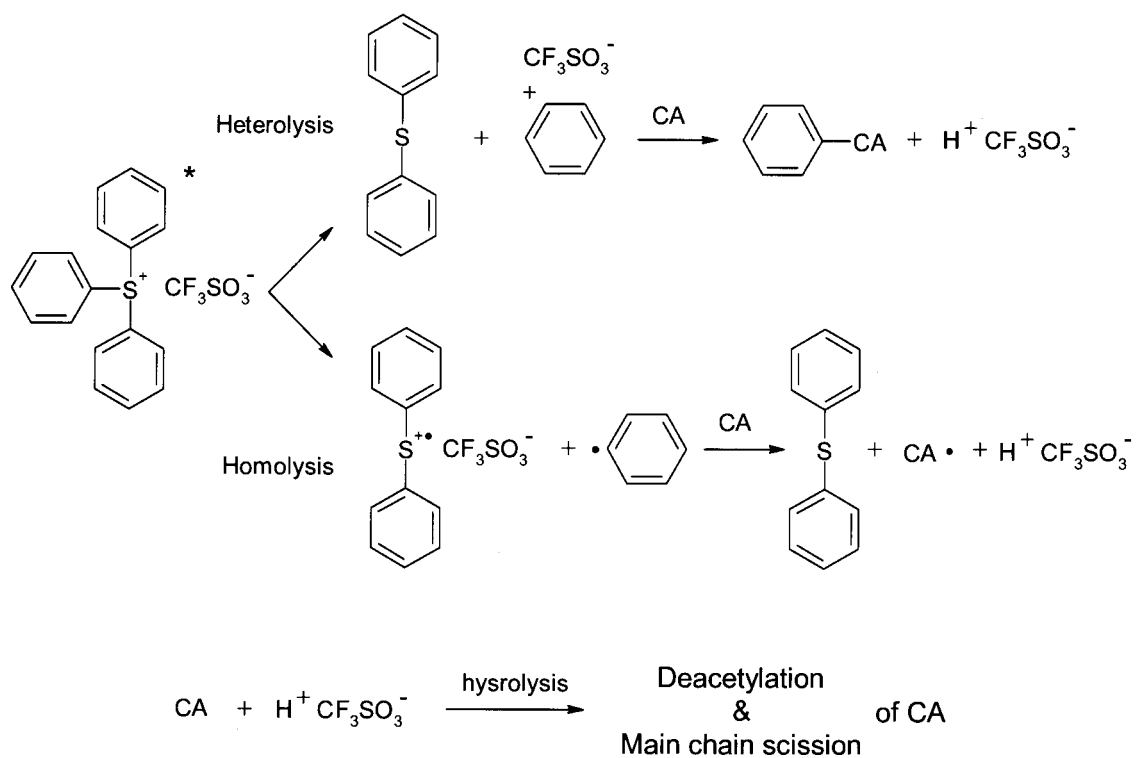

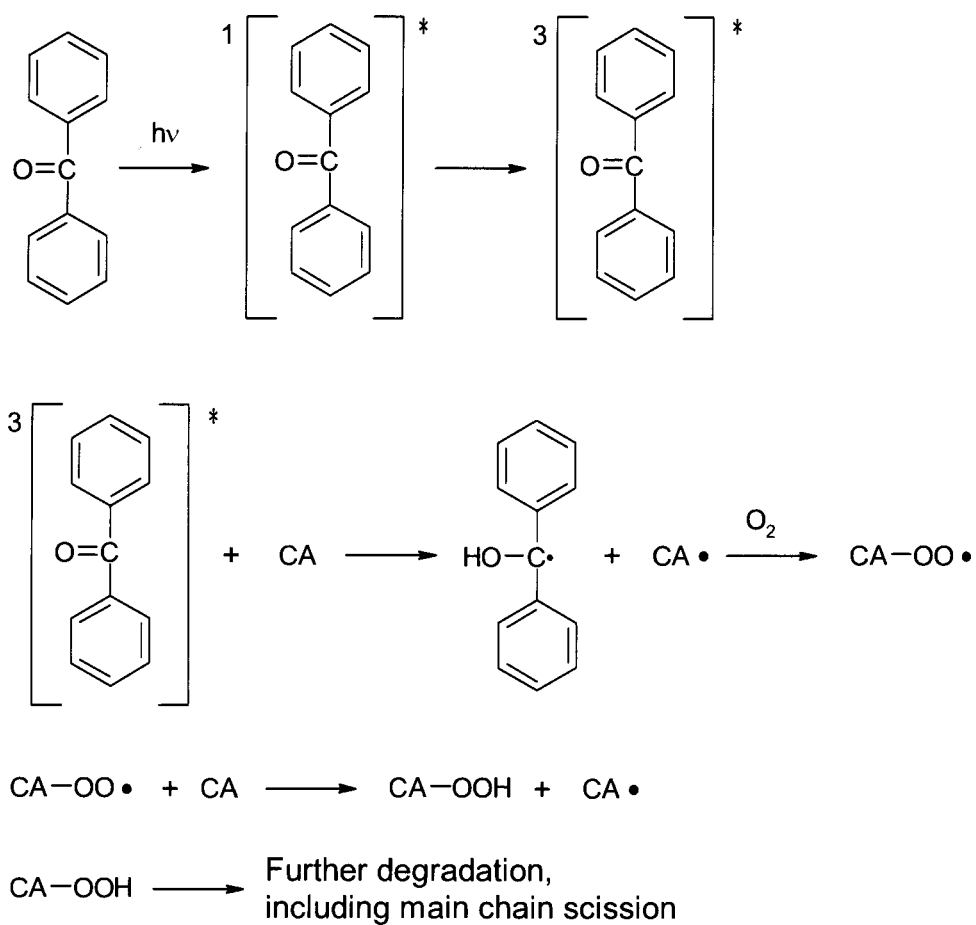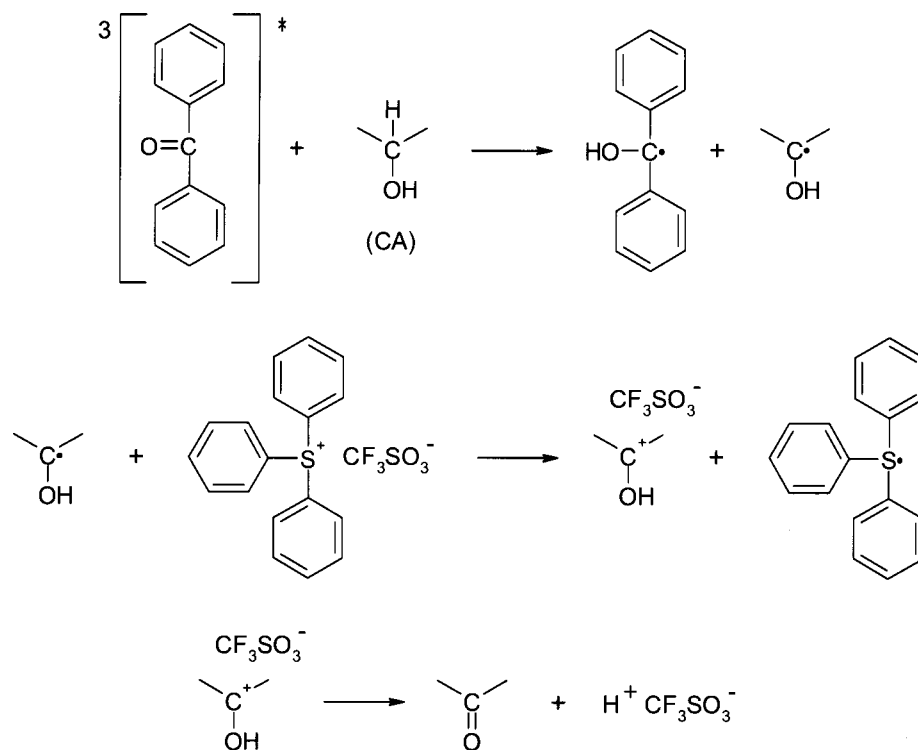**Figure 8** Molecular weight distributions along with the changes in M_n. M_n and M_w were determined by SEC on the basis of polystyrene standards (eluent: N,N-dimethylformamide containing 0.01M lithium bromide).

CA + H⁺CF₃SO₃⁻ →(hysrolysis)→ Deacetylation & Main chain scission of CA

Scheme 1

CA—OO• + CA ⟶ CA—OOH + CA•

CA—OOH ⟶ Further degradation, including main chain scission

Scheme 2

Scheme 3

strate.[19–24] With this in mind, in a previous article, we proposed a potential mechanism for the degradation of CA with BP, as shown in Scheme 2.[16]

The increased deacetylation of CA with TPS in the presence of BP (Figs. 4 and 5) indicated that Brønsted acid generation was more effective in the TPS/BP/CA combination than in TPS/CA alone. Although BP is an effective photosensitizer for some photoacid generators, including diphenyliodonium salts, it cannot sensitize TPS.[12,13,25,26] The photosensitization of a photoacid generator requires either a higher excited energy of sensitizers than that of the photoacid generator or a negative free energy change in the sensitizing process. However, neither of these conditions is likely between BP and TPS.[12,13,26] Therefore, the enhancement of the acid generation observed here could not be explained by the photosensitization process. A possible explanation is the oxidation of free radicals by TPS. In the field of cationic polymerization, many studies have suggested that the onium-salt-induced oxidation of free radicals can lead to the formation of cationic species.[12,13,25–30] In a representative study on a diphenyliodonium salt/BP/2-propanol system by Pappas and coworkers,[13,26] it was proposed that free radicals were induced via hydrogen abstraction from 2-propanol by BP and that these radicals were oxidized by the iodonium salt to produce protons. One of the possible pathways of Brønsted acid generation in the TPS/BP/CA system is shown in Scheme 3: (1)

excited BP abstracts hydrogen from an anhydroglucose unit of CA to induce radicals, (2) one of the radical species derived from CA is oxidized by TPS to produce a cation, and (3) then, a proton is released from the cation, and the proton acts as a catalyst for hydrolysis, which leads to the degradation of CA. Because various radical species seem to be induced by the chain oxidative degradation of CA, as described in Scheme 2, protons may be produced from other radicals than those exemplified in Scheme 3.

The oxidation of the free radicals derived from BP by TPS did not seem to occur because BP did not activate TPS by itself.[13,26] This may have been because the free energy change in the oxidation of BP radical by TPS was not negative. Identification of the radical species that were involved in the reaction discussed in this article is difficult because it is hard to measure the oxidation potentials of the species.[12] In other words, it is impossible to calculate the free energy change on the process of radical oxidation by TPS, even if the induced species could be detected.

Because the photoacid could catalyze the main-chain cleavage of CA,[11] the effective generation of the Brønsted acid was expected to enhance the decrease in molecular weight. However, the enhancement seemed to make a minor contribution, if any, when we consider the effectiveness of BP, as described in Figure 6. Different characteristics of the change in the molecular weight distribution ($M_w/$

M_n) were observed in the films with BP and those with TPS (Figs. 7 and 8); BP led to a significant increase in M_w/M_n, whereas TPS did not. In the case of the films with both compounds, the pattern of the change in M_w/M_n had characteristics of both BP and of TPS. Therefore, both mechanisms for the main-chain scission of oxidative radical reactions by BP and hydrolysis by Brønsted acid appeared to be reasonable in the copresence of TPS and BP.

Different film thicknesses may lead to different rates of degradation. In our previous study,[31] CA films containing TPS with four levels of thickness were prepared by the same procedure used in this study. As the film thickness increased, the film density decreased. With simulated solar irradiation, the decrease in the molecular weight of the thickest film was the most rapid. This result indicates that the low density of thick films made CA molecules vulnerable to the Brønsted acid generated from TPS, and main-chain cleavage by hydrolysis proceeded quickly. Similar trends were seen in the TPS/BP/CA system, although the degradation behavior of the CA films only with 40 ± 5 μm thickness was evaluated in this study.

Other than BP, some hydrocarbons and ketones have been suggested to induce acid generation from onium salts.[12–15] However, we evaluated only the effect of BP in this study because the other compounds, including anthracene and perylene, which were reported to be effective for the induction, have limited miscibility with CA. Further additive searches are of interest for our future studies.

CONCLUSIONS

The degradative behavior of CA films containing a TPS and/or BP was evaluated under simulated solar exposure by means of a xenon fadometer. Although a significant effect of the copresence of the two additives on the decrease in the molecular weight of CA could not be demonstrated, enhanced acetic acid liberation from CA was observed in the copresence of the both additives. The results indicate that Brønsted acid induction from TPS was activated by BP, and the hydrolysis (deacetylation) of CA by the Brønsted acid was accelerated. A possible mechanism was proposed as follows: free-radical species induced by the photoreaction of BP were oxidized by the TPS, and then, the Brønsted acid was released effectively. On the basis of the consideration that a lower degree of substitution of CA provides higher biodegradability, the enhancement of the deacetylation of CA by

the TPS/BP/CA system is expected to accelerate the degradation of CA under ambient environmental conditions.

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