Photodegradation of Polystyrene Containing Flame Retardants: Effect of Chemical Structure of the Additives on the Efficiency of Degradation

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ABSTRACT: The efficiency and wavelength sensitivity of photodegradation in polystyrene (PSt) in the presence of a flame retardant were studied. The effect of the concentration of a flame retardant on the degradation of PSt was also investigated. Four kinds of flame retardant containing bromine atoms in the molecule and having the same frame structure were used. Irradiation of monochromatic radiation was carried out using the Okazaki Large Spectrograph (OLS). The degradation of the PSt matrix was followed by UV-visible and FTIR spectroscopy for the chemical changes produced. Changes in the molecular weight and its distribution were estimated from the results of a gel permeation chromatography (GPC) measurement. In all additives tested, the photodegradation of PSt was accelerated by the addition of bromine-containing flame retardants. The most effective wavelength for the main-chain scission of PSt was 280 nm for the samples containing 1 phr of the flame retardant, while this wavelength shifts to 300 nm for the samples containing 2 phr of the flame retardant. A probable reaction scheme of the accelerated degradation in the presence of a flame retardant was proposed from the experimental results. The photostability of PSt containing a flame retardant appears to depend on chemical structures of the additive and compatibility of the additives to PSt. Further studies are required to solve the role of additives in polymer matrices. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 67: 1293–1300, 1998

INTRODUCTION

Fire-retardant polymer materials are widely used in various industrial fields. These materials are used under terrestrial sunlight or artificial light and the photostability of these polymers is reduced by the addition of flame retardants.

Recently, we tested the effect of nine kinds of flame retardants containing bromine in the molecule on the photodegradation of polystyrene (PSt).[1] It was found that the efficiency of degradation depends on the irradiation wavelength and the chemical structure of the additives. In most cases, degradation was accelerated by the addition of a flame retardant. We need excellent materials having both flame retardability and photostability. For this purpose, we should clarify the photodegradation mechanism of polymer materials in the presence of flame retardants.

It is well known that halogen compounds accelerate the photodegradation of PSt.[2–4] In this case, the halogen atom abstracts hydrogen from the α-position of PSt and leaves the polystyryl radical. The resulting polystyryl radical becomes a precursor of photodegradation. Consequently, the photodegradation of PSt is accelerated by the addition

Table I   Abbreviated Names and Chemical Structures of Flame Retardants

	Abbreviated Name	Name of Flame Retardant
a)	TBA	2,2-Bis(3,5-dibromo-4-hydroxyphenyl)propane
b)	TBA−BP	2,2-Bis[3,5-dibromo-4-(2,3-dibromopropoxy)phenyl]propane
c)	EPOu	TBA−epoxy oligomer (uncapped)
d)	EPOc	TBA−epoxy oligomer (capped)

a) [structure: 2,2-Bis(3,5-dibromo-4-hydroxyphenyl)propane]

b) [structure: 2,2-Bis[3,5-dibromo-4-(2,3-dibromopropoxy)phenyl]propane]

c) [structure: TBA−epoxy oligomer (uncapped)]

d) [structure: TBA−epoxy oligomer (capped)]
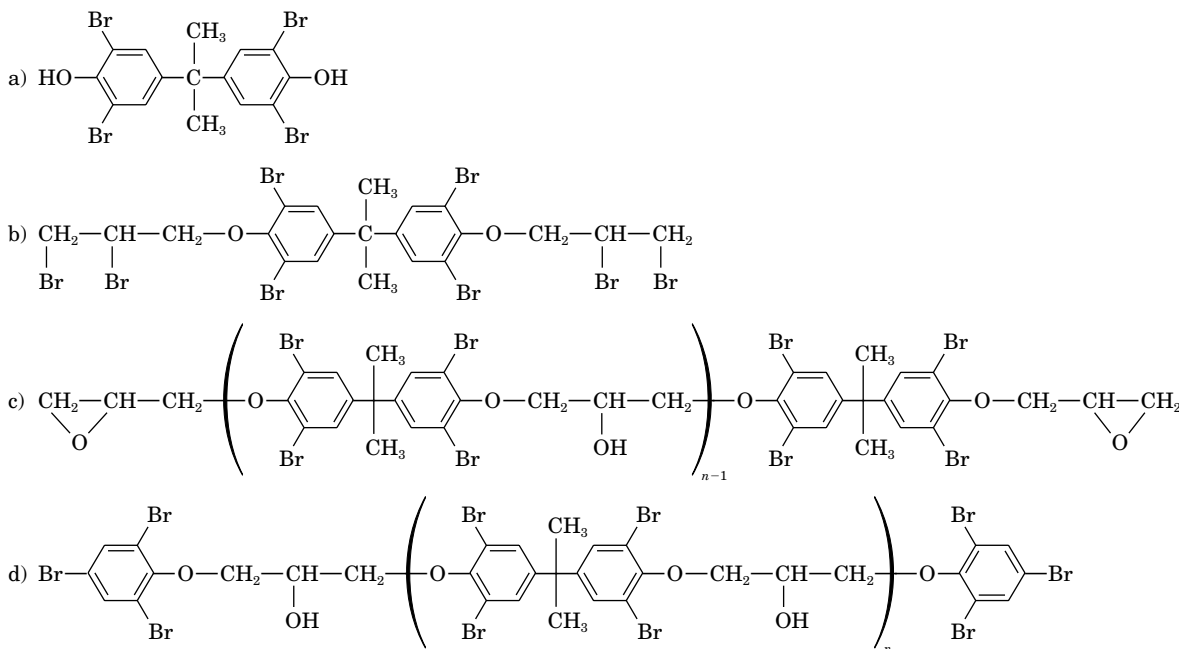
of halogen-containing additives. In the photodegradation of PSt containing a flame retardant, if bromine atoms play an important role in the photodegradation of PSt, the number of bromine atoms in the molecule and the concentration of bromine molecule in PSt should affect the efficiency of photodegradation in PSt.

In the present work, we chose four kinds of flame retardants having the same frame structure and a differing substitutional group to clarify the effect of the molecular structure of additives on the photodegradation of PSt. The wavelength sensitivity and concentration effect on the degradation of the PSt matrix were also investigated in this study.

EXPERIMENTAL

Polystyrene [(PSt) GPPS HF-55] was supplied by Mitsubishi Monsanto Chemicals as pellets. Four kinds of flame-retardants containing bromine atoms in the molecule were used as additives. The abbreviated names and chemical structures of them are given in Table I.

The details of the film preparation were already described in our previous article.[1] The thickness of films was around 0.1 mm and the concentration of additives was 1 or 2 phr. In the case of the additives TBA−BP, TBA−EPOc, and TBA−EPOu, both 1 and 2 phr samples were examined. Sample films were irradiated with monochromatic radiation from 260 to 380 nm at intervals of 20 nm at 23°C using the Okazaki Large Spectrograph (OLS). Details of the OLS and a schematic representation of sample irradiations were reported previously.[5] The photon intensity at each wavelength was measured by a Riken HK-1 photon density meter and the stability of the source was continuously monitored during irradiations at two wavelength positions. Immediately after the irradiations, samples were placed in a black envelope to avoid outer radiations and stored in a desiccator at ambient temperature.

The UV-visible spectra of the photoirradiated samples were measured using a Hitachi Model 323 and Shimadzu UV-2400PC-type spectropho-
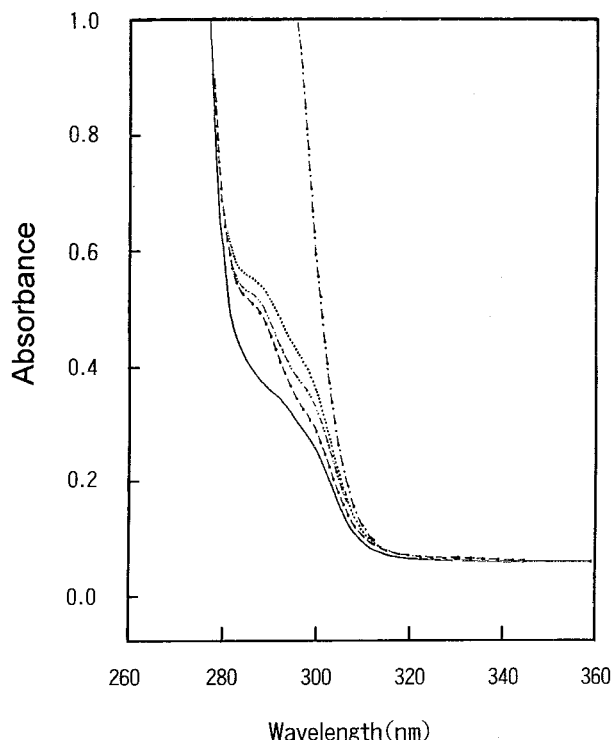
Figure 1 UV spectra of (————) PSt and PSt containing 1.0 phr of (− − − − −) EPOc, (---------) EPOu, (− −·− −·− −·−) TBA and (− −···− −···− −··) TBA-BP.

tometers. A Jasco 5300 FTIR spectrophotometer was used to measure the FTIR spectra of photoirradiated samples. Changes in the molecular weight of PSt were followed by gel permeation chromatography (GPC) measurements. A Tosoh GPC apparatus equipped with an RI 8000 detector and a set of TSK gel-GMHL columns were used for the analysis of the molecular weight change of PSt. Tetrahydrofuran (THF) at 38°C was used as an eluent. PSt with known molecular weights were used as standards.

RESULTS AND DISCUSSION

Changes in Chemical Structure

Changes in the chemical structure in PSt was followed by UV and FTIR spectroscopy. UV spectra of PSt films containing a flame retardant (four kinds) are shown in Figure 1. The typical changes in UV spectra with photoirradiation are shown in Figure 2.

The increase in absorbance around 300 nm may be attributed to the formation of a carbonyl group adjacent to the phenyl group of PSt (**I**):

$$-CH_2-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}$$

(**I**)
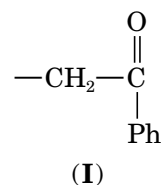
where Ph represents the phenyl group. The increase in absorbance at 310 nm (ΔOD_{310}) showing oxygenated product formation in PSt was chosen as a measure of the degradation of PSt. Changes in the ΔOD_{310} per photon and per unit thickness are plotted against the irradiation wavelength in Figures 3 and 4.

The efficiency of the degradation estimated by UV spectra is in the order of Ref < TBA–EPOu < TBA–EPOc < TBA–BP < TBA at the concentration of 1 phr. In the case when the additive concentration is 2 phr, the efficiency of the degradation became Ref < TBA–EPOu ≦ TBA–EPOc < TBA–BP. The irradiation wavelength giving maximum efficiency is 280 nm in 1 phr samples, while it shifts to 300 nm for the samples con-
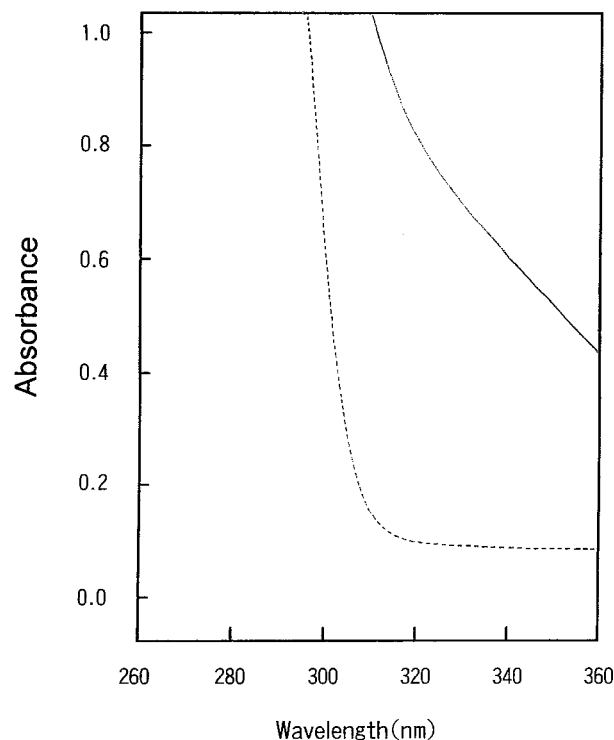

Figure 2 UV spectra of photoirradiated PSt containing 1.0 phr of TBA: (--------) unirradiated; (————) irradiated at 280 nm. Total photon fluence: 4.75×10^{19} photons/cm².

taining 2 phr of TBA–EPOc. The value of ΔOD_{310} per photon is about the same order for both 1 and 2 phr samples. The total photon fluence of the irradiated samples containing 2 phr additive was twice higher than those of the 1 phr samples. The linear relationship between irradiation dose and the degree of degradation or concentration of additives does not exist in this case.

FTIR is useful tool to detect the chemical changes produced by photoirradiation. Typical spectra are shown in Figure 5. A new band at $1685\ cm^{-1}$ was produced after photoirradiation which was also assigned to the formation of a carbonyl group adjacent to a phenyl group of PSt (**I**).[6]

This band was also used as a measure of the degradation of PSt. The carbonyl index was defined as the ratio of $A_{1685}/A_{1685\text{-}0}$, in which A_{1685} and $A_{1685\text{-}0}$ are the optical densities at $1685\ cm^{-1}$ after and before photoirradiation, respectively. Carbonyl indices were plotted against the irradiation wavelength for the samples containing 1 and 2 phr additive, respectively, in Figures 6 and 7.
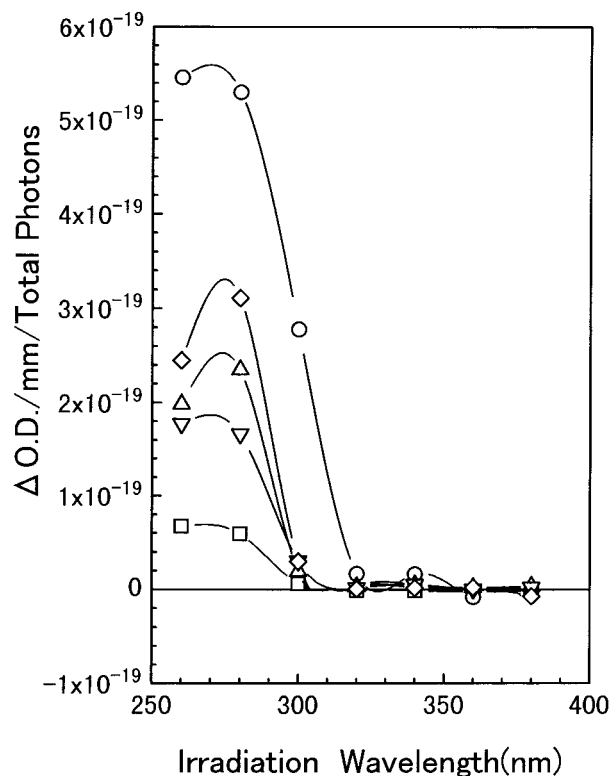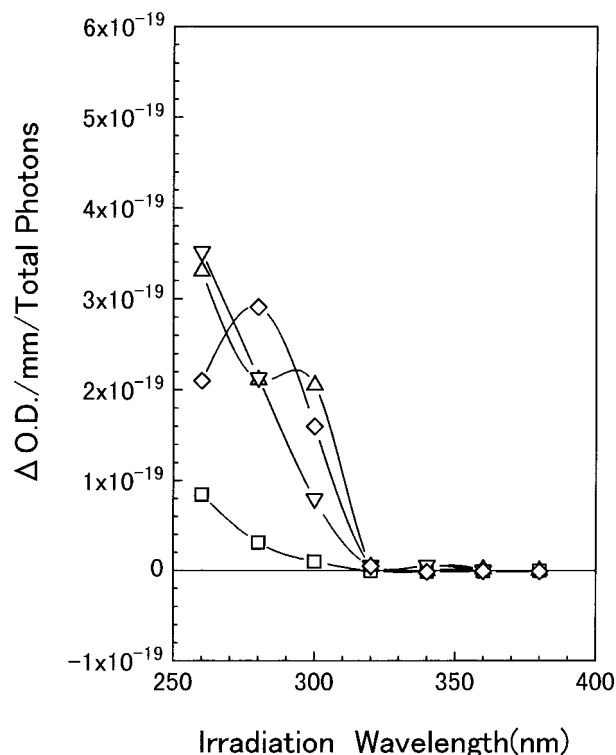

Figure 4 Changes in the optical density per photon at 310 nm at various irradiation wavelengths. Concentration of additives: 2 phr. Samples and symbols are the same as in Figure 3.
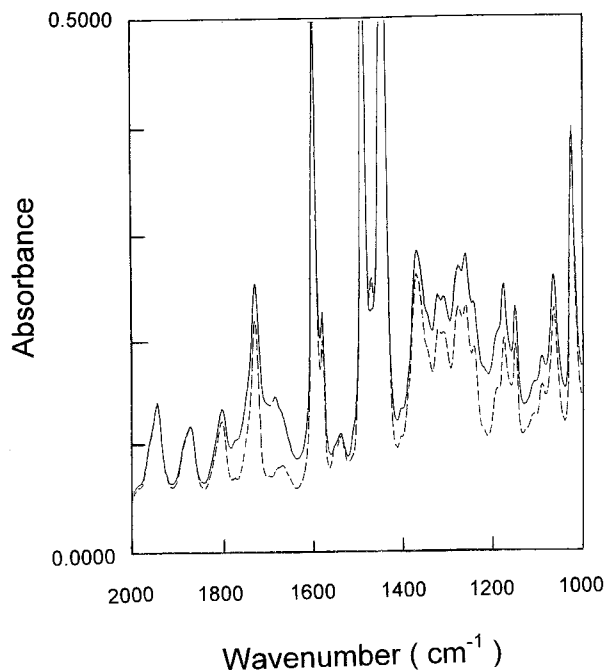

Figure 3 Changes in the optical density per photon at 310 nm at various irradiation wavelengths. Concentration of additives; 1 phr: (□) PSt; (△) EPOc–PSt; (▽) EPOu–PSt; (○) TBA–PSt; (◇) TBA–BP–PSt.

Figure 5 FTIR spectra of photoirradiated PSt containing 1.0 phr of TBA: (--------) unirradiated; (———) irradiated at 280 nm. Total photon fluence: 4.75×10^{19} photons/cm^2.

The efficiency of degradation estimated by the FTIR spectra are almost the same as those by the UV spectra. The shift of wavelength giving the maximum efficiency in the samples containing 2 phr of TBA–EPOc was also found in the FTIR measurement. From UV and FTIR measurements, it was concluded that the degradation of the matrix PSt was accelerated by the addition of the flame retardant. The threshold wavelength of the degradation estimated from these two measurements was found to be 320 nm.

Changes in Molecular Weight

Direct information of the degradation is given by the molecular weight change. GPC measurements were carried out for this purpose. In Figures 8 and 9, the number of chain scission (Cs) calculated from eq. (1) are plotted against the irradiation wavelength, where $\bar{M}_{n_0}$ and $\bar{M}_n$ represent the number-average molecular weights of PSt before and after photoirradiation, respectively:

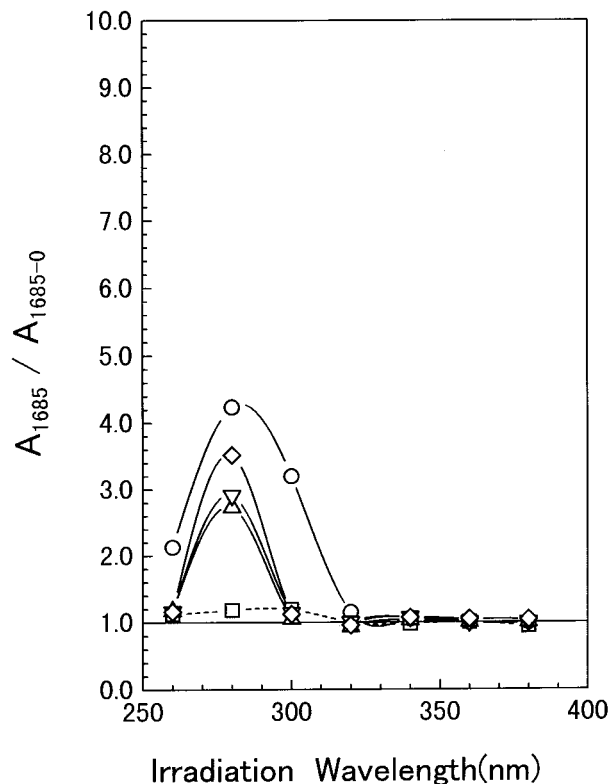$$Cs = \bar{M}_{n_0}/\bar{M}_n - 1 \qquad (1)$$

Figure 6 Changes in the carbonyl index at various irradiation wavelengths. Samples and symbols are the same as in Figure 3. Concentration of additives: 1.0 phr.

Figure 7 Changes in the carbonyl index at various irradiation wavelengths. Samples and symbols are the same as in Figure 3. Concentration of additives: 2.0 phr.
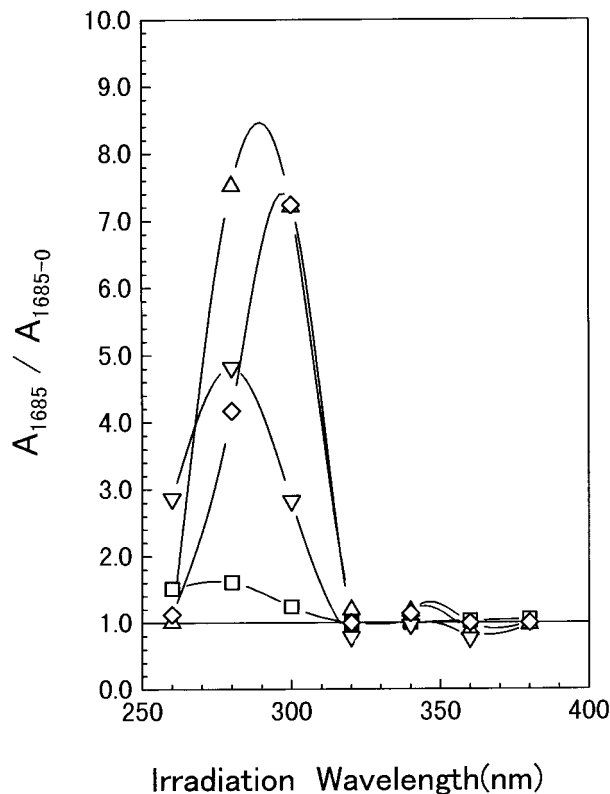
The most effective wavelength for the degradation of PSt was 280 nm, for the samples containing 1 phr additive. This wavelength shifts to 300 nm for the samples containing 2 phr additive.
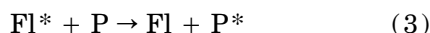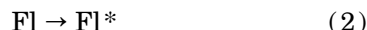
The difference is clearly found by comparing Figures 8 and 9. The shift of the maximum effective wavelength was also seen partly in the case of the spectroscopic measurement, although it was not clear as in case of molecular weight measurements. The concentration dependence of the maximum effective wavelength clearly exists in these three additives; however, it is difficult to explain the reason for this phenomenon at this time. Further information is needed on the reaction mechanism of the degradation of PSt in the presence of a flame retardant.

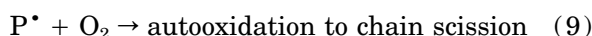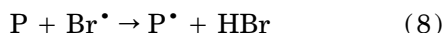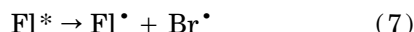## Probable Reaction Scheme of Degradation

The experimental results clearly show the acceleration of degradation of PSt in the presence of a flame retardant with the irradiation of radiation of wavelengths from 260 to 300 (320) nm. In this case, the photosensitized reaction by additives plays a role for the degradation of PSt. Generally,

photosensitized reactions are divided into two types, I and II.

Type I:

$$Fl \rightarrow Fl^* \tag{2}$$

$$Fl^* + P \rightarrow Fl + P^* \tag{3}$$

$$P^* \rightarrow P^\bullet + H^\bullet \tag{4}$$

$$P^\bullet + O_2 \rightarrow \text{autooxidation to chain scission} \tag{5}$$

Type II:

$$Fl \rightarrow Fl^* \tag{6}$$

$$Fl^* \rightarrow Fl^\bullet + Br^\bullet \tag{7}$$

$$P + Br^\bullet \rightarrow P^\bullet + HBr \tag{8}$$

$$P^\bullet + O_2 \rightarrow \text{autooxidation to chain scission} \tag{9}$$

where P and Fl represent PSt and flame-retardant, respectively.

Type I reactions include energy transfer from an excited additive molecule to the ground-state PSt molecule and an excited PSt molecule contributes to
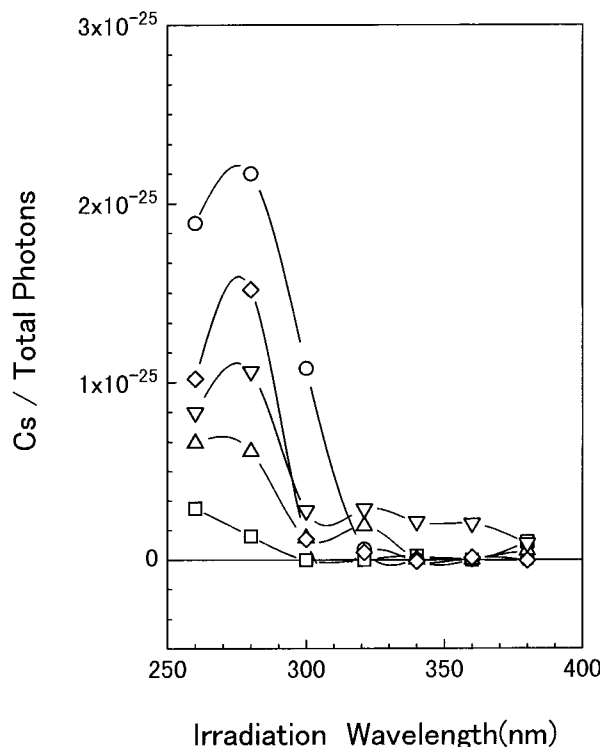
Figure 9   Number of main-chain scission per photon in photoirradiated PSt containing flame retardants. Samples and symbols are the same as in Figure 3. Concentration of additives: 2.0 phr.

the degradation reaction. Type II reactions involve an initial reaction of the excited additive to form the bromine radical and result in the formation of a free radical and the subsequent reaction of the radical with oxygen, leading to the degradation of matrix PSt. It is well known that halogen atoms accelerate the degradation reaction of polymer materials. In these cases, hydrogen atom abstraction from the α-position of polymers produces a chain radical on the polymer. An oxygen attack on this radical results in the formation of a peroxy radical and the subsequent reaction to the degradation of PSt.[7]

We will consider the possibility of a reaction scheme participating in photosensitized degradation of PSt by flame retardants. If the Type I reaction is the course of the degradation of PSt, the photon energy at 300 nm should be sufficient to dissociate the C—H bond of PSt, because the threshold wavelength of photodegradation of PSt shifts to a longer wavelength compared to that for PSt without an additive (in between 300 and 320 nm; see Figs. 8 and 9).

The degradation reaction of PSt may start from the cleavage of the C—H bond at the α-position of PSt. The bond-dissociation energy of this bond is reported to be 412 kJ/mol, whereas the photon

Figure 8   Number of main-chain scission per photon in photoirradiated PSt containing flame retardants. Samples and symbols are the same as in Figure 3. Concentration of additives: 1.0 phr.
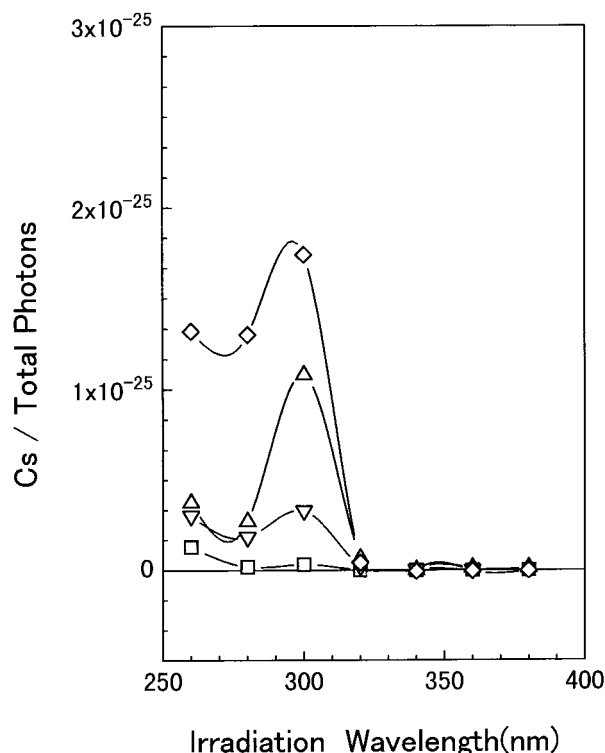
energy at 300 nm is 398 kJ/mol. This energy is insufficient to dissociate the C—H bond of PSt. Therefore, the Type I reaction may not participate in the photosensitized degradation of PSt by flame-retardants at longer wavelengths.

In the case of the accelerated degradation by the irradiation at the wavelengths of 260 and 280 nm, the Type I reaction possibly explains the acceleration, because the photon energy at 280 nm is 426 kJ/mol, which is sufficient for the chain scission of C—H bond at the α-position of PSt. The Type II reaction may play a role for the accelerated degradation of PSt at all irradiation wavelengths. The bromine atoms thus produced is small and mobile in the PSt matrix, so that the hydrogen abstraction reaction by the bromine atom can be possible in this case. Similar hydrogen atom abstraction reactions by halogen atoms were reported by several authors.[8–10] Such consideration leads to the following photosensitized degradation scheme in the PSt–flame-retardant system.
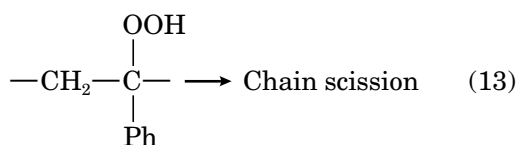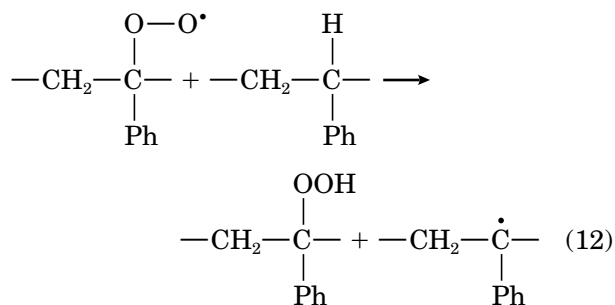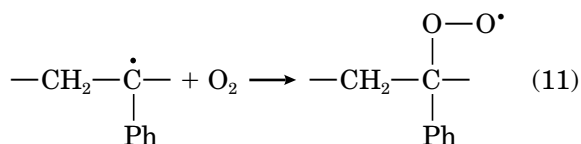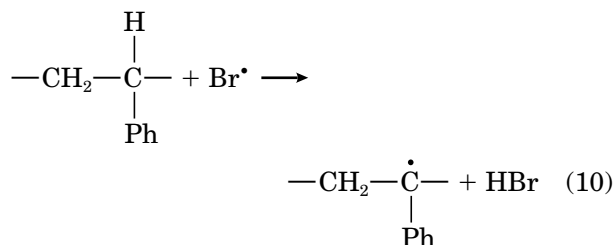
$$Fl \longrightarrow Fl^* \qquad (2)$$

$$Fl^* \longrightarrow Fl^{\bullet} + Br^{\bullet} \qquad (7)$$

$$-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}- + Br^{\bullet} \longrightarrow$$

$$-CH_2-\overset{\bullet}{\underset{\underset{\displaystyle Ph}{|}}{C}}- + HBr \qquad (10)$$

$$-CH_2-\overset{\bullet}{\underset{\underset{\displaystyle Ph}{|}}{C}}- + O_2 \longrightarrow -CH_2-\overset{\overset{\displaystyle O-O^{\bullet}}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}- \qquad (11)$$

$$-CH_2-\overset{\overset{\displaystyle O-O^{\bullet}}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}- + -CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}- \longrightarrow$$

$$-CH_2-\overset{\overset{\displaystyle OOH}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}- + -CH_2-\overset{\bullet}{\underset{\underset{\displaystyle Ph}{|}}{C}}- \qquad (12)$$

$$-CH_2-\overset{\overset{\displaystyle OOH}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}- \longrightarrow \text{Chain scission} \qquad (13)$$

Table II No. Bromine Atoms in 1 g of Flame Retardant

Flame Retardant	Molecular Weight	Mol/1 g[a]	Br/1 g[b]
TBA	544	1.84×10^{-3}	7.36×10^{-3}
TBA-BP	943	1.06×10^{-3}	8.48×10^{-3}
TBA-EPOu	1400	7.14×10^{-4}	6.52×10^{-3}
TBA-EPOc	950	1.05×10^{-3}	7.96×10^{-3}

[a] Number of molecules in 1 g of flame-retardant.
[b] Number of bromine atoms in 1 g of flame-retardant.

Difference in the Efficiency of Degradation

In the former section, we discussed the probable mechanism of the accelerated degradation of PSt by flame retardants and the bromine atom may play a role in these cases. These additives have the same frame structure as shown in Table I.

The number of bromine atoms in one molecule is greater in the order of TBA < TBA–BP < TBA–EPOc < TBA–EPOu. If the number of bromine atoms in one molecule is the cause of the difference in efficiency in accelerated degradation, the acceleration should occur in the order of TBA < TBA–BP < TBA–EPOc < TBA–EPOu. As we have seen in our experimental results, the actual efficiency of acceleration is the reverse order.

It is said that EPOu is an excellent photostabilizer, for this additive traps the bromine atoms produced by photoirradiation. In our case, the difference in photostability in EPOc and EPOu was not found in the samples containing 1 phr of the additive. The difference is seen in the samples containing 2 phr of the additives (Fig. 9). In this case, EPOu is the most effective additive of the three as a photostabilizer, especially at irradiation wavelengths of 300 nm. This fact also suggests the participation of the bromine atom in the accelerated photodegradation of PSt.

Table II shows the number of bromine atoms in 1 g of flame-retardant (molecules/g). The number of molecules of the bromine atom are almost the same in the four flame-retardants used.

The efficiency of the accelerated degradation is greatly changed in each additive. The reason is not clarified from these experimental results. One possibility is the compatibility of the flame retardants in the PSt matrix. If the flame retardant is completely compatible in the PSt matrix, the efficiency of the bromine atom formation and the successive abstraction of the hydrogen atom may easily take place. Further studies are required to solve this problem.

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