

# Photodegradation of Polymer Materials Containing Flame-Cut Agents

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## SYNOPSIS

Photodegradation of incombustible materials [polystyrene (PSt) and polypropylene (PP) containing 2 wt % of decabromodiphenyl oxide (DBDE) or tetrabromobisphenol-A (TBA) as a flame-cut agent] were studied using Okazaki Large Spectrograph (OLS). Samples were irradiated in air at 23°C with monochromatic light of wavelengths at 260, 280, 300, 320, 340, and 360 nm. UV-visible spectra and FTIR spectra were measured to identify the chemical structural changes of the polymers. Number of chain scissions, which is a measure of the polymer degradation, was estimated from the results of GPC measurements. It was found that the photostability of PP and PSt was reduced by the addition of DBDE or TBA. Photodegradation of these polymers took place by the irradiation of the light of wavelengths lower than 320 and 360 nm for the polymer containing TBA and DBDE, respectively. The most effective irradiation wavelengths for main chain scission are found to be 260–280 and 300 nm for PP or PSt–TBA samples and PP or PSt–DBDE samples, respectively. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Organic polymers have been one of the popular materials for their excellent characteristics such as moldability, low density, easiness for coloring, low prices, and so on. Since they are often used under terrestrial sunlight, fundamental studies on photodegradation of polymer materials are required for various applications of them. Polymer materials containing flame-cut agents (incombustible polymer materials) have been widely used in various industrial fields.

Studies on photodegradation of incombustible polymer materials are important from the following two viewpoints:

1. The effect of flame-cut agent on photostability of polymer materials.

2. The degradation of the used polymer materials.

It is an increasing problem to find out the method for degradation of waste materials. Although the effect of photostabilizer on photodegradation of polymer materials has been studied extensively, little is known about the role of flame-cut agent against photodegradation. We have been studying the wavelength effect on photodegradation of various polymer materials.<sup>1–7</sup> Efficiency of photo-induced degradation of a polymer material expressed as a function of the wavelength of the incident light (a kind of action spectrum) gives crucial information on spectral sensitivity of the material. Such a study can be possible using monochromatic light with high intensity. We can get monochromatic light at any desired wavelength between 250 and 1000 nm with high light intensity, using Okazaki Large Spectrograph (OLS).

In this report, we attempt to clarify the role of flame-cut agents and incident light wavelength on

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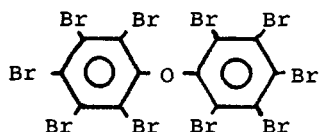
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the photodegradation of polystyrene (PSt) and polypropylene (PP).

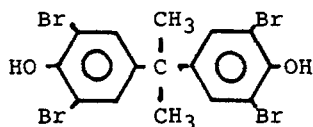
## EXPERIMENTAL

Polypropylene (J5100A) and polystyrene (GPPS HF-55) were supplied from Tosoh Corporation, and Mitsui Monsanto Chemicals, respectively, as pellets. The following two types of flame-cut agents are used as additives:

Decabromodiphenyl oxide (DBDE)



Tetrabromobisphenol-A (TBA)



Polymer pellets (PP or PSt) were mixed with flame-cut agent [decabromodiphenyl oxide (DBDE) or tetrabromobisphenol-A (TBA)] using a Laboplast mill at 200°C for 5 min. Then they are hot pressed with a pressure of 200 kg/cm<sup>2</sup> for 2 min at 200°C

and subsequently cooled at 25°C for 3 min. The thickness of films were ca. 0.1 mm.

Monochromatic light irradiation to samples were carried out using Okazaki Large Spectrograph (OLS) in Okazaki, Japan. The features of the spectrograph has been discussed previously.<sup>8</sup> Irradiation of monochromatic light with any desired wavelength was made by placing the samples at appropriate positions on a 10-m-long focal curve. The beam was focused at each wavelength by using a surface mirror (20 × 10 cm). The schematic representation of light exposure is shown in Figure 1.

Irradiations to the samples were carried out at wavelengths of 260, 280, 300, 320, 340, and 360 nm in air at 23°C. Six samples were irradiated at the same time. The light intensity at each sample position was measured by a Riken HK-1 photon density meter. Immediately after irradiations, the samples were put in black envelopes and stored in a desiccator at ambient temperature.

FTIR spectra of photo-irradiated samples were taken on a Jasco 5300 FTIR spectrophotometer. A Hitachi model 323 spectrophotometer was used to take UV spectra of the samples.

The changes in molecular weight of PP or PSt were followed by gel permeation chromatography (GPC) measurements. A Waters 150C equipped with Tosoh TSK gel-Gm<sub>XL</sub>-HT and a Tosoh HLC-802A equipped with TSK gel-GMH were used for the analysis of molecular weight distribution of PP and PSt, respectively. *o*-Dichlorobenzene (*o*DCB) at 140°C and tetrahydrofuran (THF) at 38°C were used as eluents of PP and PSt, respectively.

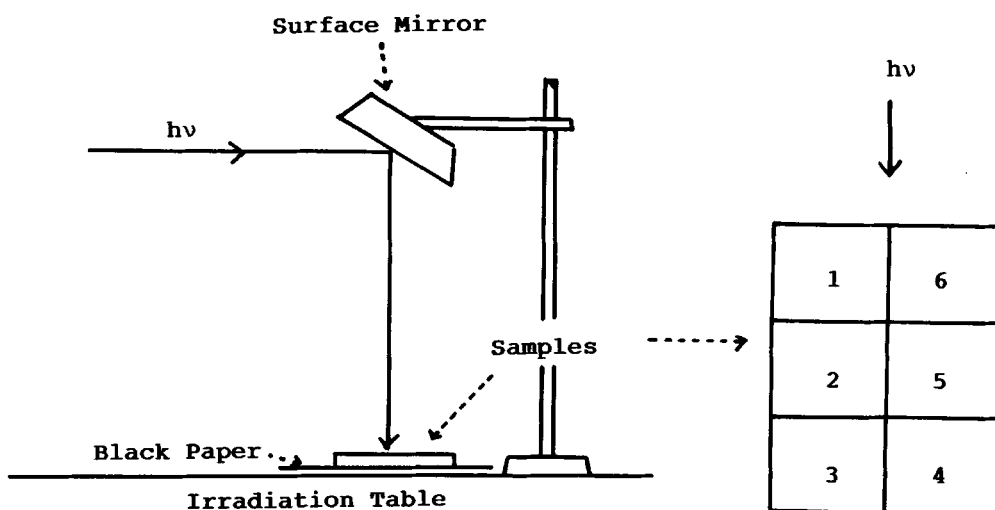
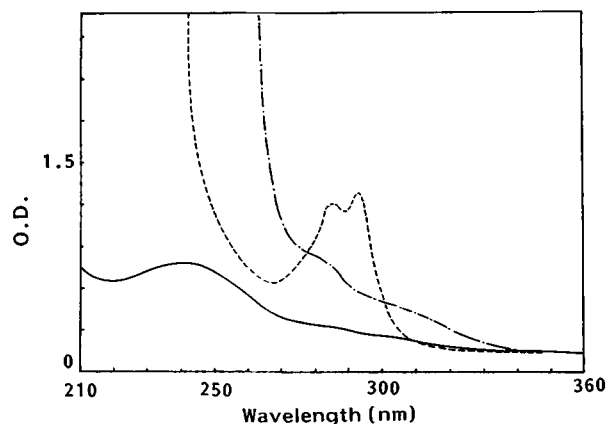


Figure 1 Schematic representation of sample irradiations.



**Figure 2** UV spectra of PP (—), PP containing 2% of DBDE (---) and 2% of TBA (.....).

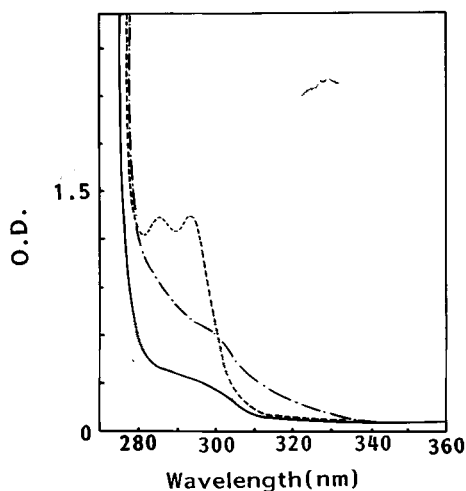
## RESULTS AND DISCUSSION

### UV and FTIR Spectral Change

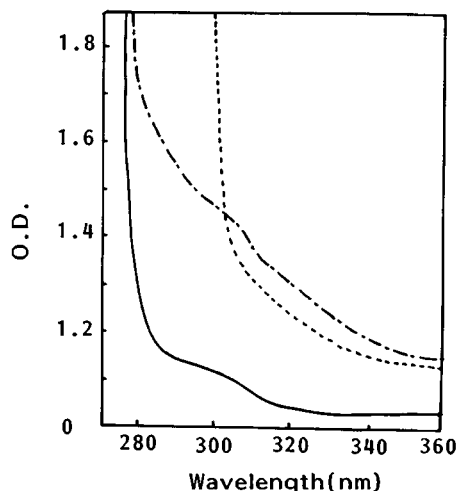
UV spectra of unirradiated PP and additive-containing PP are shown in Figure 2. Similar spectra for PSt and additive-containing PSt are also given in Figure 3.

On photoirradiation, each sample develops the increase in the intensity of absorption band in the 210–360 nm region. Typical spectra obtained after photon exposure at 23°C are shown in Figure 4.

Chemical changes produced in the samples were monitored by FTIR measurements. Formation of carbonyl groups was detected. The FTIR spectrum of photo-irradiated PP containing 2% of DBDE is shown in Figure 5, as an example.



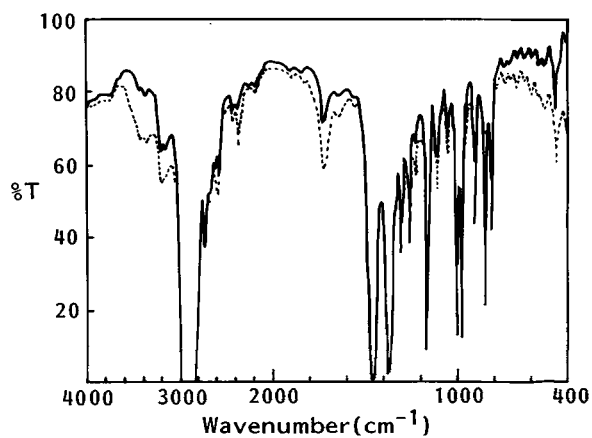
**Figure 3** UV spectra of PSt (—), PSt containing 2% of DBDE (---) and 2% of TBA (.....).



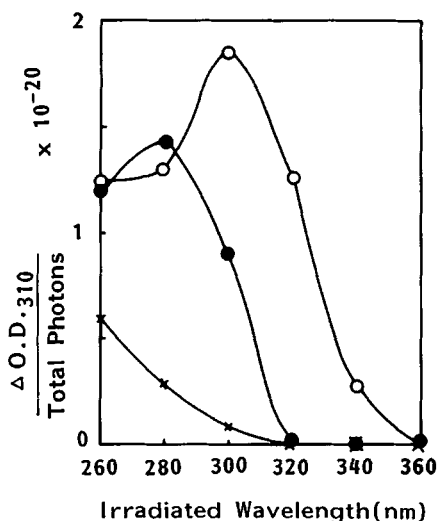
**Figure 4** UV spectra of photo-irradiated PSt (—), PSt containing 2% of DBDE (---) and 2% of TBA (.....). Irradiation wavelength, 300 nm; total photon fluence,  $9.0 \times 10^{19}$  photons/cm<sup>2</sup>.

### PSt Flame-Cut Agents System

The increase in absorbance at 310 nm of photo-irradiated PSt samples ( $\Delta OD_{310}$ ) is chosen as a measure of degradation of PSt.  $\Delta OD_{310}$  per one exposed photon are plotted at each irradiation wavelength in Figure 6. The photodegradation of PSt is accelerated by the addition of flame-cut agents. This acceleration is wavelength-dependent as shown in Figure 6. The threshold wavelengths of photodegradation are 320 and 360 nm for PSt–TBA samples and PSt–DBDE samples, respectively. The most ef-



**Figure 5** FTIR spectra of unirradiated (—) and photo-irradiated (.....) PP containing 2% of DBDE. Irradiation wavelength, 300 nm; total photon fluence,  $9.0 \times 10^{19}$  photons/cm<sup>2</sup>.

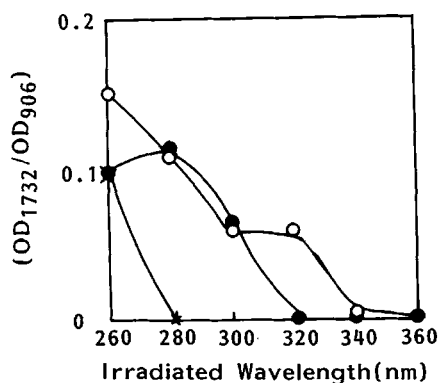


**Figure 6** Changes in the optical density at 310 nm at various irradiation wavelength.  $\times$  PSt;  $\circ$  PSt-DBDE (2%);  $\bullet$  PSt-TBA (2%).

fective wavelengths for photodegradation may be 280 and 300 nm for PSt-TBA samples and PSt-DBDE samples, respectively.

Chemical changes produced in the PSt films were monitored by FTIR measurements. Formation of carbonyl groups was used as a measure of photodegradation of PSt samples. The formation of carbonyl groups by photo-irradiation is plotted against the irradiation wavelengths in Figure 7.

Where carbonyl index represents the ratio of  $OD_{1732}$  [OD at  $1732\text{ cm}^{-1}$  ( $\nu_{C=O}$ )] to  $OD_{906}$  [OD at  $906\text{ cm}^{-1}$  ( $\nu_{C-H}$ )].<sup>9</sup> The formation of carbonyl groups



**Figure 7** Changes in the carbonyl index ( $OD_{1732}/OD_{906}$ ) at various irradiation wavelengths. Samples and symbols are as in Figure 6. Total photon fluence,  $9.0 \times 10^{19}$  photons/cm<sup>2</sup>.

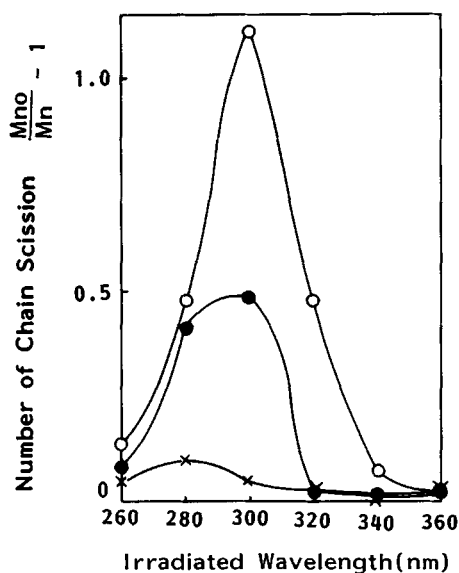
by photo-irradiation is also accelerated by the addition of flame-cut agents, although distinct wavelength dependence was not found for PSt-DBDE samples.

Figure 8 shows the number of chain scissions of PSt calculated from Eq. (1):

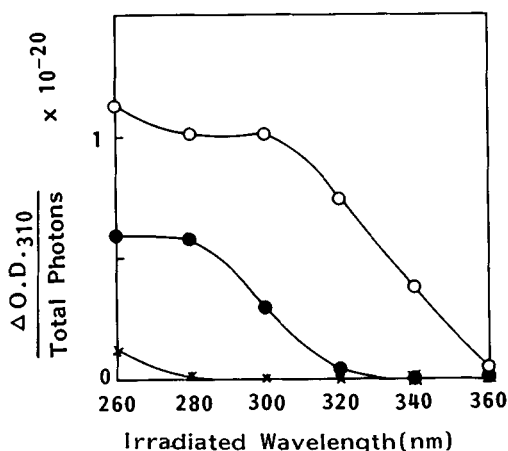
$$\bar{M}n_0/\bar{M}n - 1 \quad (1)$$

where  $\bar{M}n_0$  and  $\bar{M}n$  are the number-average molecular weights of polymers before and after photoirradiation. Photodegradation of PSt without additives scarcely occur under our experimental condition. On addition of DBDE or TBA as an additive, photodegradation of PSt is accelerated and this acceleration is wavelength-dependent as seen in Figure 8. The most effective wavelengths for photodegradation are 280–300 nm for PSt-TBA samples and 300 nm for PSt-DBDE samples.

DBDE seems to be more effective additive than TBA for photodegradation of PSt. The threshold wavelengths of photodegradation are estimated to be 320 nm for PSt-TBA samples and 360 nm for PSt-DBDE samples. These results are consistent with those from UV spectral analysis (Fig. 6). This consistency shows that we can use the  $\Delta OD_{310}$  value as a measure of photodegradation of PSt.



**Figure 8** Number of chain scission of photo-irradiated PSt and PSt containing flame-cut agents. Samples and symbols are as in Figure 6. Total photon fluence,  $9.0 \times 10^{19}$  photons/cm<sup>2</sup>.



**Figure 9** Changes in the optical density at 310 nm at various irradiation wavelengths.  $\times$  PP;  $\circ$  PP-DBDE (2%);  $\bullet$  PP-TBA (2%). Total photon fluence,  $9.0 \times 10^{19}$  photons/cm<sup>2</sup>.

### PP Flame-Cut Agents System

The increase in absorbance at 310 nm ( $\Delta OD_{310}$ ) of photo-irradiated PP and PP containing flame-cut agents are plotted against the irradiation wavelength in Figure 9. The increase in  $OD_{310}$  of PP without additive is very small on irradiation at 260 nm. When the irradiations are carried out other wavelengths than 260 nm,  $\Delta OD_{310}$  are zero. The photodegradation of PP is also accelerated by the addition of flame-cut agents and this acceleration is wavelength-dependent. The threshold wavelength of photodegradation are 320 and 360 nm for PP-TBA and PP-DBDE, respectively. This acceleration is supported by the FTIR measurements. In the case of PP-TBA and PP-DBDE samples, carbonyl groups formation favored compared with that of PP without additives.

Table I shows changes in the number-average molecular weight ( $\bar{M}_n$ ) of photoirradiated PP, PP-TBA, and PP-DBDE samples.

In PP samples without additive, main-chain scission was not observed for any irradiation wavelengths. On addition of TBA, main-chain scission of PP was observed in case of the irradiation at 280 nm. Main-chain scission of PP took place more efficiently in PP-DBDE samples than in PP-TBA samples. The most effective wavelength for main-chain scission was found to be 260 nm. The result obtained for PP-DBDE samples shows similar behavior as that obtained from UV spectral measurements (Fig. 9). The threshold wavelengths for pho-

**Table I** Changes in the Number-Average Molecular Weight of Photo-irradiated PP, PP-TBA, and PP-DBDE Samples

Irradiation Wavelength (nm)	Total Fluence (photons/cm <sup>2</sup> ) ( $\times 10^{-18}$ )	$\bar{M}_n$ ( $\times 10^{-4}$ )		
		PP	PP-TBA	PP-DBDE
	0	3.4	3.3	3.4
260	60	3.8	3.2	2.1
280	90	3.8	2.6	2.3
300	90	3.5	3.3	2.5
320	90	3.6	3.4	2.8
340	90	3.5	2.9	3.3
360	90	3.3	3.4	3.8

todegradation are 320 and 360 nm for PP-TBA and PP-DBDE, respectively.

Although the reaction mechanism of photodegradation of PP or PSt containing flame-cut agent has not been fully understood, the accelerated photodegradation of PP or PSt can take place by the addition of bromine-containing flame-cut agents.

### CONCLUSION

1. Photodegradation of PSt and PP containing flame-cut agents are accelerated at specified irradiation wavelengths.
2. The most effective irradiation wavelengths for main-chain scission are found to be 260-280 and 300 nm for PP or PSt-TBA samples and PP or PSt-DBDE samples, respectively.
3. If we adopt  $\Delta OD_{310}$  as a measure of photodegradation, the threshold wavelengths are 320 nm for polymer-TBA samples and 360 nm for polymer-DBDE samples.
4. The results were also supported by the changes in number-average molecular weights of photo-irradiated polymers.

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