

# Photooxidative Degradation of Polyethylene Containing Flame Retardants by Monochromatic Light

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## SYNOPSIS

Photodegradation of incombustible polymer materials [high-density (HD) and low-density (LD) polyethylene (PE) containing 0.5 to 2.0 phr of decabromodiphenyl ether (DBDE) or tetrabromobisphenol A (TBA) as a flame retardant] were studied using an 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. Ultraviolet and Fourier transform infrared (FTIR) spectra were taken to estimate the chemical changes caused by photoirradiation. Molecular weight change was followed by gel permeation chromatography (GPC) measurements. It was found that the photostability of PE samples was reduced by the addition of flame retardants. The threshold wavelengths of photodegradation are 320 nm and 360 nm for PE-TBA samples and PE-DBDE samples, respectively. Main-chain scission is favored when the irradiation was carried out with the light of wavelength 300 nm for HDPE-DBDE and HDPE-TBA samples. The most effective irradiation wavelengths for crosslinking are found to be 300 nm and 280 nm for LDPE-DBDE and LDPE-TBA samples, respectively. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer materials are used extensively in outdoor applications, and the lifetime of these materials involved in routine exposure is generally determined by their photostability. Incombustible polymer materials are used in conditions that require photostability. It is said that the photostability of polymer materials is reduced by the addition of flame retardants. We have studied the photodegradation of polystyrene (PSt) and polypropylene (PP) under the influence of monochromatic light irradiation<sup>1</sup> and concluded that the photodegradation of PSt and PP was accelerated by the addition of bromine-containing flame retardants.

Partial depletion of the stratospheric ozone layer will increase ultraviolet (UV) radiation levels in terrestrial sunlight. The wavelengths between 280 nm and 315 nm (UVB) are most damaging to poly-

mer materials. The increment of UVB in terrestrial sunlight will accelerate the light-induced reaction.

Efficiency of photoinduced degradation of polymer materials expressed as a function of incident light (a kind of action spectrum) gives crucial information on spectral sensitivity of the materials. From this point of view, we have been studying the wavelength effect on photodegradation of polymer materials.<sup>2-8</sup> Such studies can be possible using monochromatic light with high light intensity. Using the Okazaki Large Spectrograph (OLS), we can get monochromatic light at any desired wavelength between 250 and 1000 nm.

In this article we examine the role of Br-containing flame retardants on the photodegradation of high-density and low-density polyethylene samples.

## EXPERIMENTAL

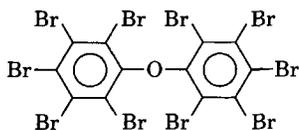
High-density (HD) and very low density (LD) polyethylene (PE) films were supplied by Tosoh Corporation. The commercial names and densities

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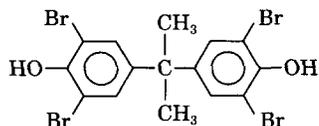
**Table I Characteristics of Polyethylene**

Sample	Commercial Name	Density (g/cm <sup>3</sup> )
HDPE	Nipolon Hard® 1000	0.963
LDPE	Lumitac® 9P369T	0.898

are listed in Table I. The following two types of flame retardants were used as additives (also supplied by Tosoh Corporation): decabromodiphenyl ether (DBDE, Flamecut 110R)



and tetrabromobisphenol A (TBA, Flamecut 120R)



Polymer pellets (HDPE or LDPE) were mixed with a flame-retardant (DBDE or TBA) using a Laboplast mill at 190°C (HDPE) or 150°C (LDPE) for 5 min. The conditions of film preparation are summarized in Table II. The thickness of films was approximately 0.01 mm, and the concentrations of additives were 0.5, 1.0, and 2.0 phr [additive (g)/polymer (g) × 100].

Monochromatic light irradiations to samples were carried out using an Okazaki Large Spectrograph (OLS) at the National Institute for Basic Biology (NIBB) in Okazaki, Japan. The features and details of the spectrograph have been introduced previously.<sup>9</sup> Irradiations of monochromatic light with any desired wavelength from 250 nm to 1000 nm were made by placing the samples at appropriate positions on a 10-m-long focal curve. The stability of the source was continuously monitored during irradiations

at preselected wavelengths. Constant intensity was obtained in this experiment. The beam was focused on the irradiation table at each wavelength by using a surface mirror (20 × 10 cm). (Schematic representations of sample irradiations were given in our previous article.<sup>1</sup>) Irradiations to the samples were carried out at wavelengths of 260, 280, 300, 320, 340, and 360 nm in air at 23°C. The light intensity at each sample position was measured by a Riken HK-1 photon density meter. Immediately after irradiation, the samples were put in a black envelope and stored in a desiccator at ambient temperature.

FTIR spectra of photoirradiated 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 HDPE and LDPE were followed by gel permeation chromatography (GPC) measurements. A Waters 150C equipped with Tosoh-TSK-gel GMHHR-H (S) was used for the analysis of molecular weight distribution of PE. *o*-Dichlorobenzene (*o*-DCB) at 140°C was used as an eluent. The photoirradiated PE samples were extracted with hot *p*-xylene for 30 h to test the gel formation.

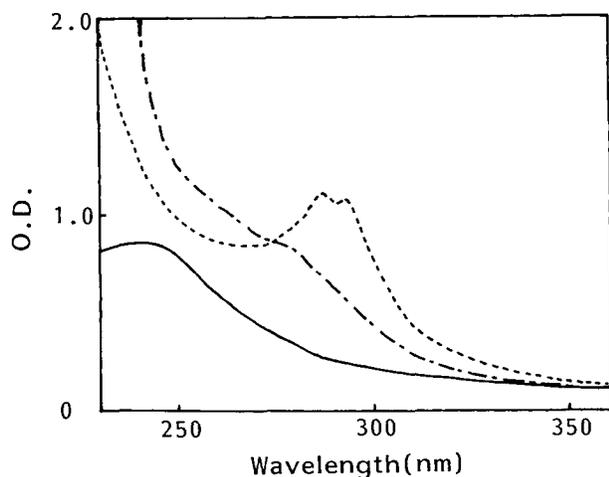
## RESULTS AND DISCUSSION

### UV Spectral Change

UV spectra of unirradiated LDPE and LDPE containing additives are shown in Figure 1. On photoirradiation, each sample developed an increase in the intensity of absorption band at 260 to 350 nm. Typical spectra obtained after photoirradiation at 23°C are shown in Figure 2. The increase in absorbance at 310 nm of photoirradiated PE samples ( $\Delta OD_{310}$ ) was chosen as a measure of degradation of PE, as in the case of PSt.<sup>1</sup> Although we have not assigned this absorption, one possibility is conjugated double bonds and/or ketonic-type compound formation.

**Table II Conditions of Film Preparation**

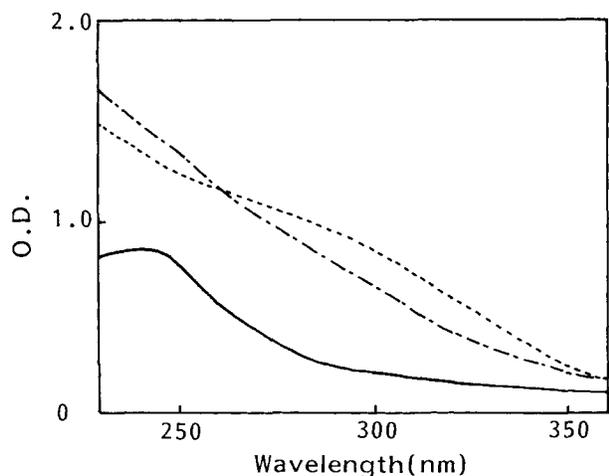
Sample	Preheating (min)	Press			Cooling	
		Pressure (kgf/cm <sup>2</sup> )	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)
HDPE	1	30	160	3	20–30	3
LDPE	1	20	160	2	20–30	3



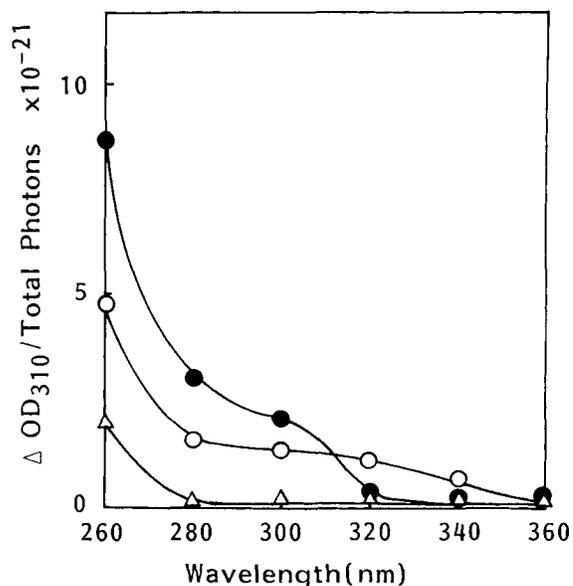
**Figure 1** UV spectra of LDPE (—) containing 1.0 phr of DBDE (---) and 1.0 phr of TBA (.....).

The  $\Delta OD_{310}$  values for each exposed photon are plotted against each irradiation wavelength in Figures 3 and 4. The  $\Delta OD_{310}$  was zero for the samples without additives, except for irradiation with the wavelength at 260 nm. In the case of additive-containing PE samples,  $\Delta OD_{310}$  increased by photoirradiations at specified irradiation wavelengths.

The photodegradation of PE samples was accelerated by the addition of flame retardants, and this acceleration was wavelength dependent, as shown in Figures 3 and 4. This acceleration was also dependent on additive concentration. One example of the effect of concentration on  $\Delta OD_{310}$  is given in Figure 5.

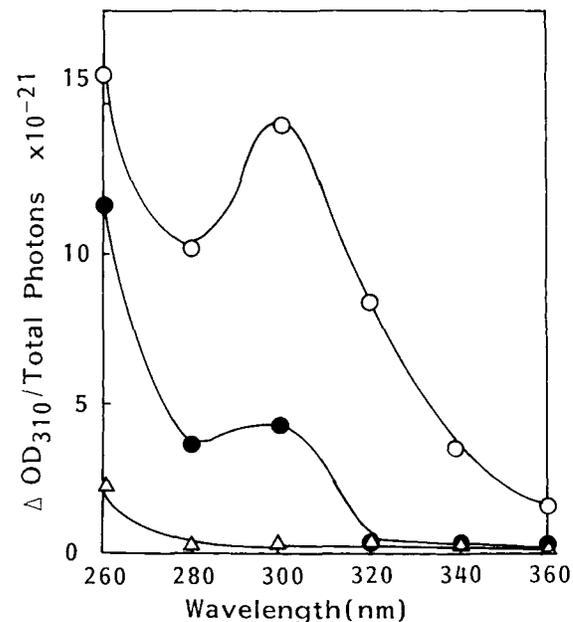


**Figure 2** UV spectra of photoirradiated LDPE (—), LDPE containing 1.0 phr of DBDE (---) and 1.0 phr of TBA (.....). Irradiation wavelength, 300 nm; total photon fluence,  $8.0 \times 10^{19}$  photons/cm<sup>2</sup>.

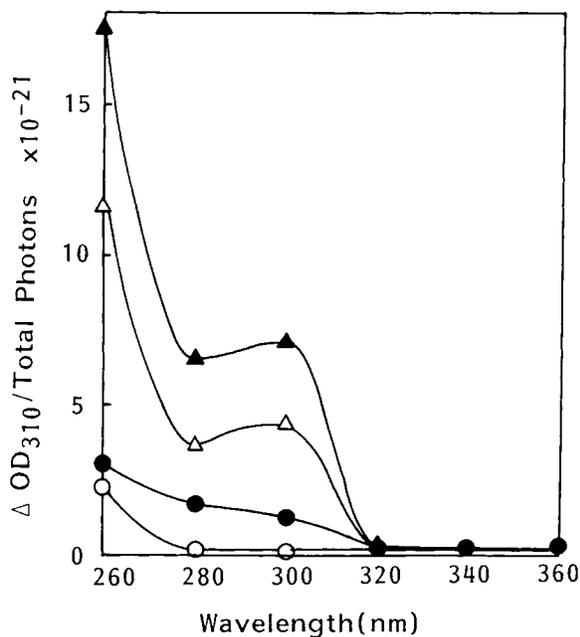


**Figure 3** Changes in the optical density at 310 nm at various irradiation wavelengths.  $\Delta$ , LDPE;  $\circ$ , LDPE-DBDE (1.0 phr);  $\bullet$ , LDPE-TBA (1.0 phr).

The threshold wavelengths of photodegradation were around 320 nm and 360 nm for PE-TBA samples and PE-DBDE samples, respectively. The photoirradiated additive-containing PE samples developed a yellow color at specific irradiation wavelengths. The coloration was found when the



**Figure 4** Changes in the optical density at 310 nm at various irradiation wavelengths.  $\Delta$ , HDPE;  $\circ$ , HDPE-DBDE (1.0 phr);  $\bullet$ , HDPE-TBA (1.0 phr).

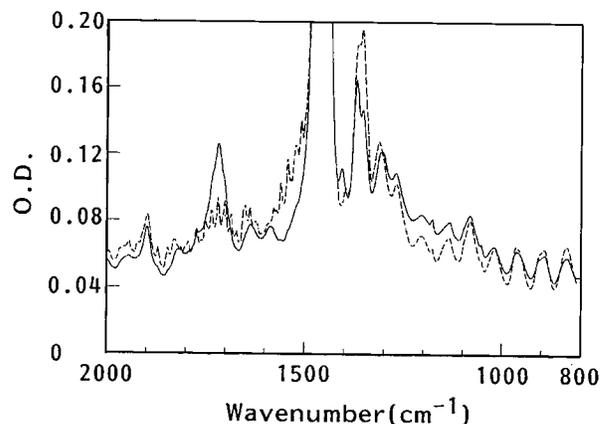


**Figure 5** Effect of additive concentration on changes in the optical density at 310 nm.  $\circ$ , HDPE;  $\bullet$ , HDPE-TBA, 0.5 phr;  $\triangle$ , HDPE-TBA, 1.0 phr;  $\blacktriangle$ , HDPE-TBA, 2.0 phr.

irradiations were carried out with wavelengths below 320 nm for all additive-containing HDPE samples. No coloration was observed for HDPE without additives. The deepest coloration was observed when irradiating the HDPE-containing DBDE sample at 300 nm. This coloration was scarcely observed for LDPE samples, except the LDPE-containing TBA irradiated at 280 nm. The increase in the  $\Delta OD_{310}$  value may be responsible for this yellowing.

Chemical changes produced in the PE films were monitored by FTIR measurements. A typical spectrum obtained by photoirradiation is shown in Figure 6. Carbonyl group formation by photoirradiation was used as a measure of photodegradation of PE samples. Changes in the carbonyl group formation are defined as  $A_{1720}/A_{1720-0}$ , where  $A_{1720}/A_{1720-0}$  represents the ratio of absorbance at  $1720\text{ cm}^{-1}$  ( $\nu_{C=O}$ ) after photoirradiation of that unirradiated sample.  $A_{1720}/A_{1720-0}$  are plotted against irradiation wavelengths in Figure 7 for HDPE samples. Changes in  $A_{1720}/A_{1720-0}$  for LDPE samples were small compared to those for HDPE samples.

The formation of carbonyl groups by photoirradiation is also accelerated by the addition of flame retardants. Carbonyl group formation is wavelength dependent, as shown in Figure 7. The threshold wavelengths for carbonyl group formation are around 320 nm and 360 nm for PE-TBA and PE-DBDE samples, respectively.



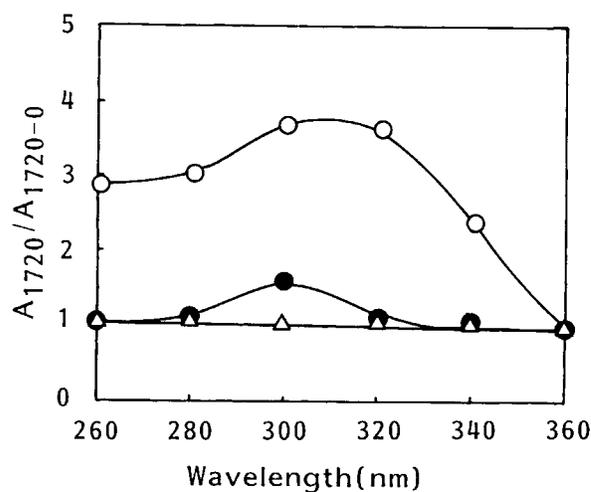
**Figure 6** FTIR spectra of photoirradiated HDPE containing 1.0 phr of DBDE. ----, unirradiated; —, irradiated with 300 nm light. Total photon fluence,  $8.0 \times 10^{19}$  photons/cm<sup>2</sup>.

An estimation of photodegradation of PE can be obtained by GPC measurement.

Changes in the average molecular weight ( $\bar{M}_n/\bar{M}_{n_0}$ ) of photoirradiated PE samples are summarized in Table III.  $\bar{M}_{n_0}$  and  $\bar{M}_n$  are the average molecular weights of polymers before and after photoirradiation.

$\bar{M}_n/\bar{M}_{n_0}$  values are nearly 1.0 in all samples. This experimental result indicates that there are no changes in the average molecular weight of PE by photoirradiation.

We have examined the changes in the molecular weight component using the molecular weight distribution (MWD) curve. Three major molecular



**Figure 7** Changes in the carbonyl index at various irradiation wavelengths.  $\triangle$ , HDPE;  $\circ$ , HDPE-DBDE (1.0 phr);  $\bullet$ , HDPE-TBA (1.0 phr). Total photon fluence,  $8.0 \times 10^{19}$  photons/cm<sup>2</sup>.

**Table III** Changes in the Average Molecular Weight ( $\bar{M}_n/\bar{M}_{n_0}$ ) of Photoirradiated PE

Sample	$\bar{M}_n/\bar{M}_{n_0}$					
	Irradiation Wavelength (nm)					
	260	280	300	320	340	360
LDPE	1.07	1.07	1.06	1.02	1.07	1.01
LDPE-DBDE*	0.98	0.95	1.00	0.93	0.98	1.04
LDPE-TBA*	0.97	1.08	1.07	1.04	1.01	0.93
HDPE	1.04	1.02	1.03	0.99	0.98	1.00
HDPE-DBDE*	1.00	0.99	0.99	1.00	1.04	1.03
HDPE-TBA*	1.04	1.06	1.05	1.07	1.07	1.03

\* Concentration of additive, 1.0 phr.

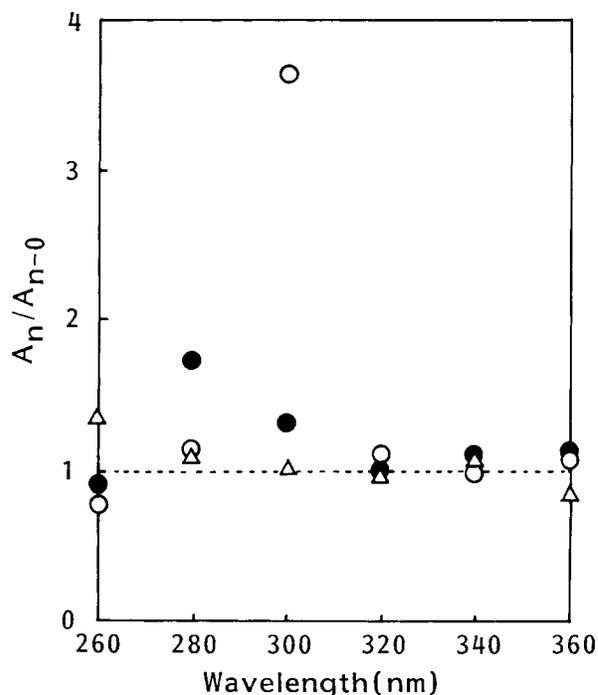
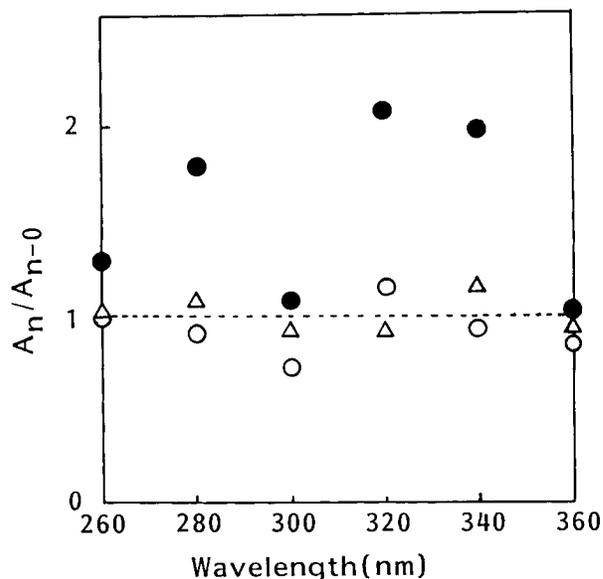
weights for each PE sample were chosen for this treatment: high molecular weight component [ $(M_n = 7 \times 10^5$  (HDPE),  $3 \times 10^5$  (LDPE))], medium molecular weight component ( $M_n = 30,000$ ), and low molecular weight component ( $M_n = 2000$ ). Changes in the molecular weight component ( $A_n/A_{n-0}$ ) are plotted against the irradiation wavelength, where  $A_{n-0}$  and  $A_n$  represent the molecular weight component at a specific molecular weight ( $M_n$ ) before and after photoirradiation.  $A_n/A_{n-0}$  for the high molecular weight component of LDPE and HDPE samples are plotted against the irradiation wavelength in Figures 8 and 9, respectively.

In LDPE without additive, a distinct change in the molecular weight component was not found. By irradiating LDPE-containing DBDE with a wavelength at 300 nm,  $A_n/A_{n-0}$  for the high molecular weight component increased. At the same time,  $A_n/A_{n-0}$  for the low molecular weight component decreased when exposing the sample to 300 nm light.

The experimental results obtained can be explained by the formation of crosslinking. In LDPE-TBA samples, a crosslinking reaction took place by irradiation with wavelengths between 280 nm and 300 nm, because the decrease of the low molecular weight component was accompanied by an increase of the high molecular weight component.

Changes in the  $A_n/A_{n-0}$  value for HDPE without additive were scarcely observed. When HDPE-containing DBDE was irradiated with a wavelength at 300 nm, the  $A_n/A_{n-0}$  value of the high molecular weight component decreased, indicating main-chain scission of HDPE. This result can be supported by FTIR measurement (Figs. 6 and 7).

Carbonyl group formation was favored for the HDPE-DBDE samples irradiated at 300 nm. In HDPE-TBA samples,  $A_n/A_{n-0}$  values of the high molecular weight component increased and those of

**Figure 8** Effect of irradiation wavelength on the changes in the high molecular weight component of LDPE ( $M_n = 3 \times 10^5$ ).  $\Delta$ , LDPE;  $\circ$ , LDPE-DBDE (1.0 phr);  $\bullet$ , LDPE-TBA (1.0 phr). Total photon fluence,  $8.0 \times 10^{19}$  photons/cm<sup>2</sup>.**Figure 9** Effect of irradiation wavelength on the changes in the high molecular weight component of HDPE ( $M_n = 7 \times 10^5$ ).  $\Delta$ , HDPE;  $\circ$ , HDPE-DBDE (1.0 phr);  $\bullet$ , HDPE-TBA (1.0 phr). Total photon fluence,  $8.0 \times 10^{19}$  photons/cm<sup>2</sup>.

the low molecular weight component decreased with irradiation between 260 and 340 nm. These results indicate that a crosslinking reaction may take place due to the addition of TBA. The increase of the high molecular weight component obtained by irradiation at 300 nm is rather small compared with samples irradiated at other than at 300 nm. Main-chain scission of HDPE may participate in this case.

Specific reactivity for additive-containing PE was observed when the irradiations were carried out at 300 nm. The insoluble fraction in hot *p*-xylene was not found in all samples, against our expectation for gel formation. If the irradiations are carried out at higher exposure doses, a more distinct increase or decrease of molecular weight could be detected. As reported in our previous article,<sup>1</sup> we have already obtained the clear molecular weight changes in photoirradiated PSt-DBDE, PSt-TBA, PP-DBDE, and PP-TBA samples at the same exposure dose.

Although the exact mechanism could not be understood fully, photooxidative degradation of PE is accelerated by bromine-containing additives.

## CONCLUSIONS

Photodegradation of LDPE and HDPE containing flame retardants is accelerated by photoirradiation at specified wavelengths. If we adopt  $\Delta OD_{310}$  as a measure of photodegradation, the threshold wavelengths are 320 nm for PE-TBA samples and 360 nm for PE-DBDE samples. These results are also supported by changes in the carbonyl index of photoirradiated PE-DBDE and PE-TBA samples. Main-chain scission is favored at the irradiation wavelength of 300 nm for HDPE-DBDE and

HDPE-TBA samples. Finally, the most effective irradiation wavelengths for crosslinking are found to be 300 nm and 280 nm for LDPE-DBDE and LDPE-TBA samples, respectively.

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