# **Two-Step Photodegradation Process of Poly(ethylene terephthalate)**

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ABSTRACT: After investigating kinetics of the UV photodegradation of PET film samples having a thickness of 4.4  $\mu$ m, we found that the photodegradation process takes place in two steps: a very rapid initial step followed by a normal step. This phenomenon is explained by using a concept of "weak links." We have obtained the rate constants of degradation of the "normal links"  $k_N = 9.0 \times 10^{-7} \, \text{h}^{-1}$  and "weak links"  $k_W = 0.46 \, \text{h}^{-1}$  and the number of scissions of weak links per molecules  $P_W = 0.22$ . For the samples treated by a UV stabilizer, we found  $k_N = 2.0 \times 10^{-7} \, \text{h}^{-1}$ ,  $k_W = 0.11 \, \text{h}^{-1}$ , and  $P_W = 0.27$ . The ratios of the rate constants of the untreated to treated samples are 4.2 for  $k_W$  and 4.5 for  $k_N$ . These results indicate that the UV stabilizer slows down the photodegradation rate of each step to the same extent, but hardly affects the number of scissions of weak links. Importantly, it is an implication that the lifetime of the PET thin film can be prolonged by a factor of 4.2 to 4.5 in the irradiation conditions used after being treated by the UV stabilizer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 306–310, 1999

Key words: poly(ethylene terephthalate); photodegradation; kinetics; UV stabilizer

## **INTRODUCTION**

Poly(ethylene terephthalate) (PET) has been widely used in the form of fibers and films as well as a thermoplastic resin. A considerable problem for their outdoor application is that the light in the 290–400 nm wavelength range of terrestrial sunlight can cause a photolysis of PET, mainly giving rise to a remarkable decrease in molecular weight, that is photodegradation.<sup>1–9</sup> The different mechanisms of photodegradation have been established to account for the outcomes obtained in the previous experimental observations.<sup>5</sup> Importantly, the photodegradation tends to result in a

serious deterioration in mechanical and other properties of PET products, such as loss in strength and elasticity.<sup>1,5, 9–11</sup> For enhancing the ability of PET products to resist UV irradiation, different kinds of the UV stabilizers have been developed and simultaneously used in practical applications. To date, however, all the details of the photodegradation process and how the added UV stabilizer takes its effect on exposure are still not understood, despite the many data published. Furthermore, the increasing outdoor application of PET products requires further exploration of the mechanism and process of UV photodegradation.

In our previous work we have investigated the changes in molecular weight and in mechanical properties with the distance to the exposed surface for the stacked PET films samples irradiated for different times.<sup>9</sup> The results obviously illustrate the surface nature of UV deterioration of

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PET, i.e., the strongest degradation takes place at the exposed surface and the degradation rate decreases with increasing the distance. In this communication, we will report a phenomenon: a twostep photodegradation process occurring in the PET film sample used. In our work, the kinetics of each step of the two-step photodegradation has been studied. Meanwhile, the experimental data obtained from the PET film samples with and without a UV stabilizer were analyzed. Our results can account for how the UV stabilizer used affects the photodegradation at each step, based on analyzing results of the experimental data obtained from PET films with and without the stabilizer.

### **EXPERIMENTAL**

The PET sample used is a commercial film (TORAY LUMIRROR 4YC21) with a thickness of 4.4 mm and a density of 1.397 g/cm<sup>3</sup>. The UV stabilizer used is "Cibafast P," a suspension solution of some chemicals in water, purchased directly from Ciba. The main ingredient in Cibafast P is a derivative of 2,4,6-triiphenyl-1,3,5-triazine, as shown in Scheme 1.

Some PET film samples were treated under pressure in the suspension solution of Cibafast P with a concentration of 55 g/L water at 130°C for 60 min to study the effect of the stabilizer. After treatment, the film samples were washed with water several times and eventually dried in vacuum for 5 h.

The irradiation apparatus used in this work is the same as that used in our previous work.<sup>9</sup> The film samples were bound on the surface of a flexible paperboard with a thickness of 0.5 mm, and through which the light cannot penetrate. Therefore, only one surface of the film samples was irradiated. Irradiation was carried out in air at an operating temperature of 48-56°C, which is lower than the glass transition temperature of PET, with no control of the relative humidity. The fluorescent sunlamp (Toshiba FL20S-E) used has a spectral distribution of the radiation energy at the wavelength range of 280-400 nm and a single maximum of the radiation energy at the wavelength of about 313 nm. Here, it is important to emphasize that an accelerated testing of PET photodegradation was conducted in this work because PET is sensitive to the light in a wavelength around 314 nm.<sup>3</sup>

Solution viscosities of the PET samples before and after irradiation were measured at 25°C in *o*-chlorophenol in an Ostward viscometer. The intrinsic viscosities  $[\eta]$  of the solutions were determined by extrapolating  $\eta_{\rm sp}/c$  vs. the *c* plot to zero concentration. The number-average molecular weights were calculated from the intrinsic viscosities by<sup>12</sup>

$$[\eta] = 3.0 \times 10^{-4} \times M_n^{0.77}.$$
 (1)

### **RESULTS AND DISCUSSION**

Before we present our experimental results, it is worth noting that the intrinsic viscosity measured or the molecular weight calculated from it is an average value of the PET film sample, having a thickness of 4.4  $\mu$ m. This is because of a considerable change in molecular weight in a thin layer of about 15  $\mu$ m, owing to the surface feature of photodegradation of PET, as indicated in our previous work.<sup>9</sup> Therefore, all the parameters that will be presented below are an average value associated with the film thickness. Our results may be different from those published in literature if the film samples having different thickness were used.

In Table I, the intrinsic viscosities of PET film samples with and without the stabilizer are shown as a function of irradiation time *t*. From Table I, we can easily see that the intrinsic viscosities of the treated PET samples  $([\eta]_{tr})$  are always higher than those of the untreated samples  $([\eta]_{untr})$  in the case of the same irradiation time except the data corresponding to t = 0. This difference indicates that the chemicals in the suspension solution of the UV stabilizer have dif-

<i>t</i> (h)	$\left[\eta\right]_{tr}(cm^{3}\cdot g^{-1})$	$\left[\eta\right]_{\mathrm{untr}}(\mathrm{cm}^{3}\cdot\mathrm{g}^{-1})$
0	0.558	0.573
1	0.542	0.538
2	0.535	0.520
3	0.512	0.490
5	0.494	0.459
10	0.487	0.451
20	0.451	0.410
30	0.440	0.402
40	0.418	0.343
50	0.421	0.325
60	0.412	0.318

Table IChanges in Intrinsic Viscosity ofTreated and Untreated PET Films SamplesIrradiated for Different Times

fused into the matrix of PET samples during treating and, hence, take their effect against the UV photodegradation occurred during irradiation. At t = 0,  $[\eta]_{untr} = 0.573 \text{ cm}^3 \cdot \text{g}^{-1}$  of the untreated sample is slight higher than  $[\eta]_{tr} = 0.558 \text{ cm}^3 \cdot \text{g}^{-1}$  of the treated sample. This difference may come from hydrolysis of PET occurring during treating in the water solution of the UV stabilizer.

In Figure 1 the molecular weights,  $M_{nt}$ , of the treated and untreated PET samples are directly plotted against irradiation time t. (The footnote t denotes the irradiation time.) The two solid curves in this figure show the fitting results, which will be discussed later in conjunction with Figure 2. It is significant to note a rapid decreases in molecular weight at t < 10 h, and a slow decrease at t > 10 h for the two samples. This observed result indicates that a rapid photodeg-



Figure 1 Molecular weights after irradiation.



**Figure 2** Average number of chain scissions per molecule after irradiation.

radation has occurred at a time interval of 0 < t < 10 h in the irradiation conditions used. In other words, the photodegradation process of the PET takes place in two steps: a very rapid initial step followed by a normal step. This is a phenomenon similar to those reported in ref. 7. Moreover, it can be seen that  $\bar{M}_{nt}$  of the treated samples are always higher than  $M_{nt}$  of the untreated samples. For example, at t = 60 h,  $\bar{M}_{nt} = 11,890$  for the treated sample and  $\bar{M}_{nt} = 8490$  for the untreated sample. These indicate that the existence of the UV stabilizer in the PET matrix results in a decrease in the number of chain scissions occurring from UV irradiation. In so doing, the  $\bar{M}_{nt}$  of the treated samples is higher.

For easily studying kinetics of the photodegradation of two kinds of samples, the quantity  $M_{n0}/M_{nt}$ -1, indicating the average number of chain scissions per molecules, are plotted against irradiation time t in Figure 2 for the treated and untreated PET samples. Here,  $M_{n0}$  is the molecular weight at t = 0. Here, we can clearly see the change in the quantity  $M_{n0}/M_{nt}$  -1 for the samples with and without the UV stabilizer. At t = 60 h,  $\bar{M}_{n0}/\bar{M}_{nt} - 1$  is reduced from 1.15 to 0.48. According to the theory of random degradation,  $^{13,14}$  the quantity  $\bar{M}_{n0}/\bar{M}_{nt}$  – 1 should linearly increase with irradiation time t. However, the relation between  $\overline{M}_{n0}/\overline{M}_{nt}$  and t in Figure 2 is linear merely at about t > 10 h for the untreated sample and at about t > 20 h for the treated sample, respectively. The relation is nonlinear at 0 < t< 10 h for the untreated sample, and at 0 < *t* < 20 h for the treated sample. This phenomenon has been observed in the previous investigations of the thermal degradation of polystyrene (PS),<sup>15–17</sup> polyethyl-ene (PE),<sup>18</sup> polypropylene (PP),<sup>19,20</sup> and poly-

Table II	Three Ki	netic Para	meters Ob	otained
from Trea	ated and <b>I</b>	<b>Untreated</b>	PET Film	Samples

	$k_W$ (1/h)	$P_W$	$k_N(1/\mathrm{h})$
Treated	0.11	0.27	$2.0 imes10^{-7}$
Untreated	0.46	0.22	$9.0 imes10^{-7}$

(methyl methacrylate) (PMMA),<sup>21</sup> as well as in the investigation of the photodegradation of PS solution.<sup>22</sup> It was attributed to a random chain scission process that took place in two steps, a very rapid initial step, followed by a normal step. The rapid drop of  $\bar{M}_{nt}$  at the initial step has been associated with a concept of "weak links." An equation given by

$$\frac{\bar{M}_{no}}{\bar{M}_{nt}} - 1 = \bar{M}_{n0}k_N t + \frac{\bar{M}_{n0}p_W}{m} \left(1 - e^{-k_W t}\right)$$
(2)

has been suggested for describing the thermal degradation of synthetic and natural polymers containing "weak links" on the main chain.<sup>22-24</sup> In eq. (2),  $K_n$  and  $K_W$  are the rate constants of degradation of the "normal links" and "weak links," respectively, and  $P_W$  is the fraction of "weak links" that initially existed and m is the molecular weight of the repeating unit. The quantity  $P_W = M_{nm}P_W/m$  represents the number of scissions of weak links per molecule. Because the weak links are more easily and readily broken than the normal chain bonds,  $k_W > > k_N$ . The two solid curves in the figure are obtained by fitting the experimental data, and the three parameters obtained thus are shown in Table II for the treated and untreated samples. At the same time, the molecular weights, as shown by the solid curves, for the treated and untreated samples calculated by using eq. (2) and the parameters in Table II are plotted against irradiation time t in Figure 1. From the table we see  $k_N = 9.0 \times 10^{-7}$  h<sup>-1</sup>,  $k_W = 0.46$  h<sup>-1</sup>, and  $P_W = 0.22$  for the untreated sample, and  $k_N = 2.0 \times 10^{-7}$  h<sup>-1</sup>,  $k_W$ = 0.11 h<sup>-1</sup>, and  $P_W = 0.27$  for the UV stabilizer treated sample. Indeed,  $k_W > k_N$ . So, we can conclude that a two-step photodegradation has indeed occurred in our PET samples in the irradiation conditions used.

It is very significant to further compare the three parameters, as shown in Table II, for the treated and untreated sample. First, we show that  $k_N/k_W = 5.5 \times 10^{-5}$  for the treated sample is very close to  $k_N/k_W = 5.1 \times 10^{-5}$  for the

untreated sample. This indicates that the UV stabilizer diffusing into the PET matrix does not change the mechanism of the photodegradation. Second, two rate constants  $k_N$  and  $k_W$  of the treated sample are smaller than those of the untreated one. This indicates very clearly that the photodegradation rate occurring in the treated PET sample is much slower than that occurring in the untreated PET sample in the same irradiation conditions. In other words, the UV stabilizer slows down the photodegradation of PET. Third, the ratios of the rate constants of the untreated sample to the treated sample are 4.2 for  $k_W$  and 4.5 for  $k_N$ , respectively. In consideration of the errors possibly introduced in our sample preparation and in our viscosity measurement, we believe that the ratios of two rate constants are approximately identical. This indicates that the UV stabilizer slows down the photodegradation rate of each step to the same extent. Importantly, it is an implication that the lifetime of the PET thin film can be prolonged by a factor of 4.2 to 4.5 in the irradiation conditions used after treated by the UV stabilizer. Finally, the parameters  $P_W$  of the treated and untreated samples shown in Table II are approximately identical. This is a reasonable result because the number of scissions of weak links in the PET film should remain unchanged after treated with the UV stabilizer. On average,  $P_W$  takes a value of 0.25, meaning one weak link per four macromolecules for the PET used.

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