

Random Chain Scission of Polyethylene Terephthalate by Light Determination of Active Wavelength

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INTRODUCTION

Whenever a polymer film is photolyzed by polychromatic radiation, e.g., sunlight, it is of interest to know which wavelength or wavelength region is contributing most strongly to the bulk photolytic reaction. A study of the photolysis of polyethylene terephthalate¹ has prompted us to describe a method which in the past we have found useful for determining such a "most active wavelength." This method, although somewhat approximate in character, requires a minimum amount of experimental effort. For more exact or more extensive photolysis studies, it may be used as a preliminary screening step.

EXPERIMENTAL PROCEDURE

Five 1/4-mil (0.00063 cm.) Mylar films were arranged in a stack. The stack was stretched on an embroidery hoop and was irradiated in air for 18 hr. under a high-pressure mercury vapor lamp (General Electric Co. BH-6 lamp). A quartz plate chamber filled with circulating water was interposed between the lamp and the film samples to prevent appreciable infrared heating. No ultraviolet or visible-light filter system was employed.

Solution viscosities of the irradiated films and a nonirradiated (original) film were run at 25°C. in trifluoroacetic acid in a Cannon-Fenske viscosimeter. The inherent viscosities, $\langle \eta \rangle = (\ln \eta_{\text{rel}})/c$, were calculated for the $\eta_{\text{rel}} = (\text{solution flow time})/(\text{solvent flow time})$ at a single polymer concentration (0.200 g./dl.).

The optical density (O.D.) of the nonirradiated film was measured against air (Cary spectrophotometer model 11) over the 2500-4000 Å. wavelength range.

RESULTS AND DISCUSSION

The inherent viscosities of the original and irradiated films are presented in Table I. The film

TABLE I

Inherent Viscosities of Irradiated Mylar Films. Solutions in Trifluoroacetic Acid (0.200 g./dl.) at 25°C.

Film $\langle \eta \rangle$, dl./g.	Original	5	4	3	2	1
0.634	0.470	0.452	^a	0.314	0.253	

^a Not measured.

positions i are numbered from $i = 1$ (top of stack) to $i = 5$ (bottom of stack) relative to the incident light direction.

The inherent viscosities (for $\eta_{\text{rel}} \lesssim 1.2$) are, to a good approximation, related to the viscosity-average molecular weights of the films by a Mark-Houwink equation, $\langle \eta \rangle = K \bar{M}_v^a$. The exponent a has not been established for polyethylene terephthalate in trifluoroacetic acid, but it should lie between 0.50 and 1.00. The number of new viscosity-average molecules formed by photolysis per original viscosity-average molecule in film i is $(\langle \eta \rangle_0 / \langle \eta \rangle_i)^{1/a} - 1$. $\langle \eta \rangle_0$ is the inherent viscosity of the nonirradiated (original) film and $\langle \eta \rangle_i$ is the inherent viscosity of irradiated film i .

Light absorption by the film is assumed to obey Lambert's law at all wavelengths involved. Each film has thickness L and an absorption coefficient at wavelength λ of k_λ . If $R_{1\lambda}$ is the energy associated with wavelength λ absorbed (photons/g.) in the upper surface of film 1, the corresponding upper surface energy absorptions of the succeeding films are $R_{i\lambda} = R_{1\lambda} e^{-(i-1)(kL)_\lambda}$.

The wavelength principally responsible for the random chain scission which lowers the molecular weight of the polymer will be designated $\lambda(d)$. To determine $\lambda(d)$ we assume values of $(kL)_{\lambda(d)} = 0.2, 0.4, 0.6, 0.8,$ and 1.0 for the films. $(\langle \eta \rangle_0 / \langle \eta \rangle_i)^{1/a} - 1$ is then plotted in log-log coordinates against $R_{i\lambda(d)} / R_{1\lambda(d)}$ for these assumed $(kL)_{\lambda(d)}$ on the basis of the viscosity data in Table I. Figure 1 is such a plot for these data assuming the extremal exponents $a = 0.50$ (upper set) and $a = 1.00$ (lower set). The best straight line is drawn through the

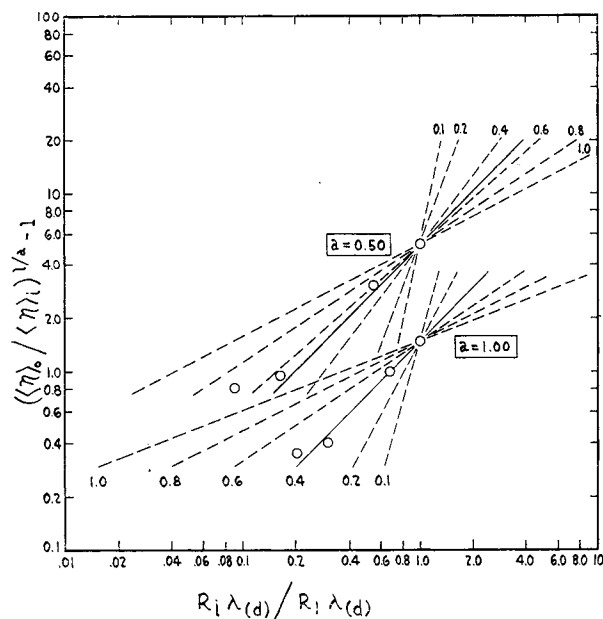


Fig. 1. Number of new viscosity-average molecules per original viscosity-average molecule plotted against relative upper-surface doses. $(kL)_{\lambda(d)}$ values assumed for the lines are shown at the top for viscosity-molecular weight exponent $a = 0.50$ and at the bottom for $a = 1.00$. The solid lines are theoretical.

data points for each assumed $(kL)_{\lambda(d)}$. Calculated points are shown only for $(kL)_{\lambda(d)} = 0.60$, $a = 0.50$ and for $(kL)_{\lambda(d)} = 0.40$, $a = 1.00$.

Theory predicts a unit slope for a plot of $\log [(\langle \eta \rangle_0 / \langle \eta \rangle_i)^{1/a} - 1]$ vs. $\log (R_{i\lambda(d)} / R_{1\lambda(d)})$ plot at low $(kL)_{\lambda(d)}$ values.² The solid lines in Figure 1 represent theory. For $a = 1.00$ the theoretical line coincides with the assumed $(kL)_{\lambda(d)} = 0.40$. For $a = 0.50$ the theoretical line lies at an assumed $(kL)_{\lambda(d)} = 0.50+$. The most likely value of a is about 0.8. The "best" choice for $(kL)_{\lambda(d)}$ is therefore 0.45. From the optical density (O.D.) vs. wavelength curve (not shown) for the nonirradiated $1/4$ -mil Mylar film we find that $(\text{O.D.})_{\lambda(d)} = (kL)_{\lambda(d)} / 2.303 = 0.195$ corresponds to $\lambda(d) = 3140 \text{ \AA}$. It is thus the 3140- \AA wavelength light (or possibly the 3131- \AA line which predominates in the continuous spectrum in this region) which is most effective in producing the chain scission observed.

Obviously approximations and limitations exist in the above treatment. Reflections at the film-air interfaces (approximately 5% at each interface) are ignored. The slight deviation of the theoretical log-log plot in Figure 1 from unit slope at finite kL is not considered. (This is definitely negligible

for small kL .) The treatment is satisfactory only for films having absorption coefficients and thicknesses such that $(kL)_{\lambda(d)}$ is reasonably small. Accurate $\lambda(d)$ determination requires a fairly rapid change of O.D. with wavelength in the region of $\lambda(d)$. The method described above will not discriminate between two wavelengths having essentially equal k_{λ} values.

Ignorance of possible concurrent crosslinking reactions competing with the predominant degradation reaction will in large measure be compensated by the above evaluation procedure unless the crosslinking $(kL)_{\lambda(c)}$ is approximately equal to or is less than $(kL)_{\lambda(d)}$. Comparable quantum efficiencies for these two processes might then cause difficulty. If $(kL)_{\lambda(c)} \gg (kL)_{\lambda(d)}$, infinite network formation can occur at the upper surface of the top film in the stack without appreciably affecting the average bulk properties of even the top film. The high attenuation of the crosslink-inducing wavelengths may then create a very thin "skin" at the upper surface of the top film. If the network structure should penetrate an appreciable fraction of the distance L into film 1, it would be advisable to plot $R_{i\lambda} / R_{2\lambda}$, $i \geq 2$, as abscissa in a graph such as Figure 1. Film 1 would then be merely a "protective filter" for the underlying film stack.

In noting the above-mentioned limitations and difficulties, we must not underestimate the power of the described evaluation procedure. Without knowledge of the integrated light flux, the quantum efficiency of scission, the spectral distribution of the light source, or an exact viscosity-molecular weight relation, it is possible to determine thereby, in many cases, the light wavelength or wavelength region responsible for the principal molecular weight degradation within a given polymer film.

References

1. Osborne, K. R., *J. Polymer Sci.*, **38**, 357 (1959).
2. Shultz, A. R., *J. Chem. Phys.*, **29**, 200 (1958).

Synopsis

A simple procedure is presented for determining the wavelength or wavelength region principally responsible for the random chain scission of a given polymer film under poorly-defined polychromatic irradiation conditions.

Résumé

Un procédé simple est présenté en vue de déterminer la longueur d'onde principalement responsable de la scission statistique de chaîne dans un film de polymère donné soumis à des conditions d'irradiation polychromatique mal définies.

Zusammenfassung

Ein einfaches Verfahren zur Bestimmung der für die statistische Kettenspaltung in einem gegebenen Polymerfilm hauptsächlich verantwortlichen Wellenlänge oder des ent-

sprechenden Wellenlängenbereiches unter schlecht definierten, polychromatischen Bestrahlungsbedingungen wird angegeben.

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