Fluorescence Measurements on the Photooxidation of Poly(ethyleneterephthalate) Films and a Photoselective Effect

M. Hennecke*, I. Keck, E. Lemmert, and J. Fuhrmann

Institute of Physical Chemistry, Technical University of Clausthal, Postfach 1252, D-3392 Clausthal-Zellerfeld, FRG

Dedicated to Prof. Dr. E. Stumpp on the occasion of his 60th birthday

Z. Naturforsch. **44b**, 745–749 (1989); received March 6, 1989

Fluorescence Spectra, Polymer Surface, Photooxidation, Photoselection, Poly(ethyleneterephthalate)

Photooxidation of PET fibres or films creates fluorescent by-products which are separated in wavelength from the intrinsic fluorescence of PET. An experimental technique is described which allows the study of the dependence of photooxidation on wavelength by the fluorescence of only a single specimen. Furthermore, using polarized fluorescence, the conservation of photoselected orientation can be investigated if the photooxidation is carried out with linearly polarized light. Evidence is presented that photooxidation of PET films takes place under partial conservation of the photoselected molecular orientation.

Introduction

The photooxidation of solid organic polymers influences many of their applications, and considerable effort has been made to study its various aspects, *e. g.* the reaction mechanism, the dependence on wavelength, and the influence on the molar mass distribution of the polymer [1]. Among the techniques for the investigation of photooxidation, fluorescence methods offer a unique sensitivity which is sufficient to monitor even a two-dimensional, diluted distribution of fluorescent molecules (fluorophores) at a polymer surface. In recent years, the sensitivity was further improved by a broad application of the single-photon counting method.

Nevertheless, fluorescence techniques in polymer science generally seem to be only a research tool because of some inherent difficulties. For example, commercial polymers usually contain fluorescing impurities or additives whose intensity of fluorescence may exceed the intrinsic fluorescence of the structural unit of the polymer by orders of magnitude [1]. Another common source of error is the light scattering power of polymers, especially semi-crystalline polymers, which sometimes requires ultimate performance of monochromators to separate the exciting light from the fluorescence.

In this paper, various fluorescence techniques are applied on the photooxidation of a film of poly(ethyleneterephthalate) (PET). The fluorescent groups which are formed as by-products by photooxidation of PET at the surface of the film have been identified for a long while [2–4]. The influence of the wavelength of the incident light and of the duration of illumination was also studied, as well as the role of air, nitrogen or oxygen atmosphere [5, 6]. This paper presents a technique to investigate the dependence of photooxidation on wavelength with only a single specimen. Furthermore, the partial conservation of photoselection (principles in [7, 8]) in the photooxidation of PET is demonstrated by illumination with linearly polarized light.

Experimental

Poly(ethyleneterephthalate) films

The material was an isotropic PET film (PET V08115) of 200 μm in thickness supplied, additive free, by Kalle AG, Wiesbaden, FRG. The degree of crystallinity, as determined by DSC, was $\alpha = 0.27$ and the glass transition temperature $T_g = 348$ K. Polarized excitation and fluorescence spectra [9] and the orientation behaviour of the intrinsic fluorophores of the PET film [10] have already been published; the main conclusions are in agreement to other papers [11, 12]. Fluorescence measurements using low-crystalline Mylar PET of low additive content (Du Pont de Nemours S.A., Luxembourg) showed no difference to PET V08115 in the normalized fluorescence spectra.

* Reprint requests to Dr. M. Hennecke.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0932–0776/89/0700–0745/$ 01.00/0

Fluorescence equipment and measurements

Corrected excitation and fluorescence spectra (also considering the polarizers) were obtained by means of a Perkin-Elmer MPF44 spectrofluorimeter specially equipped for polarized fluorescence measurements of solid samples [13]. The emission anisotropy r

$$r = \frac{I_{VV} - I_{VH}}{I_{VV} + 2I_{VH}} \quad (1)$$

was corrected for the instrumental polarization sensitivity by the method described [13]. V and H denote the vertical and horizontal positions of the polarizers in the excitation (first subscript) and the fluorescence (second subscript) beam. In Figs. 1 and 2, the position H of the polarizers is in plane. In the case of an isotropic film with diluted, immobile fluorophores, $r = r_0$, where r_0 is the fundamental anisotropy of the fluorophore.

Photooxidation and its proof by fluorescence scanning

Photooxidation of polymer films was executed in the experimental set-up described in Fig. 1. Using this polychromatic technique [14], the optical spectrum of the mercury lamp is imaged at the specimen with each of its sharp emission lines at a different position. The attribution of the mercury lines to a coordinate at the specimen and the spectral resolution can easily be verified by introducing a photographic film instead of the polymer. According to the dispersion of the quartz prism and the selected optical mapping, there is a distance of 14 mm between the slit-images of the 578 nm Hg line and the 254 nm line at the specimen.

The fluorescent products of photooxidation are analyzed by scanning over the specimen with the sample mounting device shown in Fig. 2 at constant wavelengths of excitation and fluorescence. In order to obtain better local resolution, the peripheral rays of the excitation beam in the MPF 44 spectrometer were stopped by an additional diaphragm (at the cost of intensity). As a consequence, the overall spectral resolution of the scanning curves (see Fig. 3) is not determined by the spectrometer, but by the slit width of the illumination apparatus.

Polarized excitation and fluorescence spectra (see above) can be recorded at any position across the scanning distance.

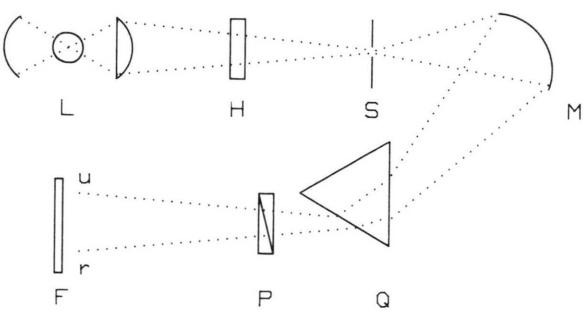

Fig. 1. Schematic diagram of the illumination apparatus for photooxidation. L: 200 W mercury lamp with focusing optics; H: heat filter; S: variable slit; M: mirror; Q: quartz prism; P: polarizer (optional); F: polymer film in thermostatable chamber with variable atmosphere; r: red edge, u: UV edge of spectrum.

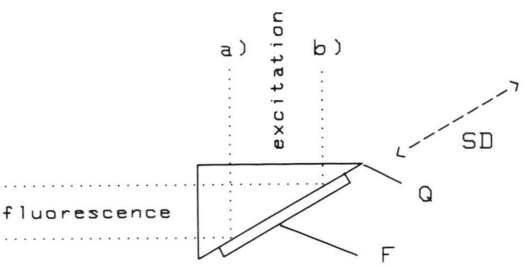

Fig. 2. Specimen mounting device on a sliding platform for incorporation into a commercial spectrofluorimeter. The maximum scanning distance in the indicated direction (SD) is 16 mm; this is scanned by a step motor driven micrometer screw. F: polymer film; Q: quartz prism; a), b): optical ways at both ends of scan. The polarizer direction V is perpendicular to the plane, H lies in the plane.

Results and Discussion

In Fig. 3 the fluorescence intensity scan across an illuminated PET film is shown; the scan was taken at the wavelength of the maximum of fluorescence of the typical by-products of photooxidation in PET (*cf.* Fig. 4). The film was illuminated for 168 h in the set-up of Fig. 1 in air and at room temperature. The slit width was adjusted to 0.4 mm; therefore, the intensity of illumination was low. By comparison to the corresponding scale of the wavelength of illuminating light, one recognizes immediately that the photooxidation is caused by light of about 310 nm, in accordance with literature [4–6]. The baseline in the scanning region 0–8 mm reflects that the intrinsic fluorescence of PET is non-zero at the selected fluorescence wavelength of 460 nm. A flat curve showing no peak is obtained by scanning over the rear surface of the film; this is evidence for the restriction of photooxidation to a surface phenomenon [8, 9], because of the limited depth of penetration of

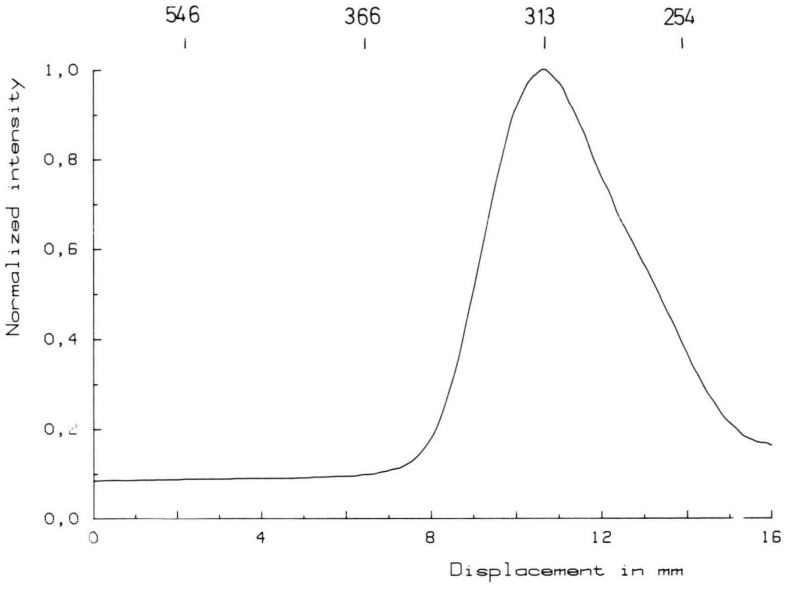

Fig. 3. Fluorescence intensity scan across an illuminated PET film (168 h in the set-up of Fig. 1). Wavelength of excitation $\lambda_{exc} = 290$ nm, slit width 1 nm; wavelength of fluorescence λ_{flu} = 460 nm, slit width 10 nm. Wavelengths of illumination corresponding to the scan coordinate are indicated at the top of the diagram.

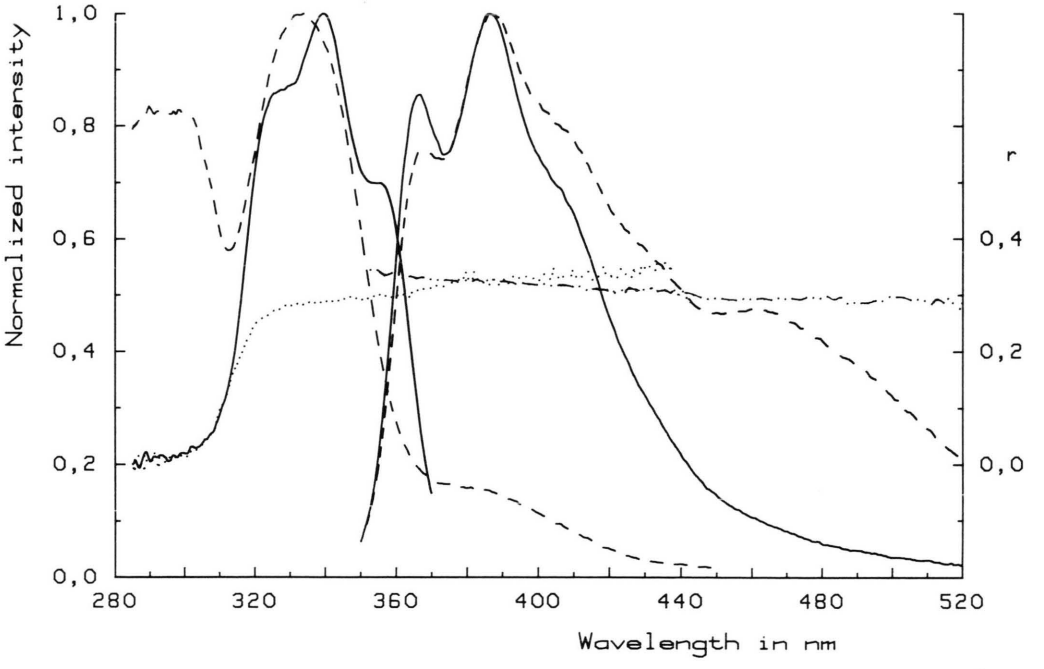

Fig. 4. Excitation and fluorescence spectra of PET films. Continuous lines: film as received; dashed lines: film illuminated for 168 h in the set-up of Fig. 1 (these spectra were measured at the displacement of 10.5 mm, *cf.* Fig. 3). Wavelength of excitation for the fluorescence spectra λ_{exc} = 338 nm, wavelengths of fluorescence for the excitation spectrum λ_{flu} = 385 nm (continuous spectrum), and 460 nm (dashed spectrum), slit widths 3 nm. Dotted curve (right ordinate): degree of polarization r of the dashed excitation spectrum; dashed-dotted curve (right ordinate): r of the dashed fluorescence spectrum. For r of the continuous spectra see [9].

the illuminating UV light of 310 nm and of the exciting light of 290 nm into the PET film.

Excitation and fluorescence spectra taken in the scanning region of 0–8 mm (Fig. 3) are identical to the spectra of PET which was not illuminated [9, 11]. The spectra in the scanning region 9–12 mm (Figs. 3, 4) show the well-known additional bands of the fluorescent by-products of photooxidation [2–4]; at longer times of illumination these peaks become more intense than the intrinsic fluorescence of PET. The relative intensity of the fluorescence of the by-products can further be influenced by the atmosphere (air, O_2, N_2, NH_3) and the temperature of illumination.

If a linear polarizer is introduced into the illuminating beam (see Fig. 1), the absorption probability of the terephthalic acid ester units depends on their molecular orientation relative to the direction of the polarizer (photoselection [7, 8]). If all the intermediate steps of the photochemical reaction leading to the fluorescent end products occur without the participation of rotationally mobile species and without intermolecular transfer reactions (including excitation energy transfer), the photoselected initial orientation distribution would be conserved (to a maximum degree) in the final products. Such behaviour cannot be expected in liquid solutions or in polymers above the glass transition temperature.

Any preferential orientation of the fluorophores generated by polarized photooxidation can easily be proved by measuring additional polarized fluorescence intensities, *e.g.* I_{HH} (see Figs. 1 and 2); instead of rotating the excitation polarizer, this can more definitely be achieved by rotating the film around its normal direction by 90°. Furthermore, the orientation can be noticed at longer times of photooxidation by its linear dichroitic effect on the polarization of the intrinsic fluorescence of PET, if the exciting light or the fluorescence passes through the photooxidized surface. At wavelengths below 400 nm, it cannot be observed by linear dichroism directly because of the small extinction and the overlap of absorption with those of PET itself.

The results of the measurements with the photoselection technique are summarized in Table I. Whilst in the case of unpolarized illumination (or no photooxidation) rotating of the sample has essentially no influence on the values of r, there is a distinct influence caused by polarized illumination. The splitting of the values in the second and fourth column of Table I is almost symmetric with respect to the isotropic values in the preceeding columns. This proves the conservation of photoselected orientation throughout the photochemical reaction sequence, at least as a partial conservation. The sign of the deviations in the second column suggests that the transition moment directions of absorption are preferentially aligned parallely to the 0° (vertical) direction. A quantitative evaluation requires knowledge of the anisotropy of absorption of the photooxidized terephthalic acid ester, *i.e.* its absorption tensor; this is the subject of current investigations.

Table I. Fluorescence polarization r (eq. (1)) of PET films, wavelength of excitation λ_{exc} = 338 nm.

Film position	λ_{flu} [nm]	385[a,c]	385[a,d]	475[b,e]	475[b,d]
0°		0.342	0.318	0.294	0.281
90°		0.343	0.356	0.293	0.301

[a] Intrinsic fluorescence of PET; [b] fluorescence of photoproducts; [c] not illuminated; [d] illuminated with polarized light; [e] illuminated with unpolarized light; error in r: ±0.004. In the film position 0°, the polarizer direction of illumination was parallel to V.

It should be noted that photoselection with linearly polarized light corresponds to a second order orientation coefficient of the absorbing chromophores of $P_2 = 0.40$, at most. P_2 is given by

$$P_2 = 0.5\,(3\,\langle\cos^2\beta\rangle - 1) \qquad (2)$$

with $\langle\cos^2\beta\rangle$ as the $\cos^2$-average of the polar orientation angle β taken over all fluorophores; β is the angle between the principal axis of the film and the transition moment direction of the chromophores.

The value of $P_2 = 0.40$ for the initially absorbing chromophores can easily be exceeded in anisotropic PET films even if natural (unpolarized) light is used for illumination. The role of the photoselection effect in the degradation and stabilization of polymers seems to be, at the moment, of purely academic interest; but it may find some importance when using extremely highly oriented polymers and high degrees of conservation of orientation during the photochemical reactions.

[1] J. F. McKellar and N. S. Allen, Photochemistry of Man-Made Polymers, Applied Science Publ., London (1979).
[2] J. G. Pacifici and J. M. Straley, Polymer Lett. **7,** 7 (1969).
[3] G. Valk, M. L. Kehren, and I. Daamen, a) Angew. Makrom. Chem. **7,** 201 (1969);
b) l.c. **13,** 97 (1970).
[4] M. Day and D. M. Wiles, Polymer Letters **9,** 665 (1971).
[5] M. Day and D. M. Wiles, a) J. Appl. Polym. Sci. **16,** 175 (1972);
b) l.c. **16,** 191 (1972);
c) l.c. **16,** 203 (1972).
[6] K. R. Osborn, J. Polym. Sci. **38,** 357 (1959).
[7] A. C. Albrecht, J. Mol. Spectr. **6,** 84 (1961).
[8] E. W. Thulstrup and J. Michl, Spectroscopy with Polarized Light, Verlag Chemie, Weinheim (1987).
[9] M. Hennecke and J. Fuhrmann, Makrom. Chem. Makrom. Symp. **5,** 111 (1986).
[10] M. Hennecke, A. Kud, K. Kurz, and J. Fuhrmann, Coll. Polym. Sci. **263,** 111 (1988).
[11] N. S. Allen and J. F. McKellar, Makrom. Chem. **179,** 523 (1978).
[12] D. J. Hemker, C. W. Frank, and J. W. Thomas, Polymer **29,** 437 (1988).
[13] M. Hennecke, Habilitationsschrift, TU Clausthal (1989).
[14] R. C. Hirt and N. Z. Searle, Appl. Polym. Symp. **4,** 61 (1967).