

Photochemical Degradation of Glassy Polyesters of Low Softening Point

S. HUSBAND, K. E. RUSSELL, J. A. STONE, and J. K. S. WAN,
Department of Chemistry, Queen's University, Kingston, Ontario, Canada

Synopsis

The photodegradation of polyesters prepared by the reaction of *o*-phthalic, adipic, and "dimer" acids with ethylene glycol has been studied. The polyesters softened at temperatures in the range of 25–50°C. Polymer films were irradiated in air by means of a medium pressure mercury lamp and the extent of formation of COOH groups determined by infrared spectroscopy. The films were also irradiated *in vacuo* and in air by means of a high-pressure mercury lamp, and the volatile products, consisting mainly of carbon monoxide and carbon dioxide, were determined by gas chromatography.

The results are interpreted in terms of simultaneous Norrish type I and type II decompositions of the polyesters. The type I process accounts for the formation of carbon monoxide and carbon dioxide in the absence of air. The enhanced yield of carbon dioxide in irradiations performed in air is ascribed to the formation of hydroperoxide which undergoes further photolysis. The type II process accounts for the formation of COOH groups. The photodegradation of these glassy polyesters parallels that of crystalline poly(ethylene terephthalate) and is relatively unaffected by changes in composition of the aromatic polyester.

INTRODUCTION

Polyesters obtained by the reaction of ethylene glycol and polyhydric alcohols with phthalic anhydride and aliphatic dibasic acids may be used as coating resins alone or in combination with aminoplast resins. The incorporation of "dimer" acid, e.g., the dicarboxylic acid resulting from the dimerization of linoleic acid, gives coatings which are sufficiently flexible to allow postforming of coated metal sheet to the desired shape.¹ Coatings based on polyesters are, however, susceptible to photodegradation. The purpose of this work was to determine the main products resulting from the photodegradation of polyesters which soften at temperatures close to room temperature and to propose mechanisms to account for the formation of these products.

The linear polyesters investigated were prepared from ethylene glycol and mixtures of dibasic acids containing a high proportion of phthalic anhydride. Chemically, these polyesters have much in common with poly(ethylene terephthalate) whose photodegradation has already been studied, but they differ in that the aromatic acid contains *o*-carboxyl groups as opposed to *p*-carboxyl groups and they contain varying amounts of aliphatic dibasic acids. The resulting matrixes are glasses of low softening point. This study reports the effects of these changes on the photodegradation.

EXPERIMENTAL

Materials

Ethylene glycol, phthalic anhydride, and adipic acid were of reagent grade; "dimer" acid (Empol 1018) was a product of Emery Industries. The polyester samples were prepared by standard techniques in an atmosphere of nitrogen; a 5% excess of ethylene glycol was employed and the amount entrained determined from the refractive index of the aqueous solution. The polymer was heated *in vacuo* to 200°C for 6 hr in order to remove very low molecular weight material. A number of polymers were prepared with softening temperatures ranging from 25°C to 50°C. Two samples were subjected to particularly detailed study; sample A contained phthalic anhydride, adipic acid, and "dimer" acid in the molar ratios 90:8:2; and sample B contained phthalic anhydride and adipic acid in the molar ratio 90:10. These possessed glass transition temperatures of approximately 40°C and 45°C, respectively.

Molecular weights of the polyesters were determined from their intrinsic viscosities in chloroform solution at 25°C by means of the approximate relationship²

$$[\eta] = 2.8 \times 10^{-4} M^{0.75} \quad (1)$$

The average molecular weights of A and B were thus estimated to be 3800 and 3000, respectively.

Polyester Films

Films of the various polymers were prepared by the melt method. A weighed sample of polyester was placed between polished Teflon plates in a metal holder and heated on an electrical hot plate. Pressure was applied through the tightening of wing nuts at the corners of the plates. On cooling, the film was readily peeled from the Teflon plates. Its thickness was estimated from its area, weight, and density (1.32 g/ml at 25°C). Films of thickness 50 μm were convenient for infrared study.

Film Irradiation

Irradiations of polyester films for the infrared studies were carried out in air using a Hanovia utility medium-pressure mercury lamp. A parallel beam was obtained by means of a quartz lens. The output of the lamp dropped by 3% during the course of a typical irradiation, as shown by uranyl oxalate actinometry.

For studies of the volatile products, irradiations of films were carried out *in vacuo* and in air using an Osram superpressure mercury lamp (200 W) in a Bausch and Lomb housing. The film was attached to a 1 cm \times 4 cm quartz plate and placed in a quartz cell fitted with metal valves which enabled the tube to be filled with CO₂-free air or to be evacuated. The beam from the lamp was passed through a quartz lens and a quartz cell containing water to minimize heating of the sample.

Product Analysis

Infrared spectra were determined by means of a Perkin-Elmer 180 spectrometer. Normally transmission spectra were obtained; a typical transmission spectrum of sample A in the 3800–2600 cm^{-1} region, before irradiation, is shown in Figure 1. The absorptions at 3540 cm^{-1} and 3290 cm^{-1} are assigned to hydroxyl and carboxyl OH stretching vibrations³ with extinction coefficients of 113 ± 18 and $150 \pm 18 \text{ l. mol}^{-1} \text{ cm}^{-1}$, respectively.⁴ The concentrations of OH and COOH endgroups in sample A before irradiation were estimated to be 0.6M and 0.06M, respectively; i.e., this sample is terminated almost entirely with OH groups derived from the ethylene glycol. Irradiation led to increases in the absorbances at 3540 cm^{-1} and 3290 cm^{-1} which were followed by obtaining infrared spectra at convenient time intervals. Minor changes in film thickness were monitored by means of the absorbance at 3070 cm^{-1} . For film surface studies, attenuated total reflectance spectra were obtained using a Wilks Model 9 internal reflectance accessory with a KRS-5 45° angle crystal.

The volatile products were analyzed by means of gas chromatography. Carbon monoxide and carbon dioxide were determined with thermal conductivity detection, the former on a molecular sieve 5A column at 60°C and the latter on a Porapak Q column at 25°C. Trace products were estimated with a Porapak Q column and flame ionization detection.

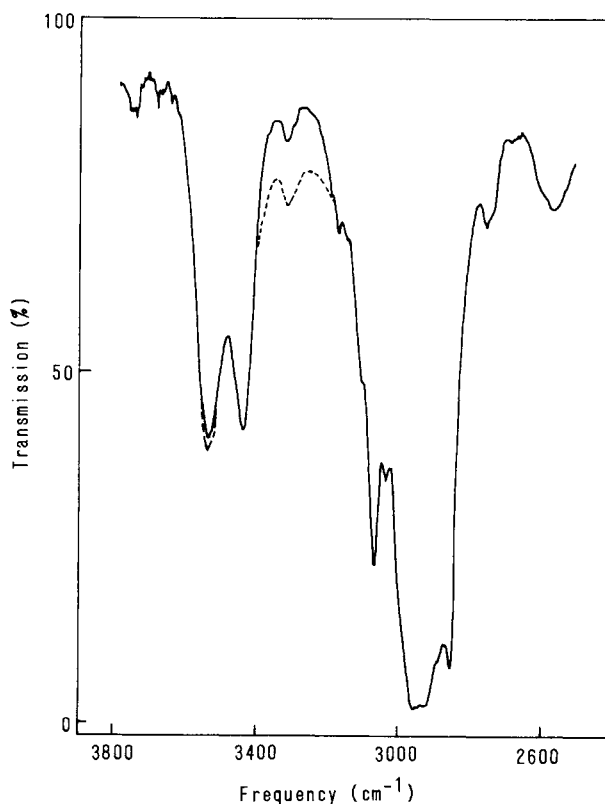


Fig. 1. Infrared spectrum of polyester A in 3800–2600 cm^{-1} region: (—) before irradiation; (- - -) after irradiation for 40 hr.

RESULTS

The polyester samples before irradiation do not absorb visible radiation significantly at wavelengths greater than 350 nm. A film of thickness 50 μm has absorbances of 0.10 at 313 nm, 0.90 at 300 nm, and >2.0 in the 220–297 nm range. Upon irradiation, the absorbance at wavelengths greater than 300 nm increases; and after approximately 20 hr with the medium-pressure lamp or 2 hr with the high-pressure lamp, the film appears light amber. The production of color is more rapid for samples irradiated *in vacuo* than in air. The films slowly become brittle, and eventually small bubbles are observed.

The two main gaseous products are carbon dioxide and carbon monoxide; carbon dioxide is the major product from irradiations performed in air, and carbon monoxide is the major product from those performed *in vacuo*. Minor products include methane, ethylene, and propylene. The yields of the various gases observed after irradiation of a film of sample A, thickness 55 μm and area 4 cm^2 , with the high-pressure lamp for 18 hr are given in Table I. The ratios of yields of CO and CO₂ to the number of moles of incident quanta are 3.8×10^{-4} and 6.5×10^{-4} , respectively, for these irradiations in air. The quantum yields of CO and CO₂ are larger than these values because only a fraction of the incident radiation is absorbed by the polymer sample. The yields of CO and CO₂ per liter of film are 0.21 and 0.35 mole, respectively. Irradiation of the film *in vacuo* gives rise to lower yields of CO and CO₂; after 18 hr, the yields per liter of film are 0.07 and 0.05 mole, respectively. The rates of formation of CO and CO₂ decrease with time. This is illustrated in Figure 2 where the yields of these gases are plotted as a function of time; corrections have been made for the decay in output from the lamp during the course of the experiments. The rate of evolution of gas appears to reach a maximum after about 10 hr of irradiation with the high-pressure lamp and to fall off considerably after about 20 hr of irradiation.

The concentrations of carboxyl and hydroxyl groups in the polymer both increase when films are irradiated by means of the medium-pressure mercury lamp (Fig. 1). The rate of production of COOH groups at the surface of the film as observed by ATR spectroscopy is only slightly greater than that observed via transmission studies, indicating that the degradation occurs fairly homogeneously when a medium-pressure lamp is the UV source. Irradiation for 150 hr causes an average increase of COOH concentration of $0.13 \pm 0.02M$. Typical results

TABLE I
Volatile Products Observed on Exposure of Polyester Film to Ultraviolet Radiation in Air

Product	Yield, ^a mole	Yield, %
CO ₂	7.0×10^{-6}	62.8
CO	4.1×10^{-6}	36.8
CH ₄	3.7×10^{-8}	0.33
C ₂ H ₆	2.6×10^{-9}	0.02
C ₂ H ₄	1.3×10^{-8}	0.12
C ₃ H ₈	3.8×10^{-10}	0.003
C ₃ H ₆	7.2×10^{-9}	0.06

^a Irradiation of film area 4 cm^2 , thickness 55 μm , for 18 hr.

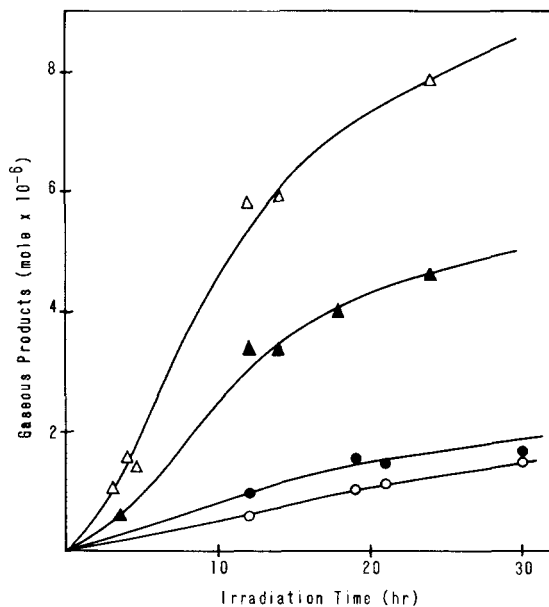


Fig. 2. Yields of CO and CO₂ as function of time of irradiation (high-pressure lamp) of polyester A: (Δ) CO₂ in air; (▲) CO in air; (○) CO₂ in vacuo; (●) CO in vacuo.

for the variation of COOH concentration with time of irradiation are shown in Figure 3. The initial rate of formation of COOH groups is high, but it decreases with time and is relatively low after 50 hr of irradiation. The increase in COOH concentration appears to be independent of the initial COOH concentration in

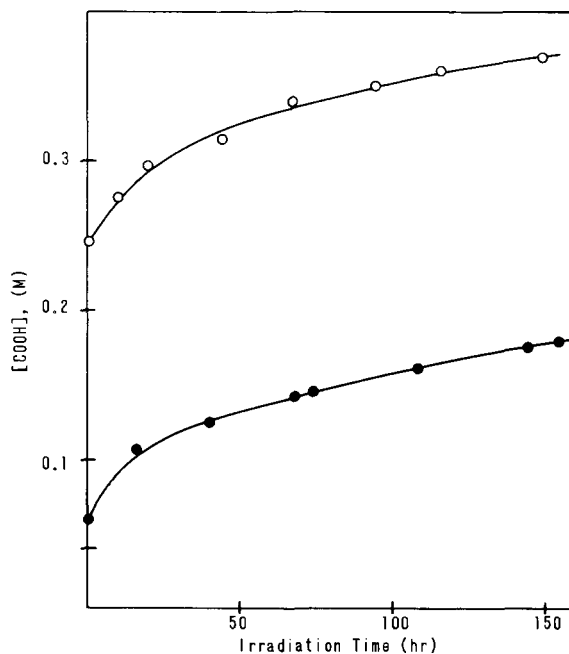


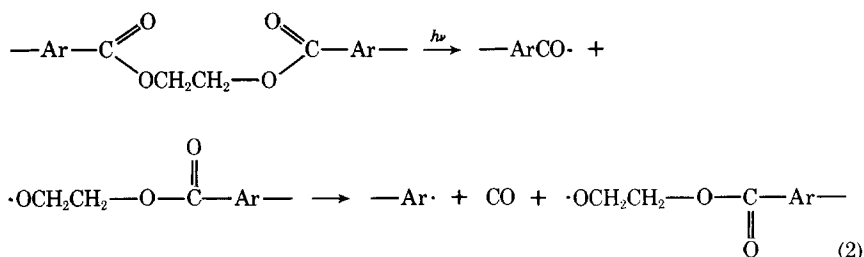
Fig. 3. Concentrations of COOH groups of polyesters A (●) and B (○) as a function of time of irradiation in air (medium-pressure lamp).

the polymer. Sample B has a higher initial concentration of COOH groups than sample A, but undergoes the same increase after irradiation for 150 hr. The concentration of OH groups increased to a somewhat lesser extent than that of COOH groups but otherwise followed the same general pattern. Similar results were obtained with other polyester samples of comparable composition.

DISCUSSION

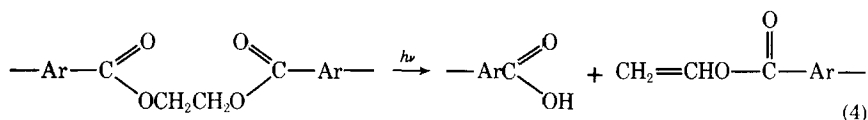
The poly(ethylene orthophthalate) samples A and B undergo photodegradation to give COOH groups, CO₂, and CO as the main identifiable products. The same products are observed in the photolysis of the aliphatic ester ethyl propionate ($\lambda < 240$ nm)⁵ and the aromatic polyester poly(ethylene terephthalate).^{6,7} Photolysis of aromatic esters,⁸ including di-*n*-butyl terephthalate,⁹ yields COOH groups and olefins. The similarities between these results indicate that the initial breakdown of the films of A and B arises from absorption of radiation by the ester chromophores in the polyesters. Absorption by unirradiated films of thickness 50 μ m becomes significant at wavelengths less than 320 nm and is very strong at wavelengths below 300 nm. Thus, radiation of wavelength > 320 nm should cause no significant photodegradation of the polyesters, at least during the early stages of an irradiation; radiation of wavelength 313 nm should be weakly and fairly uniformly absorbed, and radiation of wavelength < 300 nm should be absorbed almost entirely by the front surface of the film. Infrared studies showed that COOH production is slightly higher at the front surface of the film than in the bulk when the source is a medium-pressure mercury lamp. The extent to which nonuniform absorption of radiation from the high-pressure lamp affects the production of CO and CO₂ was not investigated. It was noted, however, in comparable studies with poly(ethylene terephthalate)⁷ that the full radiation from a high-pressure mercury lamp gives approximately the same quantum yields of CO and COOH as radiation of wavelength > 300 nm, but that the quantum yield of CO₂ is significantly increased both for irradiations *in vacuo* and in air.

The main gaseous products of photodegradation of films of polyesters A and B are CO and CO₂. The yields of 0.07 mole CO and 0.05 mole CO₂ per liter of film for 18-hr irradiations *in vacuo* compare with yields of 0.15 mole CO and 0.08 mole CO₂ observed by Day and Wiles in irradiation of poly(ethylene terephthalate) film, thickness 21 μ m, with a 500-W high-pressure lamp.⁷ Under roughly comparable experimental conditions, ethyl propionate gives a CO:CO₂ ratio of 3.8:1.¹⁰ The CO and CO₂ probably arise in Norrish type I decompositions of the polyesters with the production of free-radical intermediates, as shown in eqs. (2) and (3):



low molecular weight and thus contain a higher proportion of endgroups than standard poly(ethylene terephthalate) films, but this did not influence the nature of the gaseous products in any noticeable fashion.

Photolysis of films of A and B in air leads to a build-up of COOH groups; the initial rate of build-up is high, but the rate decreases with time of irradiation. Photolysis of aliphatic esters,⁵ aromatic esters,^{8,9} and poly(ethylene terephthalate)⁷ results in all cases in the formation of COOH groups. A comparable decrease in rate with time of irradiation is observed with the poly(ethylene terephthalate) film.⁷ One source of COOH groups is the type I decomposition, since $-\text{ArCOO}\cdot$ radicals may abstract hydrogen from the polymer as well as decompose to yield gaseous CO_2 . A more likely source is the type II decomposition represented by eq. (4):



The type II decomposition has been shown to be important in the photolysis of di-*n*-butyl terephthalate in air where the quantum yields of 1-butene (0.0050) and COOH (0.0056) are almost equal.⁹ It is also considered to be the main source of COOH groups in the photolysis of poly(ethylene terephthalate) for which the quantum yield is estimated to be 0.0020. The increase in concentration of noncarboxylic OH groups observed in the present work is explained if the alkoxy radicals formed in reaction (2) abstract hydrogen from the polymer. The hydroperoxide intermediate will also contribute to the absorbance in the 3540 cm^{-1} region.

The polymers investigated in this study contain ester groups primarily derived from *o*-phthalic acid but also from adipic and to a small extent "dimer" acid. They are glasses and soften at temperatures just above room temperature. The main aspects of their photodegradation are similar to those of poly(ethylene terephthalate) which has 50% crystallinity. The photodegradation of phthalate polyesters thus appears to be determined primarily by the $-\text{ArCOO}-\text{CH}_2\text{CH}_2\text{OOC}-$ repeating units in the polymer structure and relatively little by (a) the presence of ortho rather than para substituents in the $-\text{Ar}-$ groups, (b) the presence of ester groups derived from adipic and "dimer" acids, (c) the low softening temperatures of A and B as compared with poly(ethylene terephthalate). The polyesters absorb to a significant extent at wavelengths $>300\text{ nm}$ and will undergo a slow photodegradation in sunlight. They do, in fact, degrade when exposed to radiation from the mercury lamps which has been passed through a Pyrex filter, but the rates of degradation are inconveniently low for detailed study.

This research was supported by grants from the National Research Council of Canada and from Queen's University. The authors are greatly indebted to Claire Babineau and Elizabeth Kennedy for their initiative and perseverance in much of the experimental work.

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Received October 8, 1975

Revised February 18, 1976