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THE REACTION OF CARBONYL GROUPS IN POLYETHYLENE FILMS—I

THE REACTION WITH 2,4-DINITROPHENYLHYDRAZINE

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Abstract—A method is detailed for the study of the reaction of 2,4-dinitrophenylhydrazine with polyethylene films containing carbonyl groups. The difference between films u.v.-irradiated in air and those made with a ketone-containing copolymer is studied. There is also a study of the effects of thickness of film. Progress of reaction was monitored by u.v.-spectroscopy. The u.v. absorbance increased with time of immersion in the 2,4-dinitrophenylhydrazine solution, and with increasing thickness of film. An explanation is advanced for the difference between the two types of film; it is related to differences between the distribution of carbonyl groups through the films. Most of the carbonyl groups in the photo-oxidised films made from polyethylene were on the surface. There is evidence that 2,4-dinitrophenylhydrazine can penetrate and react throughout the films.

INTRODUCTION

There have been some reports on the reaction of photo-oxidised [1–3] and chromic acid oxidised [4] polyethylene (PE) films with 2,4-dinitrophenylhydrazine (DNPH). The reaction was monitored by measuring the absorbance at 365 nm. In an earlier study, [5]^{14}C-labelled DNPH was used to follow the reaction of PE oxidised with chromic acid or with oxygen under X-ray irradiation. In these studies, the concentrations and distributions of carbonyl groups were unknown.

The reaction of DNPH with carbonyl groups known to be distributed through a film has not been previously studied. This kind of distribution must be present in films formed from random copolymers. In this paper, a comparison of the reaction of DNPH with ethylene/vinyl ketone (2.2 mole-% ketone) copolymer films, and with photo-oxidised PE film is reported. Study of the effects of film thickness is included.

EXPERIMENTAL

Films

Low density polyethylene (LDPE)(ICI-XDG 33) was used. A commercial sample of a copolymer of ethylene with methylisopropenyl ketone (MIPK) was used. The two polymers had similar densities (0.923 and 0.927 g/cc respectively). The films were extruded to thicknesses of 50, 100 and 200 μm, and contained no additives.

Photo-oxidation of PE homopolymer

The homopolymer was irradiated using a medium-pressure mercury lamp (Hanovia U.V.S.-220, with arc tube 504/4). The films were exposed at ambient temperature ($\sim 25°$) in the atmosphere for 2 hr, at 15 cm from the lamp.

DNPH solution

A standard solution was prepared thus: G.P.R. DNPH (1 g) was refluxed for 1 hr with absolute ethanol (100 ml), hydrochloric acid (5 ml) and water (5 ml), exactly copying Kato's recipe [1–4]. The solution was prepared immediately prior to use.

Reaction conditions

The DNPH solution was placed in a large test-tube and immersed in a water bath at 72°. The attached condenser was stoppered after the solution had reached temperature.

The films were degreased with acetone and then dried in a vacuum oven. The film samples, usually 5 × 2.5 cm, were supported by a glass framework and immersed in the solution. Pieces (1 × 2.5 cm) were cut off at intervals, washed and dried as described below, and the u.v. spectra were recorded.

Each piece was immersed in 95% ethanol (40 ml) for 10 min, and then transferred to a second batch of ethanol (40 ml) for a further 10 min. It was then dried overnight in a vacuum oven at room temperature. This treatment removed the excess DNPH which had dried on the film.

The DNPH solution deteriorated after 4–5 days giving an insoluble black coating, which covered the films and could not be dissolved in ethanol, so that satisfactory u.v. measurements were impossible for times in excess of 3 days although i.r. measurements could be made.

Detection of reaction

The reaction was followed by measurement of the absorbance at 325 nm in the u.v. of the films using a Perkin–Elmer SP800 spectrophotometer. Maximum absorbance was found at 354 nm (Kato quotes 365 nm [1–4]) but it increased so rapidly that the peak went off-scale after a few minutes; it was more practicable to make measurements at 325 nm. The relationship between the absorbances at 325 nm and 354 nm was roughly linear.

Before measurements were taken, a base-line was drawn with the reference beam balanced against the sample beam using unreacted films of the requisite thickness. The unreacted film in the sample beam was then replaced with the reacted film, and the spectrum recorded. The thicknesses of all these films were the same within ± 5 μm.

The pieces of film were Soxhlet extracted with 95% ethanol for 24 hr after the recording of the u.v. spectra, to remove any remaining unreacted DNPH; the spectra were then re-recorded. Infra-red measurements were taken using a Perkin–Elmer 457 Grating spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows plots of absorbance at 325 nm vs time of immersion of films in DNPH solution over a period of 50 hr; results are shown for a film of PE photo-oxidised for 2 hr, a film of copolymer and a film of the original PE.

The results suggest that initially there is a higher concentration of carbonyl groups in the photo-oxidised film. As the time of immersion increases, there is a pronounced levelling off in the plot of the absorbance of the photo-oxidised film, but not for the film of the copolymer.

An i.r. study of the photo-oxidised PE and the copolymer films before reaction with DNPH shows an absorption in the carbonyl stretching region. For the copolymer film, the absorption (1705 cm^{-1}) is ~70%, whereas for the photo-oxidised film (1735–1715 cm^{-1}) it is only ~5%. After 2 days immersion in the DNPH solution, the copolymer absorption decreases to ~60% but the photo-oxidised film shows nearly negligible absorption, indicating that most of its carbonyl groups have reacted with DNPH. Even after 1 week of immersion, the carbonyl absorption of the copolymer film is still substantial, indicating that some of its carbonyl groups react very slowly with DNPH.

An explanation of the differences observed in the u.v. absorbance upon reaction with DNPH (see Fig. 1) is that there is an uneven distribution of carbonyl groups in the photo-oxidised film, and that most of them are near the surface. This conclusion has been reached for polypropylene [6] and for other polymers [7]. Thus the rapid rise in the absorbance would be attributed to the relatively high concentrations of carbonyl groups in the surface layers reacting readily because of their accessibility. The copolymer film shows a steady rise in absorbance with time until decomposition of the DNPH solution becomes the limiting factor. The fact that there is no rapid levelling off in u.v. absorbance is a good indication that the reagent is able to penetrate the film and react throughout it. The limiting of the u.v. absorbance of the photo-oxidised film is most probably due to the absence of reactive groups in the body of the film.

Soxhlet extraction of reacted films reduces the absorption by less than 0.05, which is not significantly greater than experimental error. This fact, in conjunction with the faint colour of the blank, shows that there is little trapped DNPH to interfere with the absorbance measurements. The blank film must contain a few carbonyl groups due to oxidation during processing, and these groups could be responsible for the residual absorbance after Soxhlet extraction.

The fact that after 1 week the carbonyl absorption of the copolymer is still quite marked suggests that the DNPH cannot react with all the carbonyl groups. This effect may be due to steric hindrance caused by the bulky dinitrophenyl group.

Films of various thicknesses were used in order to confirm that DNPH is able to penetrate the film throughout its thickness. The carbonyl groups in the copolymer film are evenly distributed, and so the effect of change in thickness must be to produce an absorbance directly proportional to thickness, providing that the DNPH can penetrate and react throughout the film. The results are shown in Fig. 2 which refers also to the original PE films of similar thicknesses. There is a strong dependence of absorbance on thickness. The ratio of absorbances is very close to 1:2:4, as expected from the ratio of the thicknesses. Reaction must therefore have occurred throughout the film, and it must be concluded that DNPH is able to diffuse through the film.

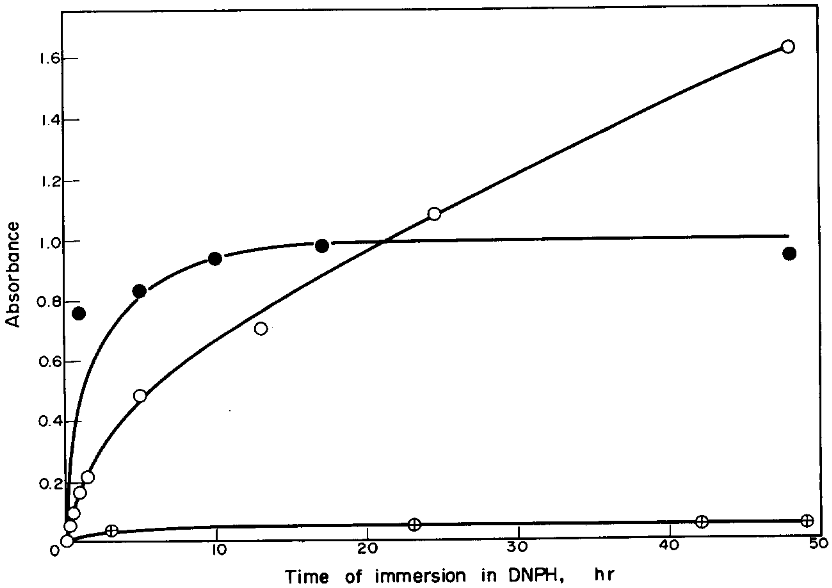

Fig. 1. Plot of absorbance at 325 nm for 50 μm films of the original PE (⊕), photo-oxidised PE (●), and copolymer (○) vs time of immersion in DNPH solution.

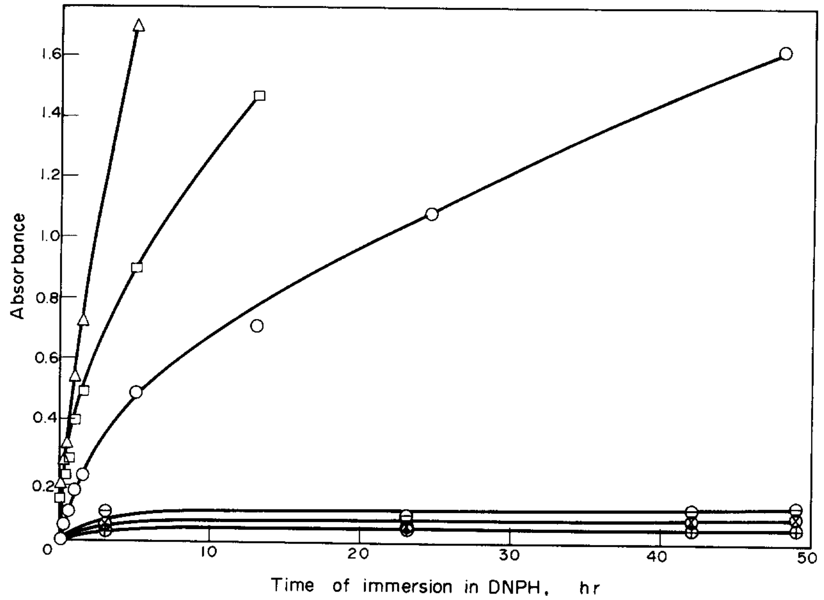

Fig. 2. Plot of absorbance at 325 nm for the original PE films of 50 μm (⊕), 100 μm (⊗), and 200 μm (⊖), and copolymer films of 50 μm (○), 100 μm (□), and 200 μm (△) vs time of immersion in DNPH solution.

The carbonyl groups in the copolymer film are distributed uniformly but the plots in Fig. 1 are consistent with the photo-oxidised film having a non-uniform distribution of carbonyl groups, probably predominantly in the surface layers [6–7]. Thus photo-oxidised films of PE would be expected to show roughly the same absorbance for all thicknesses; results for such films are shown in Fig. 3 which differs markedly from Fig. 2, and shows that the u.v. absorbance of each photo-oxidised film is quite similar, with only a slight increase with increase in thickness. Thus it can be concluded that the carbonyl groups are non-uniformly distributed. The carbonyl absorption of the photo-oxidised films shows only a slight increase with thickness, indicating that the oxidation is independent of thickness. This result suggests that oxidation takes place mainly at the surface of the films, with little reaction inside the film. A similar conclusion on the distribution of carbonyl groups in u.v.-irradiated films of differing thicknesses has been reached using oxygen uptake as the measurement of oxidation [8].

Several studies on the photodegradation of polyethylene [7–12] have shown that the carbonyl absorption

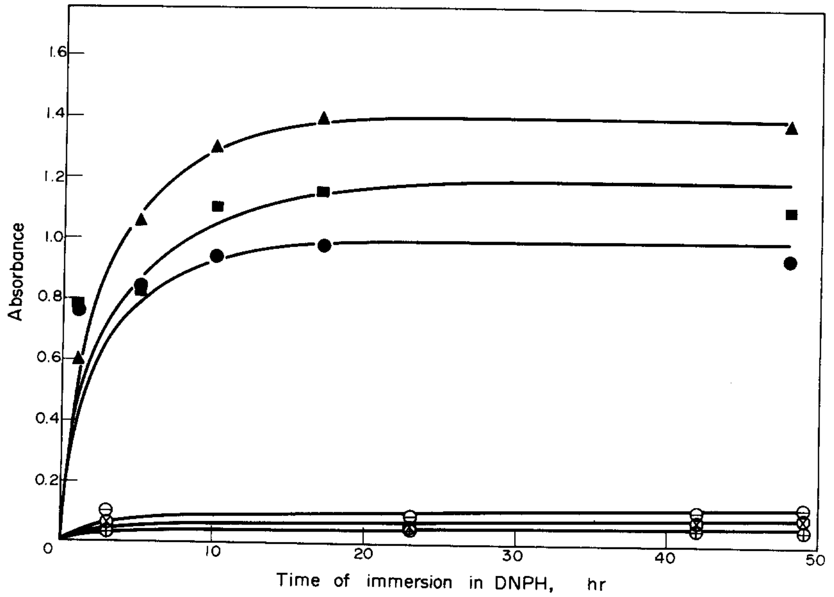

Fig. 3. Plot of absorbance at 325 nm for the original PE films of 50 μm (⊕), 100 μm (⊗), and 200 μm (⊖), and photo-oxidised PE films of 50 μm (●), 100 μm (■), and 200 μm (▲) vs time of immersion in DNPH solution.

can be attributed to several species, viz. ketones, aldehydes, acids, esters, lactones and anhydrides, as well as α,β-unsaturated species. These products have been reported for samples exposed to u.v. for periods of 300–1000 hr. It is not known precisely what groups are present in samples exposed for short periods, as in this study, but there is some evidence for acids.

In the i.r. study of photo-oxidised films, there is a disappearance of the absorption at 1730–1715 cm^{-1}, with development of a peak at 1740–1735 cm^{-1}, attributed to esters produced from acid groups by the HCl-catalysed esterification with the ethanolic DNPH solution. This appearance has been shown to be independent of the presence of DNPH, and further work is in progress.

The reaction of hydrazines with ketones yields hydrazones, and with acids yields hydrazides. The influence of hydrazides would be most significant in the u.v. absorbance, since they have an absorption maximum at ~330 nm [13–14]. There is no indication in this study of a substantial difference in absorbance maximum for the copolymer and the photo-oxidised films, but a significant difference might develop when longer irradiations are involved. This possibility should be examined carefully before drawing firm conclusions.

CONCLUSIONS

1. The u.v. irradiation of a PE film in air produces carbonyl groups which are situated mainly at the surface.
2. DNPH can react with carbonyl groups in a film throughout its thickness, as shown by experiments involving PE containing a co-monomer with carbonyl groups.
3. Some carbonyl groups appear to be unable to react with DNPH, even after extended reaction periods. This is most apparent in the copolymer films.

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