

Formation of 2,4-Dinitrophenylhydrazones and Regeneration of Carbonyl Groups in Polyethylene Film Irradiated with Ultraviolet Light

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Synopsis

2,4-Dinitrophenylhydrazine was reacted on polyethylene films irradiated in air with ultraviolet light. The changes in amount of carbonyl groups and 2,4-dinitrophenylhydrazones formed in the films were inferred by comparing their absorptions in the infrared and ultraviolet spectra, respectively. The amount of hydrazones formed increased with increase in the reaction time, and rates of the increase gradually decreased with increase in the reaction time. A comparison of the change in amount of hydrazones formed in the irradiated films with the change in amount of carbonyl groups formed in the irradiated films and the change in wettability with H-bonding liquids of the irradiated films showed that the amount of hydrazones formed seemed to be affected by amount of carbonyl groups in the surface zone of the film. The carbonyl groups were regenerated from the hydrazones with increase in the regeneration times, and rates of the regenerations gradually decreased with increase in the regeneration times. The regeneration was facilitated by raising the temperature in the levulinic acid solution, by adding dilute hydrochloric acid to the levulinic acid, or by raising the temperature in the levulinic acid solution containing hydrochloric acid.

INTRODUCTION

It has been known¹ that carbonyl groups are formed in polymer films when the films are irradiated in air by ultraviolet light. However, the formation of 2,4-dinitrophenylhydrazones in polymer film when the film is irradiated in air by ultraviolet light has received relatively little attention. Therefore, in previous reports,²⁻⁴ the formation of 2,4-dinitrophenylhydrazones in irradiated polystyrene films, the regeneration of carbonyl groups from the 2,4-dinitrophenylhydrazones on the irradiated films, and the spectral changes in the ultraviolet and infrared spectra by formation of 2,4-dinitrophenylhydrazones in irradiated polyethylene films has been reported. In this paper, the effect of time of reaction between 2,4-dinitrophenylhydrazine and irradiated polyethylene film on the formation of 2,4-dinitrophenylhydrazones in the irradiated film, a comparison of the change in amount of 2,4-dinitrophenylhydrazones formed in the irradiated polyethylene films with the change in amount of carbonyl groups formed in the irradiated films and the change in wettability with H-bonding liquids of the

irradiated polyethylene surfaces, and the regeneration of carbonyl groups from 2,4-dinitrophenylhydrazones in the irradiated polyethylene films are described.

EXPERIMENTAL

Polyethylene Films. Low-density polyethylene film (density 0.926 g/ml, thickness 0.10 mm) received from Nippon Olefin Company was used in this work. The film contained no additives.

Irradiation of Polyethylene Films. A low-pressure mercury lamp (Ushio UL 2-1SQ) was used which emits more than 90% of its light at 2537 Å. No filter was necessary. Every sample was exposed at a distance of 6 cm from the Ushio lamp in air. The temperature in the atmosphere was maintained at about 20°C during the irradiation.

Formation of 2,4-Dinitrophenylhydrazones in Irradiated Polyethylene Film. The reagents were prepared by the method carried out in previous work.² 2,4-Dinitrophenylhydrazine solution was prepared by mixing the reagents at 2,4-dinitrophenylhydrazine, 1 g, hydrochloric acid, 5 ml, water, 5 ml, and ethyl alcohol, 100 ml. The solution was prepared just before use in every experiment. The irradiated films were immersed in the 2,4-dinitrophenylhydrazine solutions and removed from the hydrazine solutions after 5 min had elapsed. The films were repeatedly washed with ethyl alcohol until the hydrazine IR absorption at 1200 cm^{-1} band had disappeared, and dried.

Absorption Spectra. Ultraviolet absorption spectra of all the samples were recorded by means of a Hitachi Model EPS-3 recording ultraviolet spectrometer. Infrared absorption spectra of all the samples were recorded by means of a Hitachi Model EPI-G₂ infrared spectrometer.

Measurement of Effect of Reaction Time on Formation of 2,4-Dinitrophenylhydrazones. The polyethylene films were irradiated for 8 hr. The irradiated films were immersed in 2,4-dinitrophenylhydrazine solutions, removed from the hydrazine solutions after different periods of time had elapsed, and washed and dried. The absorptions⁴⁻⁶ of 2,4-dinitrophenylhydrazones at 365 $\text{m}\mu$ in the films were measured, and the change in the amount of hydrazones formed in each film was determined by comparing their absorptions.

Measurement of Effect of Irradiation Time on Formation of Carbonyl Groups. The polyethylene films were irradiated for different periods of time. The intensity of absorption^{4,7} at 1715 cm^{-1} in the each film was measured. The calculation of absorbance was done by the baseline method. The baseline of the absorption band was drawn so as to join neighboring minima of the absorption curve. The change in the amount of carbonyl groups formed in each film was determined by comparing their absorptions.

Measurement of Effect of Irradiation Time on Formation of 2,4-Dinitrophenylhydrazones. The 2,4-dinitrophenylhydrazones were formed in the films irradiated for different periods of time. The absorptions at 365 $\text{m}\mu$ in

the films were measured, and the change in the amount of hydrazones formed in each film was determined by comparing their absorptions.

Measurement of Effect of Irradiation Time on Change in Critical Surface Tension. The critical surface tensions of surfaces of films irradiated for different periods of time were obtained by the method carried out in previous work.³

Regeneration of Carbonyl Groups. Levulinic acid solution A was prepared by adding 1 volume of water to 9 volumes of melted levulinic acid. Levulinic acid solution B was prepared by adding 1 volume of 1.0*N* hydrochloric acid to 9 volumes of levulinic acid. The 2,4-dinitrophenylhydrazones were formed in polyethylene films irradiated for 6½ hr. The film-formed 2,4-dinitrophenylhydrazones were immersed in the levulinic acid solutions heated at 14°, 40°, and 70°C. The films were then removed from the levulinic acid solutions after different periods of time had elapsed, washed by the method carried out in previous work,³ and dried. The absorptions at 365 mμ in the films were measured and the change in the amount of carbonyl groups regenerated from the hydrazones in the each film was determined by comparing their absorptions.

RESULTS AND DISCUSSION

Effect of Reaction Time

The spectral changes near 365 mμ in the ultraviolet spectrum caused by formation of 2,4-dinitrophenylhydrazones in irradiated polyethylene films are shown in Figure 1, where PE-DNPH is the abbreviation for the polyethylene film-formed 2,4-dinitrophenylhydrazones. Plots of A/dl at 365 mμ in PE-DNPH versus times of reactions between 2,4-dinitrophenylhydrazine and irradiated polyethylene films are shown in Figure 2, where A is

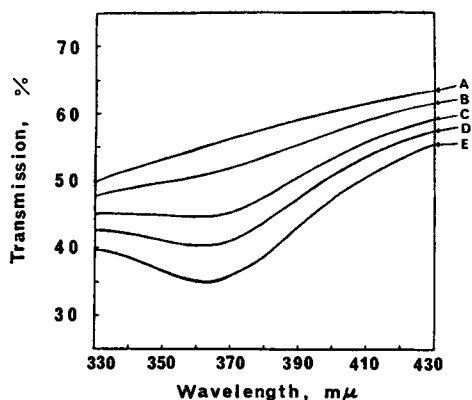


Fig. 1. Ultraviolet spectra of irradiated film and PE-DNPH: (A) irradiated for 8 hr; (B) immersed in hydrazine solution for 1 min; (C) immersed in hydrazine solution for 5 min; (D) immersed in hydrazine solution for 10 min; (E) immersed in hydrazine solution for 30 min.

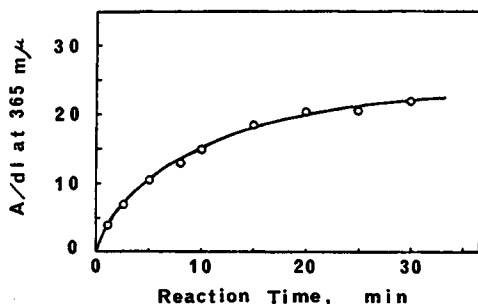


Fig. 2. Plot of A/dl for PE-DNPH at $365\text{ m}\mu$ vs. reaction time.

the absorbance at $365\text{ m}\mu$ in each film, d is the density of the film, and l is the thickness of the film. The absorptions at $365\text{ m}\mu$ increased with increase in reaction time, and the rates of the increase of the absorptions gradually decreased with increase in reaction time. The increases in absorption at $365\text{ m}\mu$ continued above about 30 min.

It has been reported⁸ that water is considered to be absorbed on hydroxyl and ester groups in molecular chains by hydrogen bonding and then replaced by dye, according to mechanism of dyeing of polymers containing hydroxyl and ester groups in the molecular chains. Carbonyl, carboxyl, and ester groups are formed in polyethylene film^{1,4} when the film is irradiated in air with ultraviolet light. Therefore, it can be considered that the following changes occurred in irradiated polyethylene film when the irradiated film was immersed in 2,4-dinitrophenylhydrazine solution. Alcohol and water in the hydrazine solution are absorbed on carbonyl, carboxyl, and ester groups in the amorphous region in the surface zone of the irradiated film by hydrogen bonding, and then the alcohol and the water are replaced by 2,4-dinitrophenylhydrazine, and 2,4-dinitrophenylhydrazones are formed by reaction between the hydrazine and carbonyl groups. The rates of the formation of 2,4-dinitrophenylhydrazones gradually decrease with increase in reaction time, because the penetration of the 2,4-dinitrophenylhydrazine solution into deeper positions buried in molecular chains is hindered by the molecular chains.

Comparison with Amount of Formed Carbonyl Groups and Wettability

Plots of absorptions of carbonyl groups at 1715 cm^{-1} versus irradiation times are shown in Figure 3. The absorptions at 1715 cm^{-1} increased with increase in irradiation time, and rates of increase of the absorptions gradually decreased with increase in irradiation time. The rates of increase of absorptions at 1715 cm^{-1} after about 7 hr were lower than the rates of increase of absorptions at 1715 cm^{-1} within about 7 hr. It seems that carbonyl groups increase with increase in irradiation time and rates of increase of the carbonyl groups decrease with increase in the irradiation time.

Plots of A/dl at $365\text{ m}\mu$ in PE-DNPH versus irradiation times are shown in Figure 4. The rates of increase of absorptions at $365\text{ m}\mu$ after about 1 hr were higher than the rates of increase of absorptions at $365\text{ m}\mu$ within

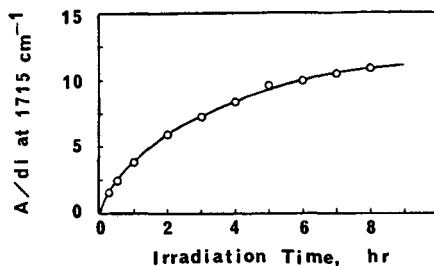


Fig. 3. Plot of A/dl for irradiated films at 1715 cm^{-1} vs. irradiation time.

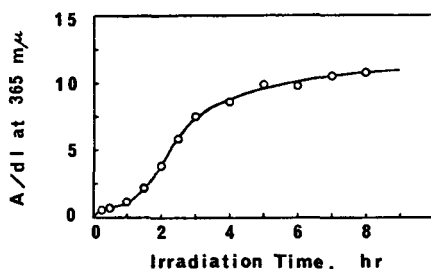


Fig. 4. Plot of A/dl for PE-DNPH at $365\text{ m}\mu$ vs. irradiation time.

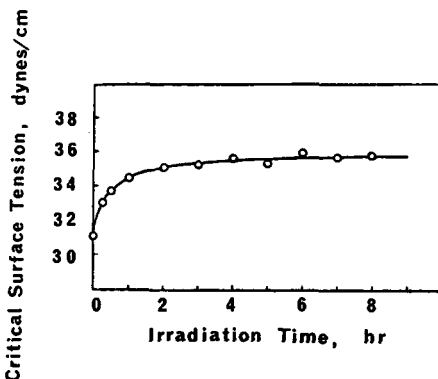


Fig. 5. Critical surface tension on irradiated polyethylene films.

about 1 hr. It is probable that 2,4-dinitrophenylhydrazine solution penetrated easily into spaces among molecular chains in amorphous region in the irradiated polyethylene film because hydrogen bonding groups increased on the molecular chains when the film was irradiated above about 1 hr. The rates of increase of absorptions at $365\text{ m}\mu$ after about 4 hr were lower than the rates of increase of absorptions at $365\text{ m}\mu$ within about 4 hr. It is probable that the rates of increase of carbonyl groups in the surface zones of the films decreased after the films were irradiated for about 4 hr. The increase of absorptions at $365\text{ m}\mu$ continued above about 6 hr.

Plots of critical surface tensions versus irradiation times are shown in Figure 5. The critical surface tension increased with increase in irradiation time within about 4 hr and the rates of the increase gradually decreased

with increase in irradiation time. The increase of the critical surface tension seemed to continue above about 4 hr. It seems that the increase of the critical surface tension was influenced by the amount of carbonyl groups formed on the surface zone of each film.

Regeneration of Carbonyl Groups

The spectral changes near $365\text{ m}\mu$ in the ultraviolet spectrum caused by regeneration of carbonyl groups from 2,4-dinitrophenylhydrazones in irradiated polyethylene films are shown in Figure 6. Plots of A/dl at $365\text{ m}\mu$ versus regeneration times are shown in Figure 7. In the early stages of the regeneration, the absorptions at $365\text{ m}\mu$ decreased with increase in regeneration time. After the early stages of the regeneration, the rates of decrease of absorptions at $365\text{ m}\mu$ gradually decreased with increase in regeneration time. The decrease of absorptions at $365\text{ m}\mu$ in the films continued after

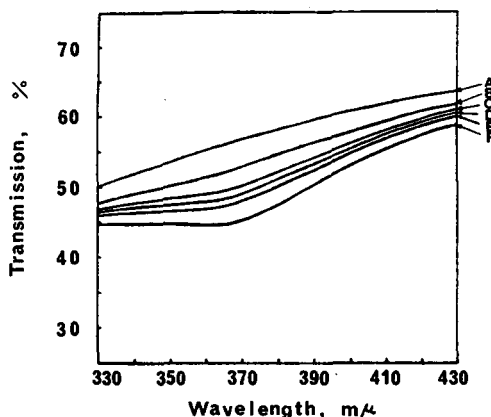


Fig. 6. Ultraviolet spectra of hydrazone bands during regeneration: (A) irradiated for $6\frac{1}{2}$ hr; (B) regenerated in solution B at 70°C for 10 min; (C) regenerated in solution A at 70°C for 10 min; (D) regenerated in solution B at 40°C for 10 min; (E) regenerated in solution A at 40°C for 10 min; (F) PE-DNPH.

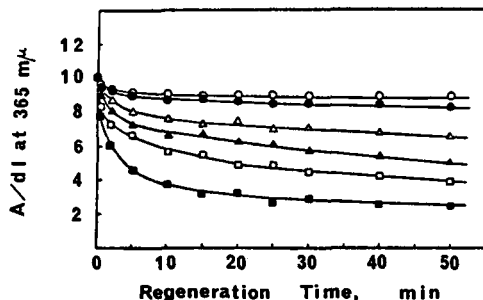


Fig. 7. Plot of A/dl for PE-DNPH at $365\text{ m}\mu$ vs. regeneration time: (○) regenerated in solution A at 14°C ; (●) regenerated in solution B at 14°C ; (Δ) regenerated in solution A at 40°C ; (▲) regenerated in solution B at 40°C ; (□) regenerated in solution A at 70°C ; (■) regenerated in solution B at 70°C .

the films were immersed in levulinic acid solutions for 30 min. It seems that the penetration of levulinic acid solutions into spaces among the molecular chains in amorphous region in the film continue above about 30 min. In the early stages of the regeneration, the decrease in the absorption at $365\text{ m}\mu$ was facilitated by raising the temperature in the levulinic acid solution or by adding dilute hydrochloric acid to the levulinic acid, or by raising the temperature in the levulinic acid solution containing hydrochloric acid.

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