Formation of 2,4-Dinitrophenylhydrazone on Surface Zone of Polystyrene Film Irradiated by Ultraviolet Light. I. Effects on Formation of 2,4-Dinitrophenylhydrazone

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Synopsis

The hydrazones of the acetophenone-type 2,4-dinitrophenylhydrazone, formed by the reaction between 2,4-dinitrophenylhydrazine and carbonyl groups, was formed on the surface zone of irradiated polystyrene film. The changes in the amount of hydrazones formed on the films were inferred by comparing the absorptions in the ultraviolet and infrared spectra. The amounts of hydrazones formed increased with increase in irradiation time within about 3 hr and approached an asymptote with increase in irradiation time upward of about 4 hr. For the samples irradiated for $6^{1}/_{2}$ hr, the changes in the absorptions of the hydrazones stopped in about 3 min after the films were immersed in the 2,4-dinitrophenylhydrazine solution, the amounts of hydrazones formed increased with increase in the amount of benzene in the 2,4-dinitrophenylhydrazine solutions, the amounts of hydrazones formed slightly increased with rising temperature below 60°C in the solutions, and the rate of increase slightly increased with rise in temperature above 60°C in the solutions.

INTRODUCTION

The oxidation degradation of polystyrene film by ultraviolet irradiation has been reported by several investigators.[1-5] It has recently been reported[6] that the structure of the final product formed in the polystyrene film upon irradiation is an acetophenone-type structure. The reactions between 2,4-dinitrophenylhydrazine and carbonyl compounds are well known. However, the formation of 2,4-dinitrophenylhydrazone on the surface zone of polystyrene film when the film is irradiated in air by near-ultraviolet light has not been reported yet. Therefore the reaction between 2,4-dinitrophenylhydrazine and the carbonyl groups formed on the film was investigated. This paper describes the effects of irradiation time, time of reaction between 2,4-dinitrophenylhydrazine and the irradiated film, amount of good solvent in 2,4-dinitrophenylhydrazine solution, and of temperature variation in 2,4-dinitrophenylhydrazine solution on the formation of 2,4-dinitrophenylhydrazone on the surface zone of the irradiated polystyrene films.

EXPERIMENTAL

Materials

The styrene monomer was washed with alkali to remove inhibitor and distilled at 20 mm. Then monomer was polymerized in bulk under an oxygen-free atmosphere without use of catalyst. The polymer was isolated by running the solution into stirred methanol. The polymer was then filtrated and washed with methanol and dried.

Preparation of Films

Films Used for Ultraviolet Absorption Measurements. The thickness of the film to be used was decided by considering the absorption of ultraviolet light into the film. The thin films were prepared by dissolving in benzene the weight of polymer necessary to give the film the thickness required, depositing the solutions on clean quartz plates and allowing them to evaporate slowly at room temperature for 24 hr. They were found to be reasonably uniform. In order to remove the last traces of benzene, the cast films were placed in a high-vacuum system until the benzene absorption at 254 mμ in the ultraviolet spectrum had disappeared. Removing benzene from the film could be much accelerated by pressurizing the system with nitrogen at 300–600 mm, evacuating at intervals, and warming to 60°C. Film thicknesses were measured by weighing a section of known area and checked by measuring the absorption at 2537 Å. Good agreement between the two methods was achieved. These cast films were used for ultraviolet absorption measurements.

Films Used for Infrared Absorption Measurements. The thickness of the polystyrene film to be used was decided by considering the absorption of infrared light into the film. The films were prepared by dissolving in benzene the weight of polymer necessary to give the film thickness required and pouring the solution on clean glass plate. Then, the benzene in the films was removed by using the same method described in the preceding paragraph. Removal of the benzene from the film was identified by disappearance of benzene absorption at 670 cm^{-1} in the infrared spectrum. Film thickness was measured by weighing a section of known area.

Irradiation of Polystyrene Films

Irradiation Source. 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.

Irradiation Procedure. Every sample was exposed at a distance of 6 cm from the Ushio lamp in air atmosphere. For the films used in the infrared absorption measurements, the irradiations were conducted on both sides of the film. The temperature in the atmosphere was maintained at about 20°C during the irradiation.

Reagents and 2,4-Dinitrophenylhydrazine Solution

Recrystallized Kokusan Kagaku Label 2,4-dinitrophenylhydrazine (melting point 199°C) was used in this work. Carbonyl-free ethyl alcohol was prepared by refluxing 600 to 700 ml of absolute alcohol for 2 hr with 5 g 2,4-dinitrophenylhydrazine and a few milliliters of concentrated hydrochloric acid and then distilling off the alcohol. 2,4-Dinitrophenylhydrazine solution was prepared by mixing the reagents at ratios of 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.

Absorption Spectra

Ultraviolet absorption spectra of the samples were recorded by means of a Hitachi Model EPS-3 recording ultraviolet spectrometer. Infrared absorption spectra of the samples were recorded by means of a Hitachi Model EPI-G$_2$ infrared spectrophotometer.

Measurement of Effects

Effect of Irradiation Time. The films used for infrared absorption measurements were irradiated for different periods of time. Cast films were not used, because the transmittance at 237 mμ of the irradiated film amounts to about 0% when the film is irradiated for a long time. The irradiated films were immersed in 2,4-dinitrophenylhydrazine solutions. After 5 min, they were removed from the 2,4-dinitrophenylhydrazine solutions, washed, dried, and measured.

Effect of Reaction Time. Cast films were irradiated for 30 min. The films used for infrared absorption measurements were irradiated for 6$^1/_2$ hr. The irradiated films were immersed in 2,4-dinitrophenylhydrazine solutions, removed from the 2,4-dinitrophenylhydrazine solutions after different periods of time had elapsed, and washed, dried, and measured.

Effect of Good Solvent Mixed in 2,4-Dinitrophenylhydrazine Solution. Cast films were irradiated for 30 min. The films used for infrared absorption measurements were irradiated for 6$^1/_2$ hr. Different amounts of benzene were added to each 2,4-dinitrophenylhydrazine solution. The irradiated films were immersed in the solutions, removed after 5 min, and washed, dried, and measured.

Effect of Temperature on the 2,4-Dinitrophenylhydrazine Solution. The films used for infrared absorption measurements were irradiated for 6$^1/_2$ hr. Cast films were not used, because the thermal expansion coefficient of polystyrene considerably differs from the coefficient of quartz. The irradiated films were immersed in 2,4-dinitrophenylhydrazine solutions heated to different temperatures. After the films were immersed for 5 min, they were removed from the 2,4-dinitrophenylhydrazine solutions, washed, dried, and measured.

Washing of Films. The cast films were taken out of the 2,4-dinitrophenylhydrazine solutions and then repeatedly washed with ethyl alcohol until the hydrazine absorption at the 350-mμ band in each film had disappeared. The films used for infrared absorption measurements were repeatedly washed with ethyl alcohol until the hydrazine absorption at the 1200-cm^{-1} band in each film had disappeared.

Measurements. For the cast films, the absorptions at 237 and 378 mμ in each film were measured, and then the change in the amount of hydrazone formed on each film was inferred by comparing their absorptions. For the films used for infrared absorption measurements, the absorption at 1720 cm^{-1} in each film was measured and the change in the amount of hydrazone formed on each film was inferred by comparing their absorptions.

RESULTS AND DISCUSSION

Absorption Spectra

The spectral changes in the ultraviolet and infrared spectrum are shown in Figures 1 and 2, respectively. The ultraviolet spectrum in the irradiated film showed that an absorption band appears at 237 mμ. The infrared spectrum in the irradiated film showed that the carbonyl band appears at 1720 cm^{-1}. The spectral changes in the ultraviolet and infrared spectrum in the films show the existence of the carbonyl structure of acetophenone in the irradiated films. The ultraviolet spectrum of the polystyrene film (PS–DNPH) showed that 2,4-dinitrophenylhydrazone formed on the surface zone and that the following changes in the spectrum took place. The absorption at 237 mμ decreased because the 2,4-dinitrophenylhydrazine and the carbonyl group formed the hydrazone on the surface zone. The ab-
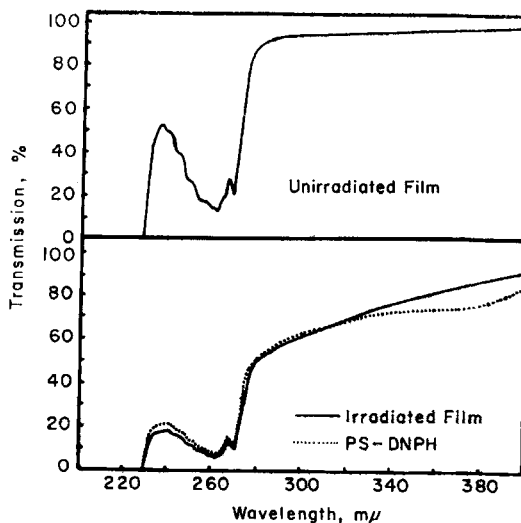

Fig. 1. Ultraviolet spectra of unirradiated film (top), irradiated film (bottom, solid line), and PS–DNPH (bottom, dashed line).
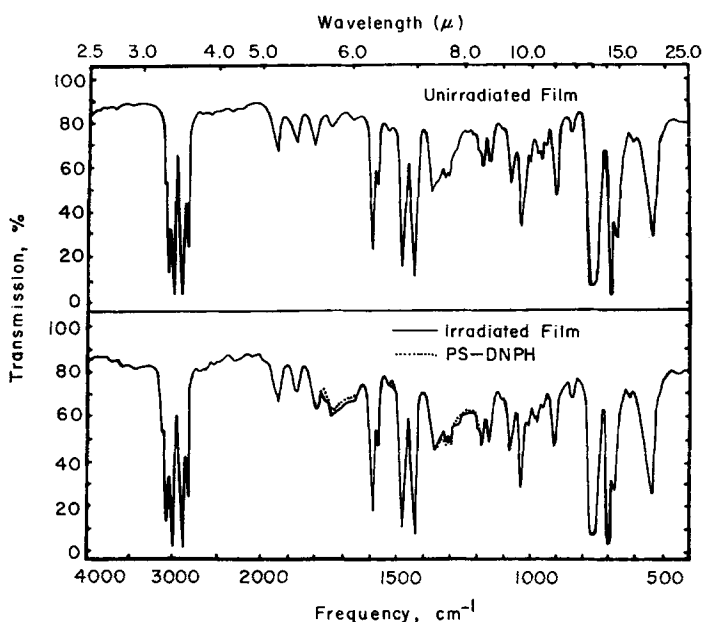
Fig. 2. Infrared spectra of unirradiated film (top), irradiated film (bottom, solid line), and PS–DNPN (bottom, dashed line).

sorption[9] of the hydrazone appeared at 378 mμ. The infrared spectrum of the PS–DNPH showed the following changes in the spectrum. The absorption at 1720 cm^{-1} decreased because the hydrazone formed between 2,4-dinitrophenylhydrazine and the carbonyl group on the surface zone. The absorptions[10] of the phenyl C=C stretching vibration and nitro groups appeared at about 1520 cm^{-1}. The absorptions[10] attributed to the nitro groups appeared at about 1330 to 1310 cm^{-1}. Their changes also showed that 2,4-dinitrophenylhydrazone formed on the surface zone of the film.

Various Effects

Plots of log E'/log E versus irradiation time, reaction time, good solvent mixed in the solution, and solution temperature are shown in Figures 3 to 10, where log E' is the optical density of each irradiated sample and of PS–DNPH and log E is the optical density of each unirradiated sample. In the figures, the open circles show the absorptions of irradiated samples and the filled circles show the absorptions of the samples (PS–DNPH), all demonstrating that 2,4-dinitrophenylhydrazones fromed on the irradiated surface zones.

Effect of Irradiation Time. The result is shown in Figure 3. For the irradiated samples, the absorption at 1720 cm^{-1} increased with increase in irradiation time within about 1 hr and approached an asymptote with increase in irradiation time thereafter, probably because of the limited penetration of 2537-Å light.[11] For the PS–DNPH, the absorptions at 1720
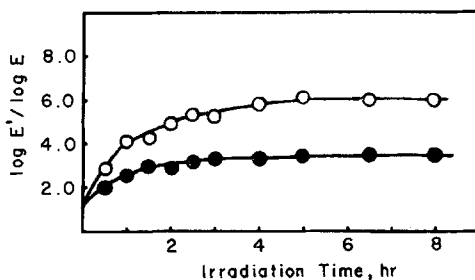
Fig. 3. Log E'/log E for irradiated films and PS–DNPH at 1720 cm^{-1} vs. irradiation time.

cm^{-1} in the PS–DNPH decreased. It is probable that these phenomena were caused by the following: The penetration of 2,4-dinitrophenylhydrazines into the spaces between the molecular chains is hindered, and therefore the carbonyl groups form and accumulate deeps that the reaction between the carbonyl group and 2,4-dinitrophenylhydrazine does not take place. The amount of carbonyl groups newly formed on the surface zone decreases with increase in irradiation time, therefore the absorptions approached an asymptote.

Effect of Reaction Time. The changes in absorptions at 1720 cm^{-1} in the infrared spectra are shown in Figure 4, and changes in absorptions at 237 and 378 mμ in the ultraviolet spectra are shown in Figures 5 and 6, respectively. From these spectra it can been seen that the changes in the absorptions stopped in about 3 min. It is probable that the pene-
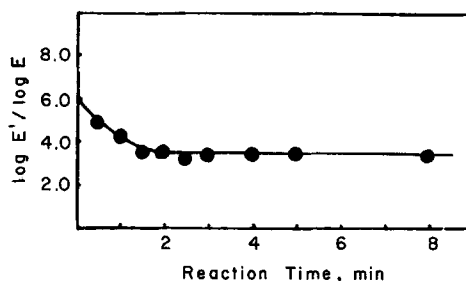

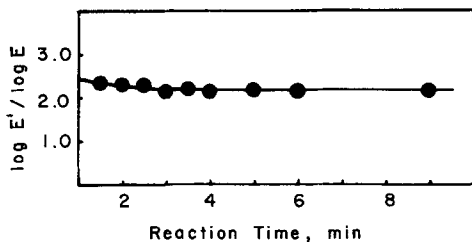Fig. 4. Log E'/log E for PS–DNPH at 1720 cm^{-1} vs. reaction time.

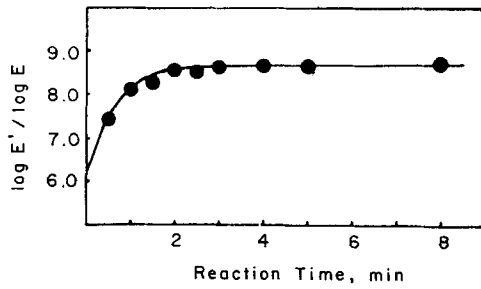Fig. 5. Log E'/log E for PS–DNPH at 237 mμ vs. reaction time.

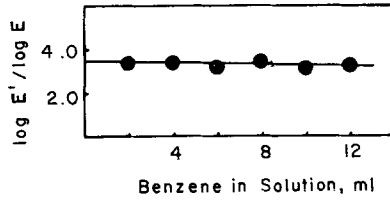Fig. 6. Log E'/log E for PS-DNPH at 378 mμ vs. reaction time.

Fig. 7. Log E'/log E for PS–DNPH at 1720 cm^{-1} vs. volume (ml) of benzene in 2,4-dinitrophenylhydrazine solution (100 ml).
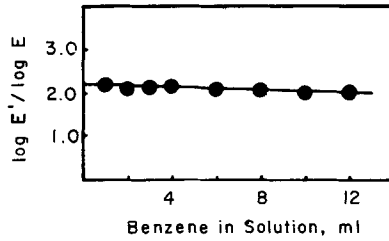

Fig. 8. Log E'/log E for PS–DNPH at 237 mμ vs. volume (ml) of benzene in 2,4-dinitrophenylhydrazine solution (100 ml).
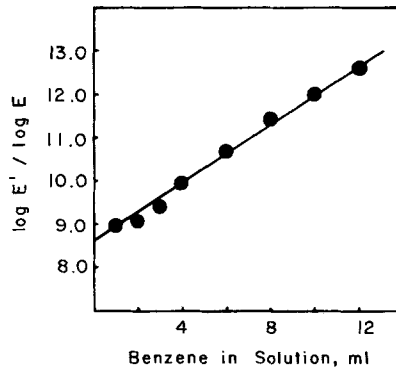

Fig. 9. Log E'/log E for PS–DNPH at 378 mμ vs. volume (ml) of benzene in 2,4-dinitrophenylhydrazine solution (100 ml).
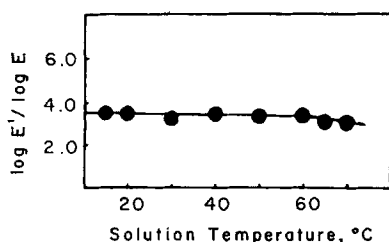
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Fig. 10. Log E'/log E for PS–DNPH at 1720 cm^{-1} vs. temperature in 2,4-dinitrophenyl-hydrazine solution.

tration of 2,4-dinitrophenylhydrazines into spaces among the molecular chains was hindered and that carbonyl groups that did not condense with 2,4-dinitrophenylhydrazines remained.

Effect of Good Solvent Mixed in 2,4-Dinitrophenylhydrazine Solution. The change in absorptions at 1720 cm^{-1} in the infrared spectra is shown in Figure 7, and changes in absorptions at 237 and 378 mμ in the ultraviolet spectra are shown in Figures 8 and 9, respectively. From these spectra it can be seen that the amount of 2,4-dinitrophenylhydrazones formed increased with increase in the amount of benzene. It seems that the penetration of 2,4-dinitrophenylhydrazine solution into spaces between the molecular chains increases with increase in the amount of benzene.

Effect of Solution Temperature. The result is shown in Figure 10. The absorptions at 1720 cm^{-1} slightly decreased with rise in temperature in the solutions below about 60°C, and the rate of decrease slightly increased with rise in temperature in the solutions above about 60°C. It is probable that these phenomena were caused by the following: The penetration of the reagent into spaces between the molecular chains slightly increased with rise in temperature below about 60°C, and the rate of this penetration increased above 60°C.

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