

Formation of 2,4- Dinitrophenylhydrazone on Surface of Polystyrene Film Irradiated with Ultraviolet Light. II. Regeneration of Carbonyl Groups and Comparison with Wettability

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Synopsis

The 2,4-dinitrophenylhydrazones formed on irradiated polystyrene films were regenerated to carbonyl groups by immersing the films in levulinic acid solutions. The changes in the amount of carbonyl groups regenerated from the hydrazones were inferred by comparing the absorptions of the hydrazones at 378 $m\mu$. The carbonyl groups were regenerated from the hydrazones with increase in regeneration times in the early stages of the regenerations and gradually regenerated with increase in the regeneration times thereafter. The regeneration of the carbonyl groups 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. When the polystyrene films were irradiated for different periods of time, the increase in the critical surface tension of the films with increase in irradiation time showed a trend similar to the increase of amount of hydrazones formed on the surface zones with increase in irradiation time.

INTRODUCTION

It is known¹ that 2,4-dinitrophenylhydrazones are formed by reaction of 2,4-dinitrophenylhydrazine with carbonyl groups and that regeneration of the carbonyls from the 2,4-dinitrophenylhydrazones is possible. In a previous report,² it has been shown that 2,4-dinitrophenylhydrazones were formed on polystyrene film irradiated in air with ultraviolet light. However, regeneration of carbonyl groups from 2,4-dinitrophenylhydrazones on irradiated polystyrene film has not yet been reported. Regeneration of carbonyls from 2,4-dinitrophenylhydrazones has been reported by several investigators,³⁻⁷ and Keeney⁸ has reported that saturated carbonyls are easily regenerated by heating levulinic acid solutions containing 2,4-dinitrophenylhydrazones of saturated carbonyls and that addition of dilute hydrochloric acid to the levulinic acid facilitated regeneration of both saturated and conjugated unsaturated carbonyls. In this work, the regeneration of carbonyl groups from 2,4-dinitrophenylhydrazones on irradiated polystyrene film was attempted, and the effects of regeneration time, addition of dilute hydrochloric acid to the levulinic acid, and of

temperature variation in the levulinic acid solutions of the regeneration were investigated.

It is known⁹ that the formation of carbonyl groups on polymer surface when the surface is oxidized by various treatments is correlated with increase in wettability observed with H-bonding liquids. In a previous report,² it has been shown that the amount of 2,4-dinitrophenylhydrazones formed on the surface of polystyrene films when the films were irradiated in air with ultraviolet light was affected by the amount of carbonyl groups formed on the surface by the irradiation. Therefore, when the polystyrene surfaces are irradiated in air for different periods of time with ultraviolet light, it is possible that the change in wettability with H-bonding liquids of the film surface shows a trend similar to the change in amount of 2,4-dinitrophenylhydrazones formed on the surface. In this work, in addition to the problem of regeneration of carbonyl groups from 2,4-dinitrophenylhydrazones on irradiated polystyrene films, a comparison was undertaken of the change in amount of 2,4-dinitrophenylhydrazones formed on the irradiated polystyrene surface with the change in wettability with H-bonding liquids of the irradiated polystyrene surfaces. The results are reported in this paper.

EXPERIMENTAL

Preparation of Films and Plates

Polymer. The polystyrene was prepared by the method carried out in previous work.²

Films. The thickness of the polystyrene film to be used was decided upon by considering the absorption of ultraviolet light at 378 $m\mu$ 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 a clean glass plate. Then the benzene in the films was removed by using the same method described in the previous work.² Film thickness was measured by weighing a section of known area.

Plates. Each 3-mm-thick plate was molded from polystyrene polymer powder in a press at 190°C and 100 kg/cm² pressure. Each plate was removed from the mold and washed with ethyl alcohol and dried. Resulting film surfaces were smooth and clean.

Irradiation of Films and Plates

All samples were irradiated by the method previously described.² The irradiations were conducted on both sides of each film.

Formation of 2,4-Dinitrophenylhydrazones on Irradiated Polystyrene Film

The reagents and the 2,4-dinitrophenylhydrazine solutions were prepared by the method carried out in previous work.²

The irradiated films were immersed in 2,4-dinitrophenylhydrazine solutions and removed after 5 min solutions. The films were repeatedly washed with ethyl alcohol until the hydrazine absorption at the 1200 cm^{-1} band had disappeared, and dried.

Regeneration of Carbonyl Groups

Reagents. 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.

Regeneration Procedure. The polystyrene films were irradiated for 6 $\frac{1}{2}$ hr. The 2,4-dinitrophenylhydrazones were formed on the irradiated films. The films that formed 2,4-dinitrophenylhydrazones were immersed in the levulinic acid solutions heated at 28°, 40°, and 50°C. The films were removed from the levulinic acid solutions after different periods of time had elapsed, and were repeatedly washed with ethyl alcohol until the absorption of 2,4-dinitrophenylhydrazone of levulinic acid at 358 $m\mu$ in each film had disappeared, and then dried and measured.

Measurements. The absorption of the hydrazone at 378 $m\mu$ in each film was measured and the change in the amount of carbonyl groups regenerated from the hydrazones in the each film was inferred by comparing their absorptions.

Comparison with Wettability

Measurement of Amount of 2,4-Dinitrophenylhydrazones Formed on Irradiated Films. The polystyrene films were irradiated for different periods of time, and 2,4-dinitrophenylhydrazones were formed on the irradiated films. The change in the amount of the hydrazones formed on each film was inferred by comparing absorptions at 378 $m\mu$.

Measurement of Critical Surface Tension on Irradiated Plates. Polystyrene plates irradiated for different periods of time were prepared as samples. Different amounts of dipropylene glycol were dissolved in water, and the surface tension of the solutions was measured by the ring method, by applying the correction factors of Harkins and Jordan.¹⁰ A drop of dipropylene glycol solution was carefully placed on the surface of the sample. The contact angle θ of the drop was measured by using an Erma Model G-1 contact angle meter. Further measurements were made by successive additions to the same drop, the mean of five measurements being taken in each case. The measurements of the contact angle varied no more than $\pm 2^\circ$ from the mean. All measurements were made at about 50% R.H. and 20°C, within 10 sec of placing each drop. The contact angles of the other dipropylene glycol solutions were measured in the same way. The surface tension versus the cosine of the contact angle was plotted for each dipropylene glycol solution. The critical surface tension¹¹ was obtained by extrapolating the curve to the abscissa at $\cos \theta = 1$ ($\theta = 0$). The critical surface tensions of all samples were obtained in the same way.

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 spectrophotometer.

RESULTS AND DISCUSSION

Absorption Spectra

The spectral changes at 378 $m\mu$ in the ultraviolet spectrum are shown in Figure 1, where PS-DNPH is the abbreviation for the polystyrene film-formed 2,4-dinitrophenylhydrazones. The absorption² of the 2,4-dinitrophenylhydrazones at 378 $m\mu$ in the film decreased with increase in the regeneration time and approached the absorption of the irradiated film with increase in the regeneration time. The infrared spectrum showed

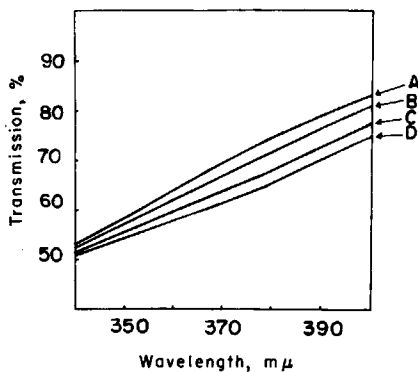


Fig. 1. Ultraviolet spectra of hydrazone band during regeneration: (A) irradiated for 6½ hr; (B) regenerated in solution A at 28°C for 2 min; (C) regenerated in solution A at 28°C for 10 sec; (D) PS-DNPH.

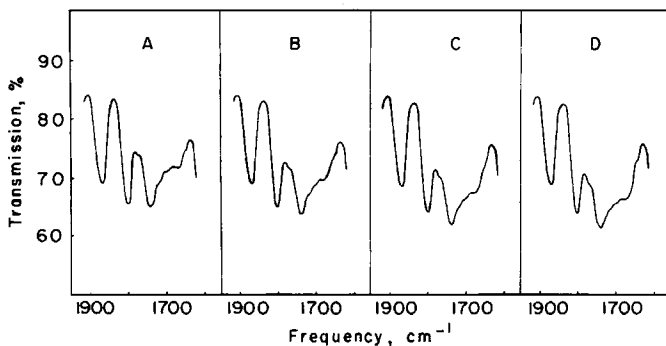


Fig. 2. Infrared spectra of carbonyl band during regeneration: (A) PS-DNPH; (B) regenerated in solution A at 28°C for 30 sec; (C) regenerated in solution A at 28°C for 5 min; (D) irradiated for 6½ hr.

the following changes in the spectrum: The absorption of the carbonyl band at 1720 cm^{-1} increased with increase in the regeneration time as shown in Figure 2. The weak absorptions² of nitro groups at about 1520 cm^{-1} and about 1330 to 1310 cm^{-1} decreased with increase in regeneration time. Their absorptions also approached the absorptions of the irradiated film with increase in regeneration time. The changes showed that the 2,4-dinitrophenylhydrazones formed on the irradiated polystyrene films were regenerated to carbonyl groups by immersing the films in levulinic acid solution.

Regeneration of Carbonyl Groups

Plots of $\log E'/\log E$ at $378\text{ m}\mu$ versus regeneration times are shown in Figures 3 to 5, where $\log E$ is the optical density at $378\text{ m}\mu$ in each unirradiated film and $\log E'$ is the optical density at $378\text{ m}\mu$ in each film with carbonyl groups regenerated from the hydrazones on the film. In the figures, the open circles show the absorptions of the films with carbonyl groups regenerated from hydrazones on the films by immersing the films in solution A, and the filled circles show the absorptions of the films by immersing the films in solution B. In the early stages of the regeneration, the absorptions at $378\text{ m}\mu$ decreased with increase in regeneration time. After the early stages of the regeneration, with increase in regeneration

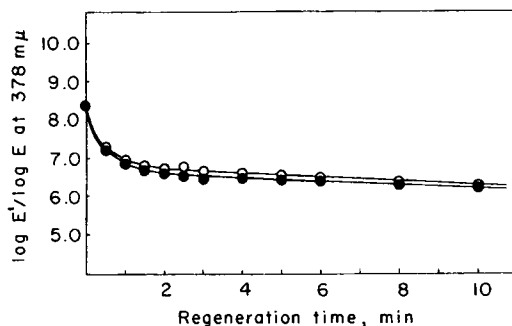


Fig. 3. Regeneration of carbonyl groups at 28°C .

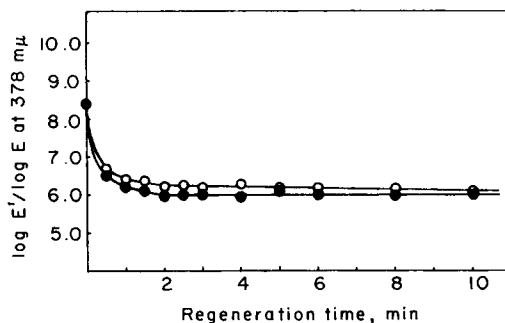


Fig. 4. Regeneration of carbonyl groups at 40°C .

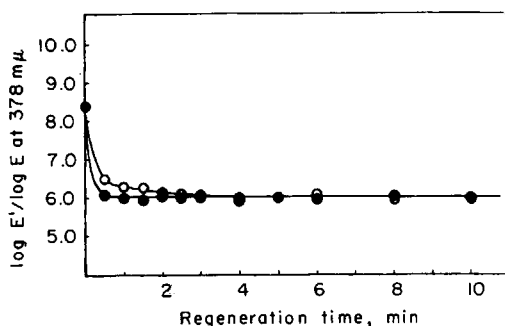


Fig. 5. Regeneration of carbonyl groups at 50°C.

time, the absorptions at 378 $m\mu$ gradually approached the absorption ($\log E'/\log E = 6.0$) of the film irradiated for 6 $\frac{1}{2}$ hr. It is probable that the hydrazones hindered the regeneration of the carbonyl groups of the polymer chains neighboring the hydrazones at first, but the carbonyl groups were gradually regenerated after the early stages of the regenerations. In the early stages of the regeneration, the decrease in the absorption at 378 $m\mu$ 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. Ratios of the absorptions at 378 $m\mu$ in the films regenerated by solution B to the absorptions at 378 $m\mu$ in the films regenerated by solution A seemed to increase with rise in temperature in the levulinic acid solutions in the early stages of the regeneration.

Comparison with Wettability

Plots of critical surface tensions versus irradiation times are shown in Figure 6. Plots of absorptions at 378 $m\mu$ in PS-DNPH versus irradiation times are shown in Figure 7. The critical surface tension increased with increase in irradiation time within about 1 hr and approached an asymptote

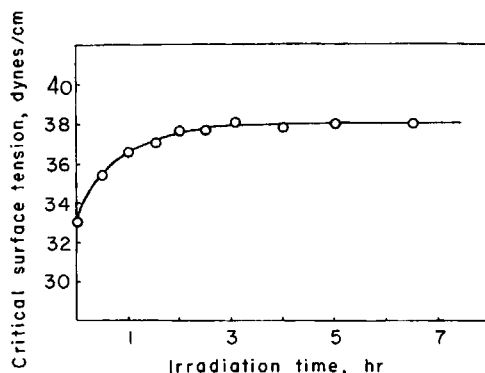


Fig. 6. Critical surface tensions on irradiated polystyrene films.

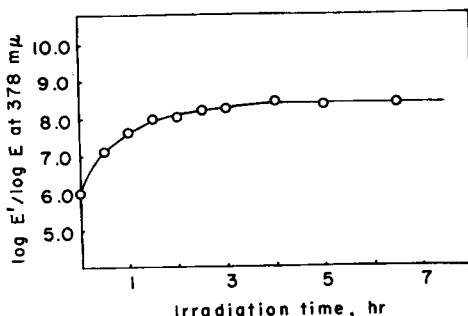


Fig. 7. Log $E'/\log E$ for PS-DNPH at 378 $m\mu$ vs. irradiation time.

with increase in irradiation time. Plots of absorptions at 378 $m\mu$ in PS-DNPH versus irradiation times showed a trend similar to plots of critical surface tensions versus irradiation times. It is probable that these phenomena were caused by the following: The amounts of the hydrazones formed on the surface zones of the irradiated films are influenced by the amounts of carbonyl groups formed on the surface zones², therefore the increase in critical surface tension showed a trend similar to that in the increase in the amounts of hydrazones formed on the surface zones.

References

1. E. Funakubo, *Detection Method on Organic Compounds*, vol. I, Yokendo Press, Tokyo, 1967, p. 255.
2. K. Kato, *J. Appl. Polym. Sci.*, **15**, 2115 (1971).
3. H. H. Strain, *J. Amer. Chem. Soc.*, **57**, 758 (1935).
4. M. Anchel and R. Schoenheimer, *J. Biol. Chem.*, **114**, 539 (1936).
5. V. R. Mattox and E. C. Kendall, *J. Amer. Chem. Soc.*, **72**, 2290 (1950).
6. J. Demaecker and R. H. Martin, *Nature*, **173**, 266 (1954).
7. R. Robinson, *Nature*, **173**, 541 (1954).
8. M. Keeney, *Anal. Chem.*, **29**, 1489 (1957).
9. H. Marumo, *Surface Chemistry of Polymers*, Sangyo Press, Tokyo, 1968, p. 30.
10. W.D. Harkins and H. F. Jordan, *J. Amer. Chem. Soc.*, **52**, 1751 (1930).
11. W. A. Zisman, *Advan. Chem. Ser.*, No. **43**, 1 (1964).

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