*Photoconductivity of Polyacenaphthylene and Its Nitrated Derivatives**

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During the last decade a renewed interest in the photoconductive properties of organic compounds has been shown, and many studies of the photoconductivities of polynuclear molecules and of miscellaneous dyes have been reported.

Recently a few photoconductive polymers have been discovered, such as poly-*N*-vinyl carbazole,[1-4] irradiated polyvinylidene chloride,[5] the thermal conversion product of polyacrylonitrile,[6] polyvinylchloride-leuco base complexes[7] and a polymer containing a triphenylpyrazoline group which has been reported on in a previous paper of ours.[8]

The semiconductivity of charge-transfer complexes of polyacenaphthylene with Lewis acids in the dark was studied by Slough.[9] The present authors, in studying the photoconductive behavior of polyacenaphthylene, have detected that the photoconduction of this polymer is small initially but that it increases with adequate nitration of the polymer.

Experimental

Polymerization of Acenaphthylene.[10]—Ten grams of acenaphthylene was dissolved in 10 ml. of ethyl benzene and emulsified with 100 ml. of a sodium stearate solution.** As an initiator, 0.4 g. of potassium persulfate was added to the emulsion, and then the mixture was agitated in a closed container for 10 hr. at 45°C. The resultant polymer was coagulated from the solution by dropping it slowly into dilute hydrochloric acid. The coagulated polymer was then filtered off, dissolved in benzene, and precipitated into methyl alcohol. Yield, 74%. $[\eta]=0.53$ (at 25°C in benzene).

Nitration of Polyacenaphthylene. — The polyacenaphthylene thus obtained was dissolved in a mixture of benzene (or monochlorobenzene) and glacial acetic acid (or acetic anhydride) ; then the mixture was stirred and concentrated nitric acid (s. g. 1.40) was slowly added. After the addition of nitric acid, the mixture was stirred at a constant temperature and then poured into methyl alcohol. The pale yellow polymer was twice reprecipitated from a monochlorobenzene solution by pouring it into methyl alcohol and then dried at room temperature. The molar per cent of sub-

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1) J. Weigl, Internationales Kolloquim über wissenschaftliche Photographie, Zürich, Sept., 1961.

2) C. Claus, *Photo. Sci. Eng.*, **7**, 5 (1963).

3) H. Mikawa et al., Symposium of the Society of Electrophotography of Japan, Tokyo, June, 1963.

4) Y. Hayashi and A. Inami, 12th Annual Meeting of the Society of Polymer Science of Japan, Tokyo, May, 1963.

5) G. Oster, G. Oster and M. Kryszewski, *J. Polymer Sci.*, **57**, 937 (1962).

6) K. Daito and Y. Oshina, 11th Annual Meeting of the Society of Polymer Science of Japan, Nagoya, May, 1962.

7) H. Greig, *R. C. A. Rev.*, **23**, 413 (1962).

8) K. Morimoto, Y. Hayashi and A. Inami, This Bulletin, **36**, 1651 (1963).

9) W. Slough, *Trans. Faraday Soc.*, **58**, 2360 (1962).

10) U. S. Pat. 2563524 (1951).

** This emulsion consisted of 600 ml. of water, 14 g. of stearic acid, and 6 g. of potassium hydroxide.

TABLE I. NITRATION OF POLYACENAPHTHYLENE

No.	Polymer/HNO_3 mole ratio	Solvent	ml.	Temp. °C	Time hr.	$-NO_2$ group mol. %
2	1/1	Benzene	60	70	2	7.9
		Acetic acid	10			
3	1/1	Acetic acid	10	75	6	16.4
4	1/1	Benzene	60	70	2	28.7
		Acetic acid	30			
5	1/1.2	Chlorobenzene	60	70	2	40.6
		Acetic anhydride	20			

stituted nitro groups were calculated from the nitrogen contents by the Dumas' microanalysis. Table I shows the reaction conditions and results. The degrees of nitration varied from 7.9 to 40.6 molar per cent, according to the condition of the reaction. The photoconductive properties of these nitrated polyacenaphthylenes were studied.

Photoconductivity of Polymers. — The photoconductivity was investigated by using the same sandwich-type cell as was used in another paper.[8] The preparation of the cell was carried out by the following technique; a 10% polymer solution of monochlorobenzene was placed uniformly flat onto a NESA conductive glass plate used as a transparent electrode, and then the solvent was thoroughly evaporated. After the solvent had been evaporated, the specimen film was 10 μ thick. The second electrode was formed thereafter by the vacuum-evaporation coating of aluminum onto the surface of the specimen film.

The sandwich-type cell thus obtained was then placed in a closed glass chamber, which was kept in a vacuo of 10^{-3} mmHg. The applied field of the specimen was 1600 V./cm., taken from a 1.6 V. drybattery source, and the current measurement was carried out with the aid of a vibration-reed electronic micro-micro ammeter (Takeda Riken, type TR-85) and an electronic X-T recorder (Toa-Dempa, type EPR-2). The light source used for measuring the photocurrent of the cell was a 100 W. tungsten lamp.

From the fact that the V-I plots in the dark passed through the point of origin, it may be seen that the dark currents of specimens obeyed Ohm's law and that the contacts between the specimen films and the aluminum layer, or the NESA conductive surface, were perfect.

Relative Surface Potential.—The resistances in the dark were so high and both rise and decay responses were so slow that the ordinary methods of the mere detection of the photocurrents described above were not enough to determine their photoconductive behaviors. In order to reexamine them, the authors introduced a method of comparing the relative surface potential in the light with that in the dark, a method which had been applied in the determination of the photosensitivity of electrophotographic conductive layers. A typical difference between the sandwich-type cell method and the relative-surface-potential method is that the internal field of the specimen in the latter (ca. 10^6 V./cm.) is much higher than in the former (ca. 10^3 V./cm.).

As has been stated in detail in another paper,[4] a thin specimen film 3 μ thick was formed on an aluminum plate. The top surface of a plate was sensitized in the dark to a potential of 200~300 V. (V_d) by negative corona-charging. Actinic light produces electron-hole pairs, which, under the influence of the electric field, are separated; the hole moves to the surface to neutralize a negative charge, and the negative electron is accelerated to the conductive aluminum base, where it neutralizes the induced positive charge. Therefore, the surface potential decreased with the illuminated time to V_l. The relative-surface-potential was defined as a ratio of potential V_l to V_d, and so the time in which V_l/V_d is reduced to one-half represents the half-decay time $(V_l/V_d)_{1/2}$, which serves as an index of photoconductivity. The experimental results obtained when the surface was illuminated with an incandescent light at 1000 luxes are shown in Table II.

Results

Photocurrents under Illumination with an Incandescent Lamp.—*Polyacenaphthylene.* — When a powerful incandescent light (10^5 luxes) is applied to the negative electrode of the cell, a photocurrent increases slowly, attaining a peak after 200 sec. Then the current tends to decay slowly; when the light is switched off, it decays to the initial value, as Fig. 1 shows.

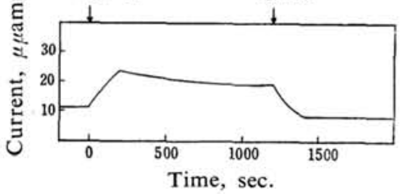

Fig. 1. Rise of the photocurrent under illumination and its decay, polyacenaphthylene.

Nitrated Polyacenaphthylenes. — The time-responses of the photocurrents of the nitrated polyacenaphthylenes are shown in Fig. 2. No photocurrent is observed in the case of Experiment No. 5. The time-responses are very slow; that is, even after 1400 sec. the photocurrents increase gradually. This is the same

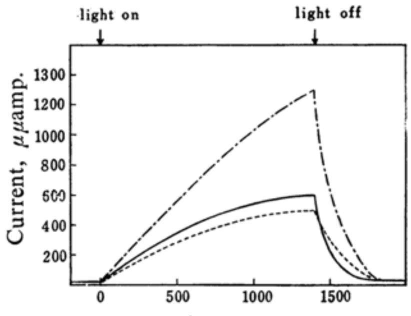

Fig. 2. Rise of the photocurrent under illumination and its decay, nitrated polyacenaphthylenes.
7.9% nitration (dotted line)
16.4% nitration (solid line)
28.7% nitration (broken line)

phenomenon as was observed in crystal violet by Vartanian,11) and so it can be seen that something in nitrated polymers seems to act as electron-traps.

When a powerful incandescent light (10^4 to 10^5 luxes) is applied to the cell, the photocurrents increase, as is shown in Fig. 3.

The photoconductive natures of these polymers are listed in Table II. In the case of the sandwich-cell method, the sample of 16.4 molar per cent nitration is the most photoconductive, while in the relative-surface-potential method, the sample of 28.7 molar per cent nitration is the most photoconductive. This difference may be due to the different measuring methods. In any case it is clear that the photoconductivity of polyacenaphthylene increases upon the nitration of the polymer.

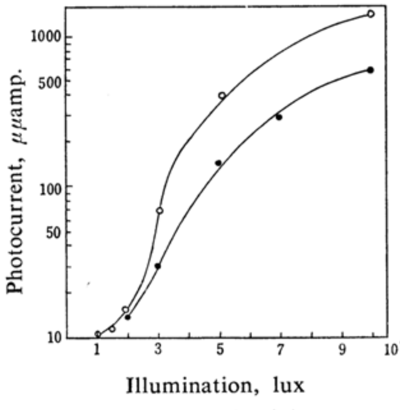

Fig. 3. Photoconductivity curve.
16.4% nitration (○)
28.7% nitration (●)

TABLE II. PHOTOCONDUCTIVE INDEXES OF POLYACENAPHTHYLENE AND NITRATED

No.	$-NO_2$ group mol. %	I_d $\mu\mu$amp.	I_l $\mu\mu$amp.	I_l/I_d	$(V_l/V_d)_{1/2}$ sec.
1	0	11	24	2	100
2	7.9	15	500	33	46
3	16.4	18	1300	72	14
4	28.7	18	600	33	4.5
5	40.6	37	37	1	74

Discussion

The number of the conjugated double bonds or mobile π electrons of polyacenaphthylene are equal to those of polyvinylnaphthalene, which our experiment establishes as having no photoconductivity. The photoconductivity of polyacenaphthylene, therefore, can not be explained by the mere existence of the mobile π electrons. It may be considered that the conductivity of this polymer depends on the stereoregularity. Between the electron clouds of the acenaphthene groups, which lie one against the other, there are, by virtue of a slight overlapping, interaction forces which cause a slight splitting of the electron orbitals of the groups and, consequently, the formation of narrow energy bands.

The fact that the nitration brings more photoconductivity may be interpreted with a charge-transfer mechanism. The nitrated acenaphthene group may be an electron-donor. When these groups are put in order, as has been discussed above, a charge-transfer complex may be formed between an acenaphthene group and a nitrated acenaphthene group.

Summary

The photoconductive properties of polyacenaphthylene and nitrated polyacenaphthylene have been studied using both the sandwich-cell method and the relative-surface-potential method. The polyacenaphthylene shows little photoconductivity, while the nitrated polymer obtained by the partial nitration of polyacenaphthylene shows considerable photoconductivity. The photocurrent depends on the degree of nitration.

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