Photoconductive Polymer: Its Preparation and Photoconductive Behavior

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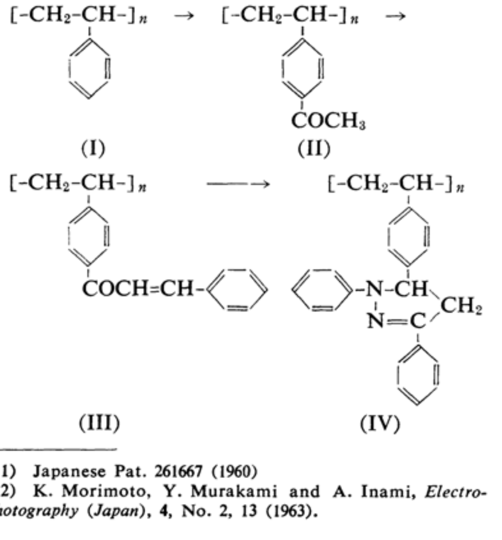
(Received July 30, 1963)

The photoconductive properties of 1, 3, 4,-triphenyl-2-pyrazoline, its derivatives and homologues have already been established,[1] and the present authors have reported in another paper[2] on their photoconductive and electrophotographic characteristics. A poly-[1, 3-diphenyl-5-(4-vinylphenyl)-2-pyrazoline] is considered to be perhaps the simplest polymer with a triphenyl-2-pyrazoline group to synthesize. Recently several polymers containing heterocyclic group have been reported,[3-5] but because vinyl monomers containing a heterocyclic group are chemically unstable, in most cases only solvent-insoluble high polymers can be obtained. The most successful synthetic route, therefore, is first to prepare polyvinylbenzalacetophenone from polystyrene, and then to let the product react with phenylhydrazine. This sequence produces poly [1, 2-diphenyl-5-(4-vinylphenyl)-2-pyrazoline] of a considerable purity. Under carefully controlled preparative conditions, a high degree of substitution is obtained without the substance's being insoluble in an organic solvent. The photoconductive behavior of this material is then measured.

Experimental

Synthesis of the Polymer. — The polymer was synthesized in three steps as follows:



Polyvinylacetophenone (II) from Acetyl Chloride and Polystyrene (I).[6] — In a stirred flask with a dropping funnel and reflux condenser, 500 ml. of carbon disulfide, 134 g. (1 mol.) of aluminum chloride, and 59 g. (0.5 mol.) of polystyrene ($[\eta]=0.68$, at 25°C in benzene) dissolved in 500 ml. of carbon disulfide were placed in that order. The mixture was refluxed gently for about one hour, and the mass was heated in water to remove the carbon disulfide. The product was broken up and washed in water, then dried to yield about 63 g. of a nearly white powder. The product was soluble in acetophenone, acetone, acetic acid and dioxane.

Found: C, 81.53; H, 6.95. Calcd. for $C_{10}H_{10}O$: C, 82.15; H, 6.90%.

$[\eta]=0.33$, at 25°C in acetone.

Polyvinylbenzalacetophenone (III) from Polyvinylacetophenone with Benzaldehyde.[7]—To a solution of 10.0 g. of polyvinylacetophenone dissolved in 100 ml. of benzaldehyde, 2 g. of concentrated sulfuric acid dissolved in 30 ml. of benzaldehyde were added. After this mixture had stood in the dark for 96 hr., 10 g. of anhydrous sodium acetate was added to decompose the sulfuric catalyst. The solid substance was removed by centrifuging, and the remaining liquid was then poured into methanol. The pale yellow precipitate was twice reprecipitated from a monochlorobenzene solution by pouring it into methanol, and then it was dried in the dark at room temperature. The product was soluble in benzene, monochlorobenzene, ethyl methyl ketone and dioxane.

Found: C, 87.47; H, 6.69. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02%.

$[\eta]=0.73$, at 25°C in dioxane.

Poly[1, 3-diphenyl-5-(4-vinylphenyl)-2-pyrazoline] (IV). — To a solution of 5 g. (0.02 mol.) of polyvinylbenzalacetophenone dissolved in a mixture of 50 ml. of dioxane and 6.5 g. of glacial acetic acid, 2.5 g. of phenylhydrazine were added. After the mixture had been stirred for 90 min. at 90°C, the solution was poured into methanol. The yellow precipitate was twice reprecipitated from dioxane solution by pouring it into methanol; it was then dried to yield about 4.8 g. of yellow powder. The product was soluble in benzene, toluene, monochlorobenzene, dioxane and methylene chloride.

Found: C, 81.67; H, 6.06; N, 8.72. Calcd. for $C_{23}H_{20}N_2$: C, 85.18; H, 6.17; N, 8.64%.

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[1] Japanese Pat. 261667 (1960)

[2] K. Morimoto, Y. Murakami and A. Inami, *Electrophotography (Japan)*, **4**, No. 2, 13 (1963).

[3] R. Kern, *J. Polymer Sci.*, **43**, 549 (1960).

[4] A. Coscia, R. Kugel and J. Pellon, ibid., **55**, 303 (1961).

[5] Brit. Pat. 915621 (1963).

[6] W. Kenyon and G. Waugh, *J. Polymer Sci.*, **32**, 83 (1958).

[7] C. Unruh, *J. Appl. Polymer Sci.*, **2**, 358 (1959).

$[\eta]=0.68$, at 25°C in benzene.

The Infrared Spectra of the Polymers. — The polymers synthesized were identified by comparing the infrared absorption bands of those compounds which do not have a vinyl group, such as acetophenone, benzalacetophenone and 1,3,4-triphenyl-2-pyrazoline. The infrared absorption spectra were measured with a Hitachi double-beam spectrometer. The polymers used were in the form of a thin film.

The Photoconductivity of Polymer, IV. — The conductivity cell used for the polymer was the so-called "sandwich-type photoconductivity cell," a schematic diagram of which is shown in Fig. 1.

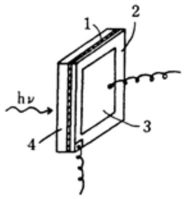

Fig. 1. The sandwich-type cell.
1, NESA coated layer; 2, polymer specimen film; 3, aluminum evaporated layer; 4, glass substratum

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 with the aid of a Baker-type film applicator; then the solvent was throughly evaporated in the drying oven. After the solvent had been evaporated, the specimen film was 20 μ thick. The second electrode was formed thereafter by the evaporation of aluminum onto the surface of the specimen film.

The sandwich-type cell thus obtained was then placed in a closed glass chamber (as shown in Fig. 2), which was kept in a vacuo of $<10^{-3}$ mmHg. The temperature of the specimen was always kept at 25°C. The applied field to the specimen was 1500 V.-cm^{-1} (taken from a 3 V. dry battery 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).

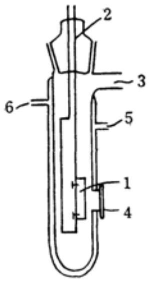

Fig. 2. The schematic diagram of the sandwich type cell placed in glass chamber.
1, Tefron casing of the cell; 2, metal-to-glass seal; 3, evacuation pipe; 4, quartz window; 5, 6, input and output of water from thermostat bath

As the resistance of the polymer in both dark and light showed a considerably high value, the glass chamber was completey shielded to avoid all noises. The light source used for measuring the photocurrent of the cell was a 100 W tungsten lamp. When necessary, an interference filter was placed in the path of the light beam to obtain monochromatic light.

The sandwich-type celles tested were stored in a dark desiccator immediately after they had been coated. The cell that had been exposed to light was tested after it had been in the dark at least 24 hr. A diagram of the entire photoconductivity apparatus is shown in Fig. 3.

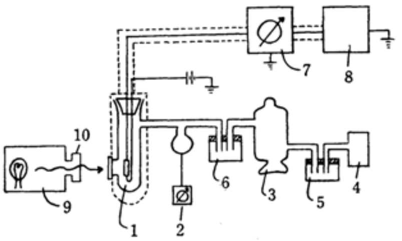

Fig. 3. Set up experimental apparatus.
1, Glass chamber containing the cell; 2, cold cathode ion gauge; 3, Hg diffusion pump; 4, rotary pump; 5, 6, cold traps; 7, vibration-reed micro-micro ammeter; 8, X-T recorder; 9, light source casing; 10, shutter

Results and Discussion

Identification of the Polymers. — *Polyvinylacetophenone.*—The infrared spectrum of polyvinylacetophenone indicates the absorptions of the acetyl group.

Wave number, cm^{-1}	Absorbing structure
1680	Carbonyl
1268	Aromatic ketone
1360	Methyl

Polyvinylbenzalacetophenone. — The absorption bands at 1304 and 975 cm^{-1} may be assigned to disubstituted ethylene, those at 765 and 696 cm^{-1}, to monosubstituted benzene, that at 1576 cm^{-1}, to benzal; that at 1663 cm^{-1}, to carbonyl, and that at 1216 cm^{-1}, to aromatic ketone. As the absorption band at 1360 cm^{-1} resulting from the methyl group is not present, it is considered that the reaction is complete.

Poly[1, 3-diphenyl-5-(4-vinylphenyl)-2-pyrazoline].—As is shown in Fig. 4, the absorption bands at 1663 and 1216 cm^{-1}, resulting from the carbonyl group, completely disappear, and the bands at 1304 and 975 cm^{-1} resulting from the disubstituted ethylene group are barely present.

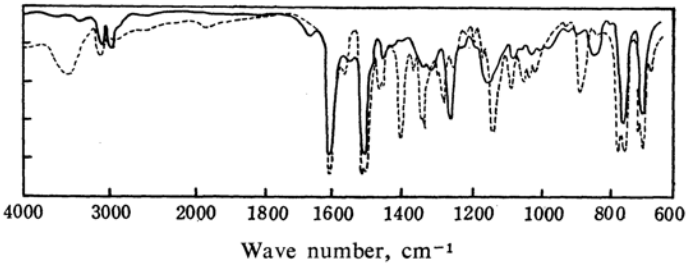

Fig. 4. IR spectra of poly[1,3-diphenyl-5-(4-vinylphenyl)-2-pyrazoline] (solid line) and of 1,3,4-triphenyl-2-pyrazoline (dotted line).

Photoconductivity Behavior. — *V-I Characteristic in the Dark.*—From Fig. 5 it may be seen that the V-I plot in the dark passes through the point of origin, showing that the dark current of the specimen obeys Ohm's law. It may, therefore, be assumed that the contacts between the specimen film and the aluminum layer or NESA conductive surface are perfect.

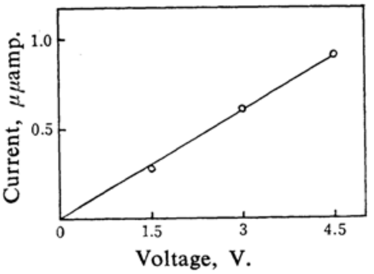

Fig. 5. Relation between voltage applied and photocurrent.

The Photocurrent in an Incandescent Lamp.—When the cell is illuminated with an intense luminous flux, the photocurrent rises instantly and reaches a maximum value in less than 2 sec. Also, when the light source is switched off, the current decreases to the initial dark value in the same period. When illuminated with a weak light beam or monochromatic light, however, it takes several seconds to attain the peak current. Also, a longer time is required for it to come to equilibrium when the light is switched off to neutralize the space charge to zero.

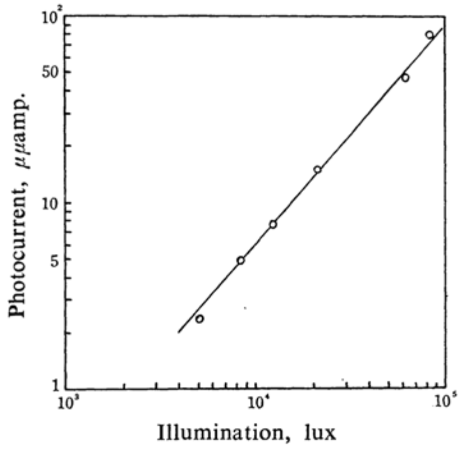

Fig. 6. Photoconductivity curve.

A large photocurrent value is observed for this type of cell when the illuminated electrode is negative. This behavior suggests that the charge carriers in this polymer are mainly electrons rather than positive holes. The same relation was observed by Northrop and Simpson,[8-10] who used this type of cell for lower molecular weight polyaromatics. The value of I_p(photocurrent)/I_d(dark current) is 34 or 147 depending on whether the illuminated electrode is positive or negative respectively.

When a powerfull incandescence (10^3 to 10^5 luxes) is applied o the cell, as is shown in Fig. 6, the empirical formula

$$I_p = KL^{1.2}$$

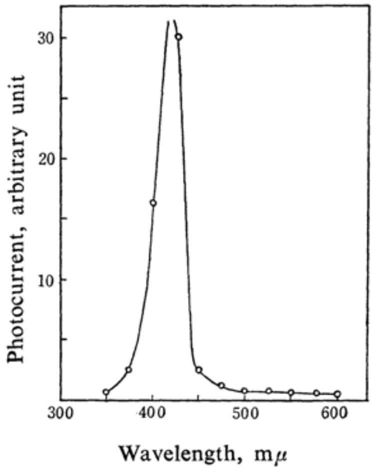

Fig. 7. Photocurrent sensitivity.

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[8] D. Northrop and O. Simpson, *Proc. Roy. Soc.*, **A234**, 124, 136 (1956).

[9] D. Northrop and O Simpson, ibid., **A244**, 377 (1958).

[10] H. Inokuchi and H. Akamatu, *Solid State Phys.*, **12**, 93 (1961).

can be applied, where K is a constant and L, the illumination.

Monochromatic Photoresponses. — The monochromatic responses of the polymer specimen are shown in Fig. 7. As may be seen from these results, remarkable responses occur in the wavelength of 400 and 425 mμ.

Summary

A photoconductive polymer, poly[1, 3-diphenyl-5-(4-vinylphenyl)-2-pyrazoline], has been synthesized from polystyrene via polyvinylacetophenone and polyvinylbenzalacetophenone. Under carefully controlled preparative conditions, a high degree of substitution has been obtained without its being insoluble. The photoconductive behavior of the polymer has been measured using a sandwich-type cell. The current obeyed Ohm's law, and the value of I_p/I_d was 34 or 147 depending on whether the illuminated electrode was positive or negative respectively.

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