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Photoconduction of Polystyrylpyrimidines

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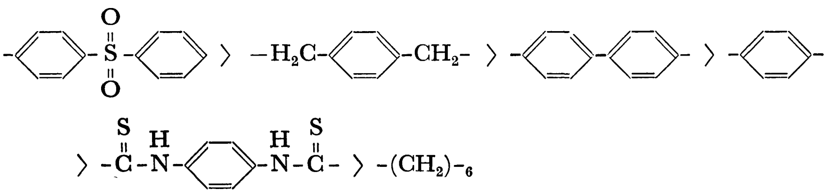
Eight polystyrylpyrimidines were synthesized from *p*-xylylpyrimidine with *p*-phenylene diisothiocyanate (DIT), terephthaloylchloride (TPC), *p*-xylylenedibromide (XDB), *p*-phenylenediamine (PDA), 4,4'-diaminodiphenyl (BD), 4,4'-diamino diphenylsulfone (DPS), hexamethylene diamine (HMD), and 4,4'-diaminodiphenylmethane (DPM). These polymer films have a fairly large photoconductive character; using a surface-type photoconductive cell, the logarithmic relation of the photo-current (I_p) to the applied potential was found to be linear. Further, it was found that the slopes (n) obtained from the logarithmic relation ($I_p=kL^n$) of the photocurrent to the light intensity (L) have values from 1.0 to 2.4. The peaks of the spectral response of the photocurrent of the eight samples exit around 500—600 mμ and/or near the ultraviolet wavelength region. The photoconduction of these polymers was enhanced by the bridging groups attached to xylylpyrimidine; the enhancement is in the following order;



These have in recent years been a large number of reports on the photoconduction of polycyclic aromatics and also of polymers.[1] However, scarcely systematic research on the relation between the photoconduction and the chemical structure has been carried out.[2]

It was been widely noted that polyvinylcarbazole shows quite a large photoresponse, one which is influenced by sensitizers.[3] The cause of this photoresponse is assumed to be that polyvinylcarbazole has a large side group which shows an energy transfer by means of dipole-dipole resonance between carbazole molecules.[4] As other organic photoconductive materials, polystyrene,[5] polyvinylacridine,[6] and polyhalogenated vinyl,[7] and so on have been investigated. However, the photoconduction of the polymer containing a hetero-ring in the main chain has not yet been investigated.

Recently, many sorts of electrophotographic techniques have been developed. The main requirements for good electrophotographic materials are as follows; the ratio between the photoconductivity and the dark conductivity should be large, and the spectral response of the photoconduction should cover a wide visible and ultraviolet wavelength region. If the relation between the molecular structure and the photoconductive character could be find, materials suitable for electrophotographic printing could be prepared.

In this report, we will describe the variation in the photoconductive characters of eight sorts of polystyrylpyrimidines as a function of the molecular structure.

Experimental

1. Synthesis of the Polymers. The polycondensations of *p*-xylylpyrimidine (1.00×10^{-2} mol) with various diamines (1.00×10^{-2} mol) were carried out for 5—10 hr 100 m*l* three-necked flask equipped with a stirrer, a nitrogen gas inlet, and a calcium chloride drying tube at 150°C. Inorganic catalysts were not used, since inorganic impurities obviously affect their electrical properties. Triethylamine (5 wt% for monomer) was used as a catalyst for polycondensation. During the synthesizine procedure, highly polar solvents dimethylformamide and dimethylacetamide were used to accelerate the reaction. The reaction mixture was poured into ethanol, and the precipitated polymer was filtered and washed successively with hot water and alcohol. The powders separated from the reaction mixture were purified by a Soxlet extraction, dried at 100°C under a vacuum, and stored over a desicant.[8] The polymer was found to have no ash content. Table 1 shows the structures and the nitrogen analyses for the polymers obtained from *p*-xylylpyrimidine reacted with and various monomers.

2. Measurement of the Semiconductive Properties and Photoconductivity. The electrical resistivity of the powdered samples compressed between stainless-steel electrodes by a pressure of 50 kg/cm^2 was measured *in vacuo*. The details of this procedure already have been presented.[9] The resistivity decreased with an increase in the temperature, and a good linear relationship was obtained between the logarithm of the resistivity (ρ) and the reciprocal of the temperature, this indicates the applicability of the following formula.[10]
$\rho=\rho_0\exp\ (\Delta E_G/2kT)$

Measurement of the Surface Photo-current: Throughout the experiments described in this report, a sample tablet (1.31

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[1] "Encyclopedia of Polymer Science and Technology," Vol. 11, ed. by H.H.Mark and N.G.Gaylord, Interscience Publ., New York (1969), p.338.

[2] V. Mylnikov and A. Terenin, *J. Polym. Sic.*, *C*, **16**, 3655 (1968).

[3] K. Okamoto, Y. Hasegawa, S. Kusabayashi, and H. Mikawa, This Bulletin, **41**, 2563 (1968).

[4] W. Klopffer, *J. Chem. Phys.*, **50**, 2337 (1969).

[5] M. Ofran, N. Ofran, and A. Weinreb, *ibid.*, **50**, 3131 (1969).

[6] B. B. Homer and M. Shinitzky, *Makromol.*, **1**, 469 (1968).

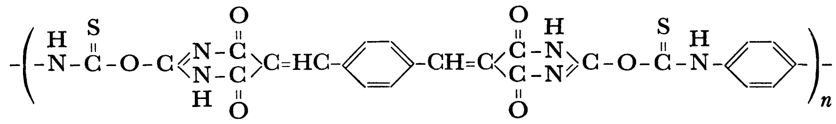
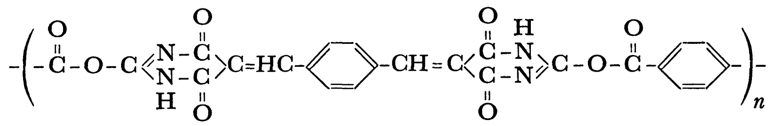
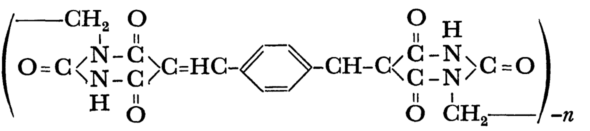
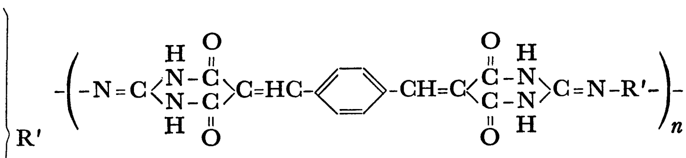
[7] M. Kryszeniski, A. Szymanski, and A. Wlochouicz, *J. Polym. Sci.*, *C*, **16**, 3921 (1965).

[8] R. Hirohashi, Y. Hishiki, and M. Haruta, *Kogyo Kagaku Zasshi*, **73**, 631 (1970).

[9] R. Hirohashi, Y. Hishiki, and S. Ishikawa, *Polymer.*, **11**, 297 (1970).

[10] R. Hirohashi, Y. Hishiki, and S. Saito, *Kogyo Kagaku Zasshi*, **72**, 1189 (1969).

Table 1. Structures and nitrogen analyses of polystyrylpyrimidines

No.	Reagent	Structure	Nitrogen analyses	
			Calcd (%)	Found (%)
P1	DIT		15.38	15.24
P2	TPC		11.57	13.55
P3	XDB		12.28	13.69
P4	PDA		19.71	18.39
P5	BD		16.73	15.28
P6	DPS		15.27	15.64
P7	HMD		19.35	20.72
P8	DPM		16.27	15.55

DIT: *p*-Phenylene diisothiocyanate, TPC: Terephthaloyl chloride, XDB: *p*-Xylylene dibromide, PDA: *p*-Phenylene diamine, BD: Benzidine, DPS: 4,4'-Diamino diphenylsulfone, HMD: Hexamethylene diamine, DPM: 4,4'-diamino diphenylmethane

cm^2 surface area and *ca.* 0.5—1.0 mm thick) was made by the compression of about 0.1 g of a finely-powdered at about 200 kg/cm^2. Silver paste (du Pont conducting silver paint No. 4817) was painted in two stripes on the surface of a tablet with a 1 mm gap. A 750 watt tungsten lamp was used, associated with metallic interference filteres in order to isolate narrow particular wavelength regions. The maximum transmissive wavelengths of the regions, which were 10—61 mμ in the half-band width, ranged from 398 mμ to 1340 mμ, with intervals of 50—100 mμ.[11] The photoconduction of the polymer was measured in a conductivity cell by illumination with a tungsten lamp or a hydrogen-discharge lamp. The electric current was measured by means of the DC amplifier. As the voltage source applied to an organic photocell, we used a DC voltage supply of up to 1000 V.

The absolute measurements of the intensity of the incident light on an organic photocell were made by means of a Nihonbunko vacuum thermopile which was placed at the position of the photocell. The maximum intensity, 3.70—4.73 × 10^{15} photons/sec·cm^2, was obtained for the light which was isolated by a 848 mμ filter.[12]

Results and Discussion

The voltage dependence of the surface photo-current and the dark-current of the polymers was measured. Most of the observations were made *in vacuo* with a

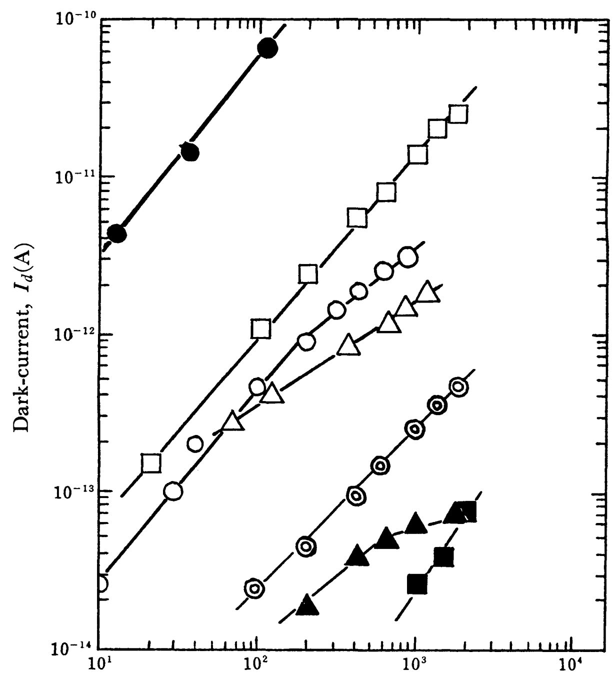


Fig. 1. Surface photo-current *vs.* applied electric field for polystyrylpyrimidines. (at 10^{-6} Torr, by tungsten lamp 750 watt)

○	●	△	▲	◎	□	■
P1	P2	P3	P4	P5	P6	P7

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[11] R. Hirohashi, Y. Hishiki, and S. Ishii, *J. Sci. Phot. Japan*, **33**, 90 (1970).

[12] M. Sano, "Dissertation," The University of Tokyo (1961).

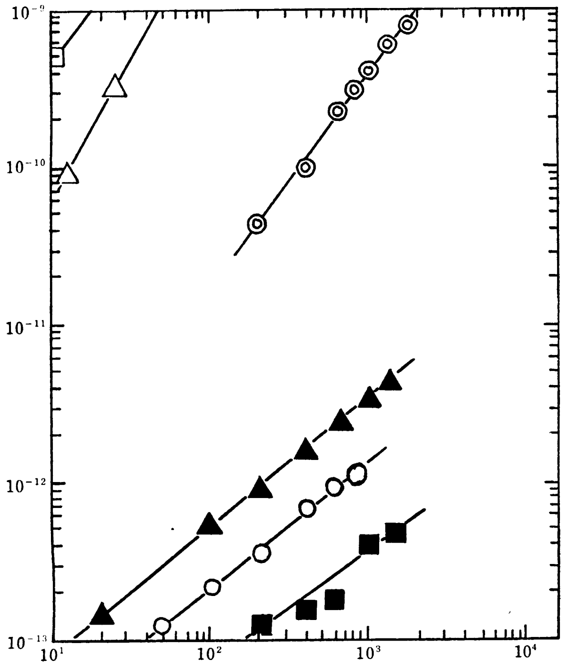
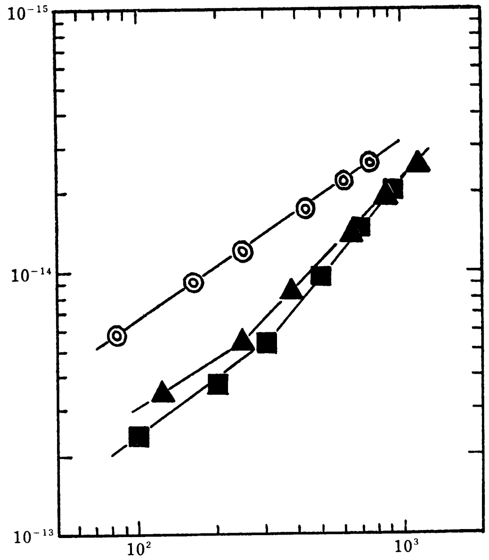


Fig. 2. Surface photo-current *vs.* applied electric field for polystyrylpyrimidines. (at 10^{-6} Torr, by tungsten lamp 750 watt)

○ △ ▲ ◎ □ ■
P1 P3 P4 P5 P6 P7

surface-type photocell in order to avoid the effects of the space charge which are occasionally observed with sandwich-type photocells. The potential dependence for the photocurrent is reproducible, as in the case of the dark-current. Figures 1 and 2 show the electric-field(V) dependence of the dark-current (I_d) and of the photo-current (I_p).

Ohmic behavior derived from the I_d-V relation was observed for all samples except the P7- and P8-samples for the dark-current. On the other hand, ohmic relations for the photo-current against the applied potential were obtained for all samples except P3. Figure 3 shows the I_d-V relation under illumination by a hydrogen-discharge lamp.



Electric field F(V/cm)

Fig. 3. Surface photo-current *vs.* applied electric field for polystyrylpyrimidines. (at 10^{-6} Torr, by hydrogen discharged tube)

▲ ◎ ■
P4 P5 P7

Table 2 shows the values of the slopes(α and β) of the I-V relation for polystyrylpyrimidines. The values of α and β were calculated from the $I_d=kV^\alpha$ and $I_p=kV^\beta$ relation respectively. The specific resistivities, the values of the energy gap, and the temperature-possessed kink of the energy gap are shown in Table 2.

A summary of the results for surface-type cells is presented in Table 3. The ratios of the photo-current (I_p) to the dark-current (I_d) reveal the effects of the molecular structures sufficiently well.

The photo-current decreases in air (I_p=4.5×10^{-13} Å) more than in a vacuum (I_p=4.3×10^{-11} Å). As a general rule, upon illumination by incandescent lamp the photo-current does not immediately rise to its equilibrium value. Usually the current-time curve shows a peak shortly after the light has been switched

TABLE 2. THE VALUES OF SLOPE(α AND β) AND SEMICONDUCTING PROPERTIES OF POLYMERS

No.	Specific resistivity ρ (ohm/cm) Temp. (°C)	Energy gap ΔE_G (eV)	Temp. °C	α Field low	α Field high	β Tungsten lamp	HDT[a)] Field low	HDT[a)] Field high
P1	1.74×10^{13} (18)	0.68	50— 91	1.3	0.9	0.8	—	—
		1.51	91—143					
P2	3.74×10^{13} (17)	0.56	17— 69	1.1		—	—	—
		1.70	69—138					
P3	6.89×10^{13} (12)	0.83	12—114	0.7		1.7	—	—
		1.65	114—143					
P4	4.27×10^{12} (9)	1.52	21—152	1.0	0.4	0.8	0.6	1.1
P5	4.48×10^{12} (12)	1.20	12—147	1.0		1.3	0.8	
P6	4.96×10^{14} (12)	1.91	45—145	1.1		1.4	—	—
P7	3.59×10^{12} (13)	1.23	36—148	2.0		1.0	0.7	1.2
P8	4.82×10^{12} (12)	1.18	12—146	1.6		—	—	—

a) HDT: Hydrogen discharged tube.

Table 3. The ratios of photo-current to dark-current for polymers

No.	Electrical field (V/cm)	I_p (A)	I_d (A)	I_p/I_d (max)
P1	10	2.67×10^{-14}	2.7×10^{-14}	1
P3	25	3.32×10^{-10}	2.7×10^{-13}	1230
P4	400	2.03×10^{-11}	6.5×10^{-14}	310
P5	400	5.85×10^{-10}	3.5×10^{-13}	1670
P6	20	1.21×10^{-9}	1.66×10^{-13}	7300

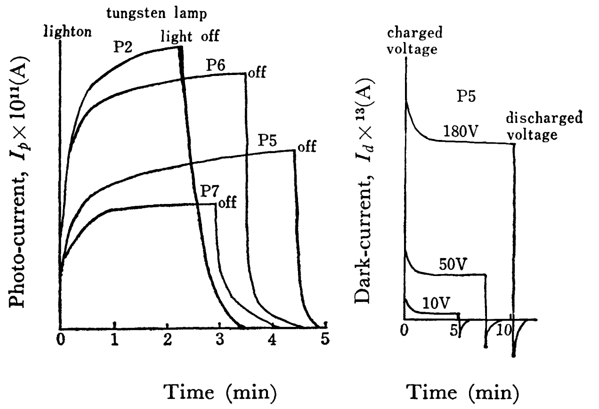


Fig. 4. Dependence of the absorption current on chemical structure and charged voltage.

on as in Fig. 4.

This indicates the formation of a space-charge effect[13] and shows the influence of the contact between electrodes and the specimen. On the other hand, the photo-current upon illumination by the photo-current to its equibrium value. After switching on the field, the currents rises to a peak value, which then slowly decreases to equilibrium. When the supply of the field is stopped, a back current is obtained. The photo-current markedly depends on the voltages and light intensities used.

The Spectral Dependence of the Photo-currents of Polystyrylpyrimidines. A number of investigations of photoconduction in organic solids have been reported. Most of them have been concerned with simple compounds, especially with the anthracene crystal. The spectral response curve of photoconduction was in a closed relation to the absorption spectrum of the anthracene crystal[14] and to those for polycyclic aromatic compounds.[15]

The absorption spectra in the ultraviolet and visible regions of polystyrylpyrimidines, dissolved in concentrated sulfuric acid, were recorded at room temperature. Figure 5 shows the absorption spectra.

Figure 6 shows the spectral dependence of the photo-current of polystyrylpyrimidines. In order to normalize the photo-current, it was divided by the incident-light intensity for each wavelength. The photo-current is produced by the light energy which is absorbed into the bulk of the polymeric solid. Generally, the main feature of the spectral response curves is that their peaks correspond to the minima of the absorption spectrum; that is, a higher extinction coefficient will lead to a lower photo-current in the region of the absorption spectrum.

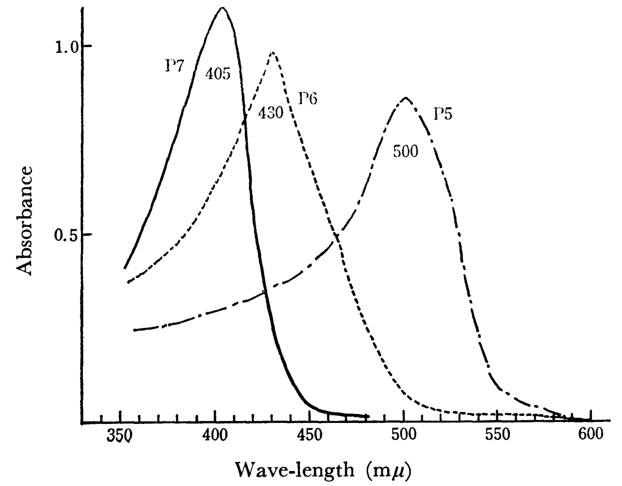


Fig. 5. Absorption spectra of polystyrylpyrimidines. (in concentrated sulfuric acid)

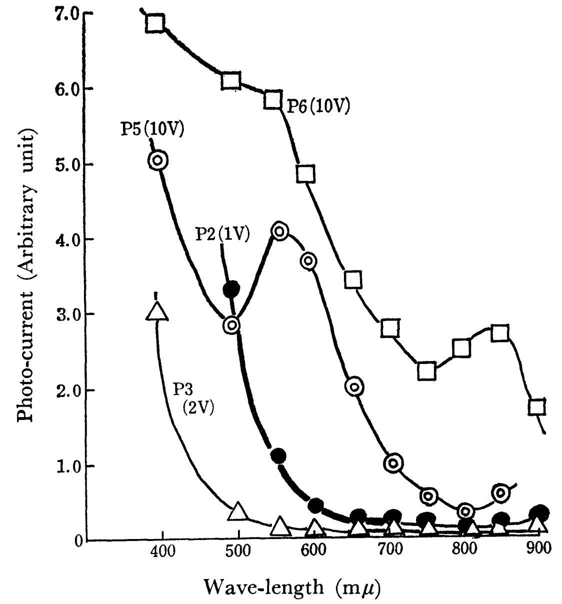


Fig. 6. The spectral dependence of the photo-current of polystyrylpyrimidines. (with metalic interfacial filters.)

The number of carriers is proportional to the number of photons absorbed into the bulk, with a definite coefficient of the quantum yield. The photo-current curve of polystyrylpyrimidines possesses quite a long tail, one extending to the near-infrared wavelength region. The sensitivity of photoconduction decreases more or less with an increase in the wavelength and continues to extend over the infrared region. In this experiment, the threshold value for photo-conduction could not be found, but the value should be located near the ultraviolet region judging from our results.

The Incident-light-intensity Dependence of the Photo-

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[13] J. Kommandeur and W. G. Schneider, *J. Chem. Phys.*, **28**, 582 (1958).

[14] D. J. Carswell and L. E. Lyons, *J. Chem. Soc.*, **1955**, 1734.

[15] H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **20**, 1481 (1952).

current. The measurements of the photo-current with a variation in the intensity of the incident light indicated that the current observed was almost proportional to the light intensity. The dependence of the photo-current (I_p) on the illumination intensity (L) is expressed by the equation; $I_p=kL^n$. Going to the longer-wavelength region, it approaches more and more linearity until, at 748 mμ, the photo-current is proportional to the light intensity. Table 4 shows the values of n for the tungsten lamp and for each wavelength.

The values of n changed as a function of the applied voltage, the wavelength, and the atmosphere. In the presence of oxygen, the value of n is less than unity; the cause of this decrease is assumed to be the fact that the oxygen absorbs on the polymer films.[16]

Table 4. The values of n

Polymer No.			
P1	—	P5	0.8 and 2.4
P2	1.1	P6	1.1
P3	1.0	P7	2.3
P4	2.0	P8	—

a) low light intensity 0.8 and high light intensity 2.4

Sample P5	Wavelength $\lambda_{\max}$ mμ	Applied voltage	n
	551	90	0.73
	653	90	0.96
	749	150	0.98

The authors wish to express their sincere thanks to Professor Hiroo Inokuchi, of the Institute for Solid State Physics, the University of Tokyo, for his valuable suggestions in the course of this work.

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[16] A. T. Vartanyan and L. D. Rozenstein, *Dokl. Akad. Nauk SSSR*, **124**, 295 (1958).