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# The Polymerization of α-Naphthylmethylvinylether and 3-Pyrenylmethylvinylether and Electrical Conductivity of Their Polymers

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A new vinylmonomer with a large pendant π-electron group was synthesized. α-Naphthylmethylvinylether and 3-pyrenylmethylvinylether were polymerized in good yields, although their polymers have fairly low molecular weights. Both polymers have a fairly high isotacticity. Poly-3-pyrenylmethylvinylether showed a large photocurrent in its absorption region and a small photocurrent even above 500 to 1000 mμ. The doped TCNE significantly sensitized its photoconductivity.

Polycyclic aromatic hydrocarbons have been much studied as organic photoconductors.[1] The conductivity of polymers with a large aromatic ring as a side chain has also been studied because of the practical interest in their ability to form a photoconductive film. Poly-*N*-vinylcarbazole is one of the most photoconductive polymers which have ever been reported and used as material for electrophotography.[2] It has been suggested that the high photoconductive property of poly-*N*-vinylcarbazole is associated with the crystallinity.[3] Poly-3-vinylpyrene is the polymer with the largest aromatic ring as a side chain which has ever been synthesized.[4] Although the polymer is ordinarily poorly crystalline, spherulite is observed in the polarizing hot-stage after heat annealing, and it is also photoconductive.[4] The relationship between the conductivity and the crystallinity has also been found in other polymers.[5]

Many studies have been done on the stereoregular polymerization of vinylethers. As has been reported in connection with the polymerization of both tri-

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[1] F. Gutmann, L. E. Lyons, "Organic Semiconductors", John Wiley & Sons, Inc., New York, (1967).

[2] K. Morimoto, Y. Murakami and M. Ikeda, *National Technical Reports*, **15**, 125 (1969).

[3] A. Kimura, Y. Yoshimoto, Y. Akana, H. Hirata, S. Kusabayashi, H. Mikawa, and N. Kasai, *J. Polym. Sci. A*-2, **8**, 643 (1970).

[4] K. Tanikawa, S. Kusabayashi, and H. Mikawa, *Polym. Lett.*, **6**, 275 (1968); This Bulletin, **41**, 2719 (1968).

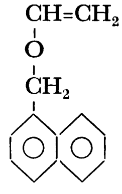
[5] K. Okamoto, S. Kusabayashi and H. Mikawa, *Kogyo Kagaku Zasshi*, **73**, 1351 (1970).

methylsilylvinylether and benzylvinylether,[6] a vinylether with a large side-chain group is expected to give an isotactic polymer by cationic polymerization in nonpolar solvents.

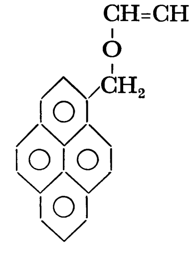
In the present paper, the authors will report on the polymerization of α-naphthylmethylvinylether (NVE) and of 3-pyrenylmethylvinylether (PVE) as well as on the high isotacticities and the electrical conductivity of their polymers.

## Experimental

*Synthesis.*



NVE



PVE

*NVE.* NVE was prepared according to the method reported by Watanabe and Conlon.[7] The crude material was purified by means of column chromatography (basic alumina, ligroin) and high vacuum distillation (bp 95°C/0.03 mmHg).

*PVE.* 3-Pyrenylaldehyde[4] was reduced to 3-pyrenylmethanol by the following procedures. A 25-g portion of 3-pyrenylaldehyde was dissolved in 800 cc of methanol with 4 g of $NaBH_4$, and the mixture was heated at about 40°C for 6 hr with stirring. After the excess $NaBH_4$ had then been decomposed by dilute acetic acid, most of the solvent was distilled away and the reaction product was extracted with benzene. The benzene solution was washed several times with water and dried over anhydrous potassium carbonate. The benzene was distilled away, and the resulting precipitate, 3-pyrenylmethanol, was washed several times with a benzene-ligroin mixture and recrystallized three times from ligroin. Yield, 15 g (60%); mp 126—127°C. Found: C, 88.27; H, 5.19%. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.17%.

3-Pyrenylmethanol was transformed to 3-pyrenylmethylvinylether by the procedures similar to those used in the case of naphthylmethylvinylether.[7] The reaction mixture of 3-pyrenylmethanol (20 g), isobutylvinylether (500 cc), and $Hg(OCOCH_3)_2$ (1.8 g) was refluxed for a day; then another 1.0 g of $Hg(OCOCH_3)_2$ was added and reflux was continued for one more day. The reaction mixture was then washed with water, and the isobutylvinylether was removed by distillation. After being purified by column chromatography (basic alumina, ligroin), PVE was recrystallized three times from ligroin. Yield, 3.33 g (15%); mp 77—78°C. Found: C, 88.28; H, 5.46%. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.17%. Its NMR signal consisted of a multiplet (ring protons) at 1.9—2.5 $\tau$, a quartet (internal vinyl hydrogen) at 3.2—3.6 $\tau$, a singlet (Py-$CH_2$-O-) at 4.8 $\tau$, and a multiplet (terminal vinyl hydrogens) at 5.5—6.6 $\tau$.

*Polymerization.* The polymerization conditions are summarized in Tables 1 and 2. The solvents were purified by ordinary methods. The initiators were distilled prior to use and were kept as a toluene solution under nitrogen. Polymerization was carried out in a vacuum sealed tube. Methanol was used as the precipitating agent.

*Preparation of Poly-3-pyrenylmethylvinylether (PPVE) Doped with Tetracyanoethylene (TCNE).* A certain amount of TCNE was added into a benzene solution of PPVE. After being stirred for an hour, the mixture was poured into a large amount of methanol or ligroin and the precipitate was washed with methanol or ligroin and dried *in vacuo*. The content of TCNE was estimated from the results of elementary analysis.

*Measurement of the Electrical Conductivity.* Both polymers were purified as much as possible by repeated precipitations before the measurement. As a thin film (10 $\mu$ thick) of poly-α-naphthylmethylvinylether (PNVE) could be formed on a nesa quartz plate by the cast method, its electrical conductivity was measured in an Au–PNVE–Nesa sandwich-type cell. As it was not possible to make thin films

TABLE 1. POLYMERIZATION OF NVE.

| No | Solvent[a] | Temp °C | Catalyst | Cat Concn mol% | Time hr | Yield % | Mol Wt[b] | Softening range °C |
|---|---|---|---|---|---|---|---|---|
| 1 | *n*-Heptane | 25 | $AlEtCl_2$ | 5 | 15 | 81 | 3760 | 90—100 |
| 2 | *n*-Heptane | 0 | $AlEtCl_2$ | 5 | 10 | 71 | | |
| 3 | $CH_2Cl_2$ | −78 | $AlEtCl_2$ | 7 | 10 | 44 | 1400 | |
| 4 | $CH_2Cl_2$ | 0 | $AlEtCl_2$ | 7 | 10 | 59 | | |
| 5 | $CH_2Cl_2$ | 27 | $AlEtCl_2$ | 7 | 10 | 43 | | |
| 6 | Toluene | −78 | $AlEtCl_2$ | 7 | 0.5 | 50 | | |
| 7 | Toluene | −78 | $AlEtCl_2$ | 7 | 1 | 67 | | |
| 8 | Toluene | −78 | $AlEtCl_2$ | 7 | 2 | 61 | | |
| 9 | Toluene | −78 | $AlEtCl_2$ | 1 | 2 | 79 | | |
| 10 | Toluene | −78 | $AlEtCl_2$ | 2 | 2 | 72 | 4000 | |
| 11 | Toluene | −78 | $AlEtCl_2$ | 8 | 2 | 78 | | |
| 12 | Toluene | −78 | $AlEt_3/TiCl_4$ | 2/2 | 2 | 73 | | |
| 13 | Toluene | −78 | $AlEt_3/TiCl_4$ | 2/4 | 2 | 27 | | |
| 14 | Toluene | 25 | $BF_3(OEt_2)$ | 1 | 10 | 70 | | 85—105 |

a) Monomer concentration; 0.1 mol/l.

b) Mol. Wt. was measured by a vapor pressure osmometer.

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[6] S. Murahashi, S. Nozakura, M. Sumi, S. Fujii, and K. Matsumura, *Kobunshi Kagaku*, **41**, 550 (1966). S. Murahashi, H. Yuki, T. Sano, U. Yonemura, H. Tadokoro, and Y. Chatani *J. Polym. Sci.*, **62**, S77 (1962).

[7] W. H. Watanabe and L. E. Conlon, *J. Amer. Chem. Soc.*, **79**, 2828 (1957).

TABLE 2. POLYMERIZATION OF PVE[a)]

| No | Temp °C | Catalyst | Cat Concn mol% | Time hr | Yield % | Mol Wt[b)] | Softening range °C |
|---|---|---|---|---|---|---|---|
| 1 | −78 | $AlEtCl_2$ | 4.7 | 22 | 52 | 1800 | |
| 2 | −25 | $BF_3(OEt_2)$ | 10 | 5 | 85 | | 160—170 |
| 3 | 25 | $BF_3(OEt_2)$ | 1 | 17 | 58 | 1570 | 170—200 |
| 4 | 25 | $BF_3(OEt_2)$ | 2 | 17 | 63 | | |
| 5 | 25 | $BF_3(OEt_2)$ | 1.5 | 15 | 75 | c ) | c ) |
| 6 | −78 | $BF_3(OEt_2)$ | 1 | 20 | 50 | | 150—170 |

a) Toluene was used as solvent. Monomer concentration was 0.1 mol/l. b) Mol. Wt. was measured by a vapor pressure osmometer. c) see Table 3.

TABLE 3. FRACTIONATION OF PPVE[a)]

| Fraction | Solubility[b)] | Wt% | Mol Wt | Softening range °C |
|---|---|---|---|---|
| I | insoluble in tetrahydrofuran | 3 | | 250—280 |
| II | soluble in tetrahydrofuran, insoluble in benzene | 51 | 2900 | 220—230 |
| III | soluble in both tetrahydrofuran and benzene | 43 | 1400 | 185—195 |

a) The polymer of No 5 in Table 2 was used as a sample.
b) Each fraction was precipitated by methanol.

of both PPVE and PPVE doped with TCNE because of the low molecular weight of PPVE, the powder of the polymer was compressed into a disk under a pressure of 7000 kg/cm², upon which a pair of comb-type gold electrodes were evaporated under $10^{-5}$ mmHg. The surface-type cell thus obtained (distance between the electrodes, 0.02 cm; electrode length, 5 cm) was used for the electrical measurement of PPVE. Dark- and photocurrents were measured in a high vacuum ($10^{-4}$—$10^{-5}$mmHg) or in the air by the DC method with a Takedariken TR81 vibrating-reed electrometer. The monochromatized light from a 500 W xenon lamp was used, its intensity being controlled by neutral filters. The voltage was applied up to about 10000 V/cm. The measurements were carried out in the range from −10° to 70°C.

## Results and Discussion

*Polymerization.* The polymerization results are shown in Tables 1 and 2. Both polymers, PNVE and PPVE, were obtained in good yields, although the molecular weight was fairly low. The difficulties in the chain growth of the monomers, especially in that of PVE, might be due to the steric effect of the large substituent groups under these catalytic conditions.

The polymerization of NVE proceeded rapidly within half an hour, but the polymer yield increased very slowly thereafter. The effect of both temperature and solvent on the polymer yield were very small.

PPVE was fractionated according to the solubility, as is shown in Table 3. Each fraction showed the same elementary composition. The main differences between fractions are found in the molecular weight, the melting point, and the IR absorption spectrum. The IR spectrum of each fraction is shown in Fig. 1. The most significant difference in the IR absorption observed at 1060 and 1135 cm⁻¹. The difference in the solubility must be due to the difference in the molecular weight of the polymer. Fraction I, insoluble both in tetrahydrofuran and in benzene, has the highest melting temperature and probably the highest molecular weight. Fractions II and III have lower melting points and lower molecular weights. It is not clear whether these differences are due to the difference in crystallinity and/or to that in tacticity.

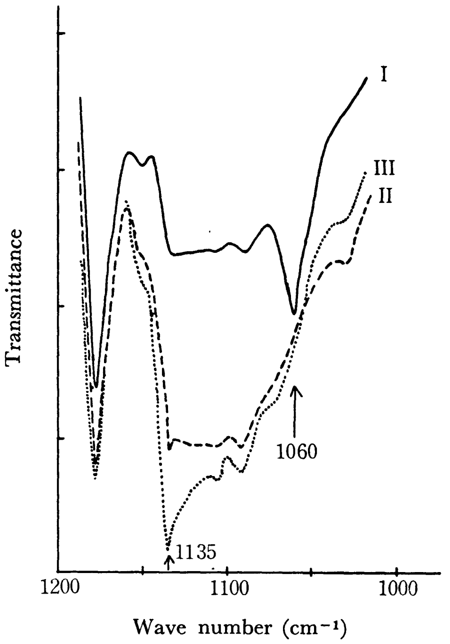

Fig. 1. IR spectra of each fraction of PPVE. Fractions I, II, and III.

The tacticity of PNVE was studied by means of the IR spectrum of the polyvinylalcohol (PVA) led from the polymer. Dry HBr gas was bubbled into a toluene solution of PNVE with stirring at room temperature. The resulting precipitate, PVA, was washed with toluene and dried in a vacuum. The IR spectrum of

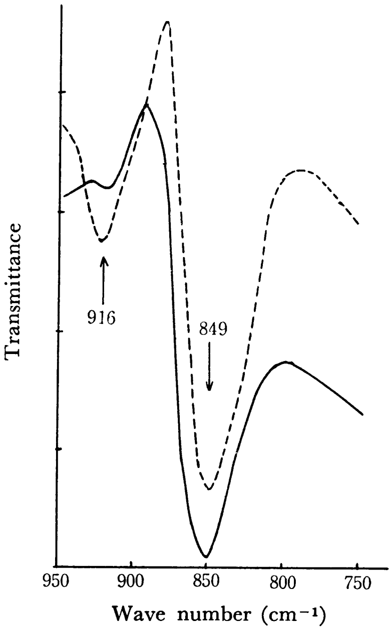

Fig. 2. IR spectrum of PVA.
solid line: PVA obtained from PNVE (No. 15 in Table 1), broken line: commercial atactic PVA.

PVA thus obtained was measured in a film; it is shown in Fig. 2. The absorbance ratio of 916 to 849 cm$^{-1}$, $D_{916}/D_{849}$, was reported to be a measure of the syndiotacticity of PVA.[8] The $D_{916}/D_{849}$ ratio was found to be 0.03 for PVA from PNVE. This value corresponds to an isotacticity of 80—90%. The PNVE obtained by the above-mentioned procedure is, therefore, highly isotactic. The high isotacticity seems to result from the effect of the large substituent group on the polymerization.

PPVE was treated by a similar method, but the difficulty in cleaving this polymer to PVA hindered us from obtaining a clear answer as to the polymer tacticity. PPVE, however, might be safely said to have a fairly high isotacticity because of the effect of the bulky substituent group, which is larger than those of the polybenzyl- and polynaphthylmethyl-vinylethers.

PNVE is amorphous judging from the X-ray diffraction pattern, although it has a high isotacticity. An appropriate heat-treatment did not improve its crystallinity.

*UV Absorption Spectra.* Figure 3 shows the absorption spectra of the polymers and their charge-transfer complexes (CT complex) in methylene chloride. The CT complex of PNVE showed the same spectrum as did the CT complex of naphthylmethylethylether. The equilibrium constants for the CT complexes were calculated by means of the Benesi-Hildebrand equation. The equilibrium constant for the PNVE-TCNE complex was found to be 1.5 l/mol at 20°C in methylene chloride. This was much smaller than that for the naphthylmethylethylether-TCNE complex (4.5 l/mol at 20°C in methylene chloride). Similar results have been reported for the CT complexes of poly-*N*-vinylcarbazole and *N*-ethylcarbazole.[9] It may be noted that the steric effect on the equilibrium is considerable, even for the polymer such as PNVE, in which the side-chain group is separated from the main chain by the –O–CH$_2$– bond.

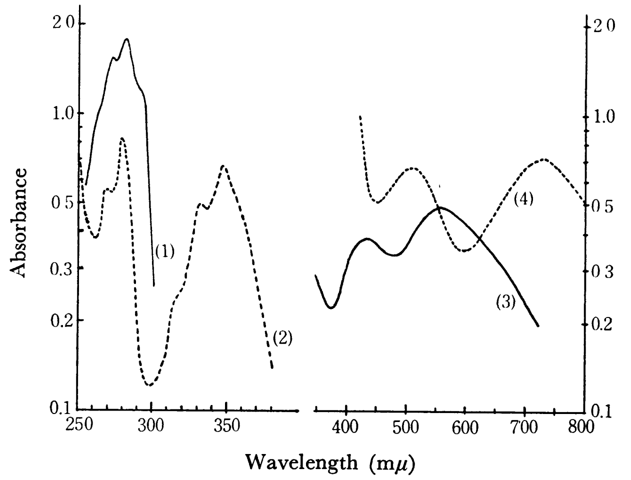

Fig. 3. UV absorption spectra of PNVE, PPVE and their CT complexes with TCNE in methylene chloride.
(1) PNVE ($2.40\times10^{-4}$ mol/l); (2) PPVE ($8.8\times10^{-4}$ mol/l); (3) PNVE ($4.60\times10^{-2}$ mol/l) and TCNE ($8.2\times10^{-3}$ mol/l); (4) PPVE ($1.0\times10^{-2}$ mol/l) and TCNE ($7.0\times10^{-2}$ mol/l).

*Dark Conductivity.* The dark current of PPVE was too small to be observed with a surface-type cell ($i_d \ll 10^{-15}$ A under 10000 V/cm). The sandwich-type cell of PNVE showed an ohmic dark current (specific conductivity at 50°C, $\sigma_{50}=10^{-18}\,\Omega^{-1}\,\text{cm}^{-1}$) whose activation energy was 1.9 eV in a high vacuum.

*Photoconductivity.* PNVE showed only a small photocurrent in the wavelengths shorter than 350 mμ.

Fractions II and III of PPVE in Table 3 were used for the measurements, no difference in electrical conductivity being observed between these fractions. The data to be presented below were obtained from Fraction III.

PPVE showed a large photoresponse, as is shown in Fig. 4. The photocurrent was proportional both to the applied voltage and to the light intensity at every wavelength, as is shown in Figs. 4 and 5. No appreciable photovoltaic current was observed. Figure 6 shows the spectral dependence of the photocurrent and the diffuse reflectance spectra. The diffuse reflectance spectra were measured using potassium bromide powder as a standard and are plotted using the Kubelka-Munk function, $f(R)=(1-R)/2R$, where $R$ is the reflectance. The long-wavelength absorption peak was observed at 380 mμ in the solid state. This corresponds to the long-wavelength and low-intensity band of the pyrene ring, which has been observed at 376 mμ for 3-ethylpyrene and poly-3-vinylpyrene in a THF solution.[10] A maximum in the photocurrent

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[8] S. Murahashi, S. Nozakura, M. Sumi, H. Yuki, and K. Hatada, *J. Polym. Sci.*, *B*, **4**, 65 (1966).

[9] A. Rembaum, A. M. Hermann, and R. Haack, *J. Polym. Sci.*, *A*-1, **6**, 1955 (1968).

[10] K. Tanikawa, Thesis, Osaka University, 1970.

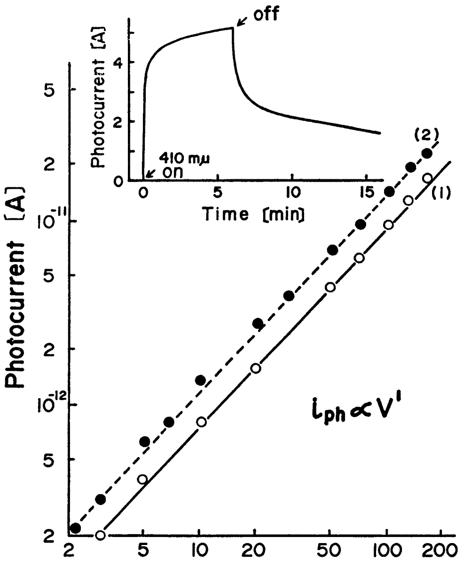

Fig. 4. Voltage dependence of photocurrent of PPVE.
(1) in high vacuum, (2) in air, under 410 mμ illumination. The photoresponse curve is also shown.

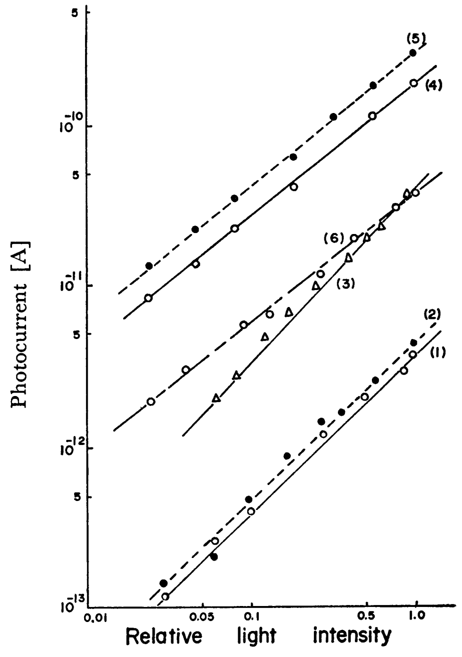

Fig. 5. Light intensity dependence of photocurrent of both PPVE and of PPVE doped with TCNE.
(1), (2), and (3); PPVE. (4), (5), and (6); PPVE doped with TCNE. (1) and (4) 420 mμ illumination in high vacuum, (2) and (5) 420 mμ illumination in air, (3) panchromatic light (from a 500 W xenon lamp) illumination in air, (6) 600 mμ illumination in high vacuum, under 2500 V/cm.

was observed at about 410 mμ, at a little longer wavelength than the absorption peak. A similar shift of the maximum in the photocurrent from the absorption peak has been also observed in poly-*N*-vinylcarbazole.[5] A small photocurrent was observed even above from 500 mμ to 1000 mμ, where PPVE has no absorption. The activation energy of the photocurrent, $\Delta E_a$, in the equation; $i \propto \exp(-\Delta E_a/kT)$ was 0.3—0.4 eV at every wavelength in a vacuum or in air (Fig. 7). The magnitude of the photo-current was larger by two factors in air than in a high vacuum. This suggests that the majority carrier in PPVE is a hole rather than an electron. This sign of the carrier is the same as that in other polymers with large π-electron systems, such as poly-*N*-vinylcarbazole.[5]

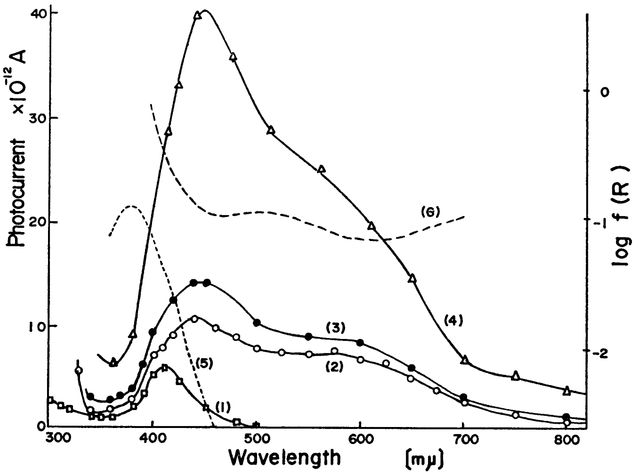

Fig. 6. Spectral response of photocurrent of PPVE sensitized with TCNE and diffuse reflectance spectra both of PPVE and of PPVE doped with TCNE.
Photocurrent was normalized for the light intensity of $1 \times 10^{14}$ photons/cm² sec. (1) PPVE in high vacuum, (2) PPVE doped with TCNE (1 mol%) in high vacuum, (3) PPVE doped with TCNE (1 mol%) in air, (4) PPVE doped with TCNE (10 mol%) in high vacuum, under 2500 V/cm. The values in the curve (4) are 1/2 of the observed ones. (5) and (6) diffuse reflectance spectra of PPVE and PPVE doped with TCNE (1 mol%).

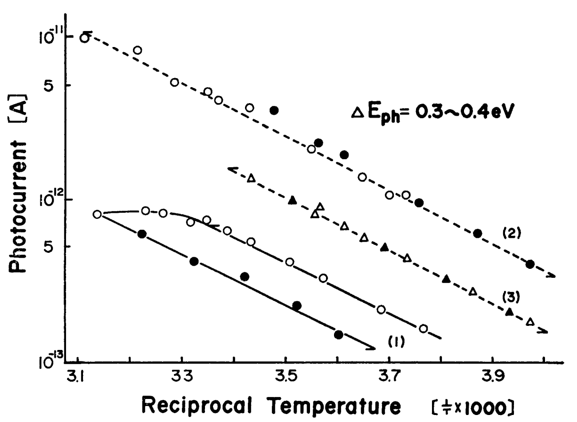

Fig. 7. Temperature dependence of photocurrent of PPVE. (1) 420 mμ illumination in high vacuum, (2) 420 mμ illumination in air, (3) 600 mμ illumination in air, under 2500 V/cm. The values in the line (1) are 1/10 of the observed ones.

Generally, polymers have many impurities which act as trapping centers. In many cases,[5,11] a re-excitation of the carriers trapped in the centers by

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[11] T. Tanaka, Y. Inuishi, *Japan. J. Appl. Phys.*, **6**, 1371 (1967).

Table 4. Sensitization factors of dark- and photoconductivities of PPVE by doped TCNE

| TCNE Content mol% | Darkconductivity[a] | Photoconductivity[a] | | | |
|---|---|---|---|---|---|
| | | 700 mμ | 550 mμ | 450 mμ | 410 mμ |
| 1 | larger than $10^2$ | 36 | 35 | 5.3 | 1.3 |
| 10 | larger than $5\times10^3$ | 186 | 250 | 40 | 5 |

a) The currents were measured under 2500 V/cm in a high vacuum at room temperature.

illumination creates the photocurrent which is sensitive to visible or IR light. PPVE showed this behavior; that is, even after the cell had been kept for many hours under no applied voltage in the dark at room temperature the photocurrent was observed for a while when the cell was illuminated with visible light under no applied voltage. This suggests that PPVE also has many deep traps, which may be the origin of the photocurrent in the visible and near IR regions.

*Sensitization of the Conductivity of PPVE.* The doping of TCNE sensitized both the dark- and photoconductivities of PPVE. The degree of sensitization increased with the doping amount, as is shown in Table 4. The sensitized dark- and photocurrents were ohmic. The sensitized photocurrent showed a sublinear dependence (0.8 power) on the light intensity, as is shown in Fig. 5.

Figure 8 shows the temperature dependence of the sensitized dark- and photocurrents. The activation energies for the dark- and photocurrents were 1.1 eV and 0.18—0.25 eV respectively, both *in vacuo* and in air. Doped TCNE decreased the activation energy for photocurrent of PPVE. A similar effect has been reported for other polymers.[13]

Its spectral dependence was not, however, consistent with the absorption spectrum of PPVE-TCNE system in the solid state, as is shown in Fig. 6. A maximum and a shoulder in the photocurrent were observed at about 450 mμ and in the 550—650 mμ region (the CT absorption region) respectively. Doped TCNE apparently caused the large increase in the photocurrent in the CT bands, especially in the shorter wavelength CT band. The CT excitation with a higher energy will generate the carriers more easily:

$$(\mathrm{D}\cdots\mathrm{A}) \xrightarrow{h\nu_{\mathrm{CT}}} (\mathrm{D}^+\cdots\mathrm{A}^-)^* \longrightarrow \mathrm{D}^+ + \mathrm{A}^- \qquad (1)$$

In addition to the spectral sensitization mentioned above, the chemical sensitization was also observed. Doped TCNE enhanced the photocurrent in the absorption region of PPVE by a factor of 1.5—2.0 in the case of 1 mol% (doping amount) and by a factor of 5 in the case of 10 mol%. Similar behavior was observed in the photoconductivity of poly-*N*-vinylcarbazole; it can be explained in terms of both the field-assisted thermal dissociation of an excited CT complex and the excitation of the donor, A⁻, by singlet excitons.[12] The same mechanism is applicable for the chemical sensitization of the photocurrent of PPVE by doped TCNE; that is,

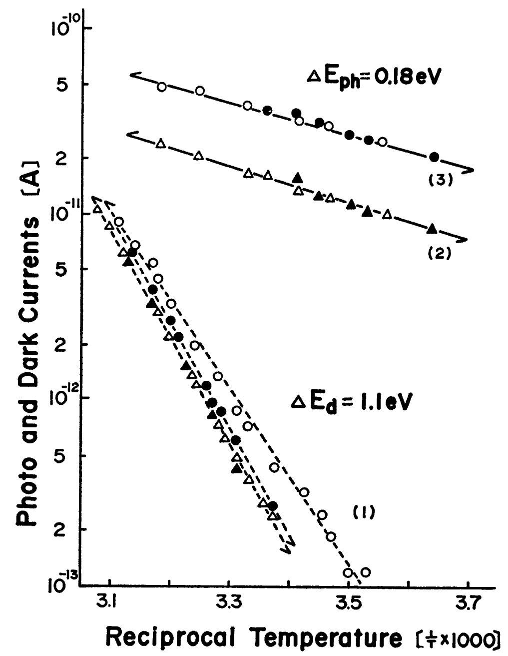

Fig. 8. Temperature dependence of photo- and dark-currents of PPVE sensitized with TCNE.
(1) dark current (○; 1-st heating, ●; 1-st cooling, △; 2-nd heating, ▲; 2-nd cooling), (2) photocurrent under 420 mμ illumination, (3) photocurrent under 600 mμ illumination, in high vacuum 2500 V/cm.

$$\mathrm{D} \xrightarrow{h\nu} \mathrm{D}^* \qquad (2),$$

$$\mathrm{D}^* + \mathrm{A} \longrightarrow (\mathrm{D}^+\cdots\mathrm{A}^-)^* \longrightarrow \mathrm{D}^+ + \mathrm{A}^- \qquad (3),$$

$$\mathrm{A}^- + \mathrm{D}^* \longrightarrow \mathrm{A} + \mathrm{D}^- \qquad (4),$$

where D is a donor molecule; D*, an excited singlet state of the donor; A, an acceptor molecule; $(\mathrm{D}^+\cdots\mathrm{A}^-)^*$, an excited CT complex; D⁺ and D⁻, ion radicals of the donor (mobile charge carriers), and A⁻ the anion radical of the acceptor (immobile). The gaseous electron affinity ($EA_G$) of TCNE and pyrene are 2.2 eV[14] and 0.58 eV[15] respectively. On the assumptions that the $EA_G$ value of PPVE is equal to the value of pyrene, and that the polarization energy due to PPVE⁻ is equal to that due to TCNE⁻ in a pellet of PPVE doped with TCNE, the energy required for the excitation of an electron from TCNE⁻ to the conduction level of PPVE is estimated to be 1.6 eV. As the energy of the singlet exciton (∼3.2 eV) is larger than this value, Process (4) is probable.

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[12] K. Okamoto, S. Kusabayashi, and H. Mikawa, submitted to this Bulletin.

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[14] G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

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