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Synthesis of 3-Vinylpyrene by Wittig's Reaction, and Syntheses and Electrical Properties of Polyvinylpyrene and Its Charge Transfer Complexes

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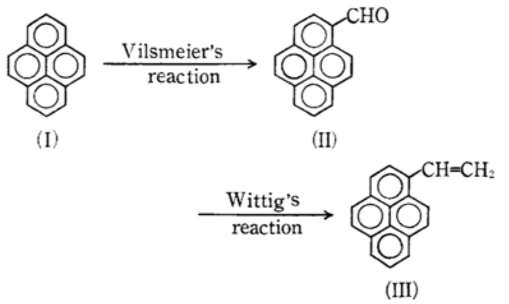
Using Wittig's reaction, we synthesized 3-vinylpyrene from pyrene-3-aldehyde in 76% yield. 3-Vinylpyrene monomer was polymerized by benzoylperoxide or di-*t*-butylperoxide catalysts. Each polymer had a melting point, being observed by the method of polarizing hot stage microscopic examination. X-ray examination showed that the polymer was crystalline, although rather poor. The charge transfer complexes, containing polyvinylpyrene as an electron donor, and iodine, tetracyanoethylene or tetracyanoquinodimethane as an electron acceptor, were prepared, each having the composition of pyrene nucleus : acceptor=16 : 3, 15 : 2, 15 : 2, respectively. Electrical conductivities of the complexes at 25°C, ρ_{25}, and band gap energies, ε, were 1.3×10^{8} Ωcm, 0.80 eV; 4.5×10^{12} Ωcm, 1.32 eV; 1.1×10^{14} Ωcm, 1.34 eV, respectively. Each complex showed ohmic current-voltage characteristics in an appropriate temperature range.

Electrical properties of several vinyl polymers having large π electron systems and of their charge transfer complexes have been reported.[1,2] In order to investigate the electrical properties[3] of polyvinylpyrene (PVP), a vinyl polymer hitherto known having largest π electron systems on a polymer chain, we synthesized PVP and its charge transfer complexes.

Synthesis of 3-Vinylpyrene. 3-Vinylpyrene monomer is known and synthesized by the dehydration of 3-(1-hydroxyethyl)pyrene with Al_2O_3.[4] The product obtained by this method is, however, difficult to purify and the yield is poor. Al_2O_3 employed by us yielded ethylpyrene (isolated and identified) as a by-product, which was very difficult to be separated from 3-vinylpyrene. As reported in the present paper, we synthesized first pyrene-3-aldehyde (II) from pyrene (I) by Vilsmeier's reaction,[5] and then 3-vinylpyrene (III) by Wittig's reaction from the aldehyde.



Both the yield and the quality of 3-vinylpyrene were much improved by using this synthesis method (76% and mp 88—89°C). Although methylenetriphenylphosphorane was synthesized in ether solution, the betaine intermediate obtained from pyrene and methylenetriphenylphosphorane had moderate stability and the decomposition of the betaine to 3-vinylpyrene was effected only at the boiling temperature of tetrahydrofuran (THF).

Synthesis and Properties of Polyvinylpyrene. The polymerization of 3-vinylpyrene was carried out by radical initiators, benzoylperoxide (BPO) or di-*t*-butylperoxide (DTBP), in benzene, toluene or xylene.

Although the polymerization of 3-vinylpyrene by BPO in benzene at 80°C was slow, the polymer obtained had moderate degree of polymerization ([η]$\sim$0.1 in THF at 25°C). By the use of DTBP catalyst in xylene at 140°C, however, the conversion was higher and the polymer began to precipitate in xylene after several hours. The polymer obtained in xylene was somewhat colored and the viscosity was lower, having lower degree

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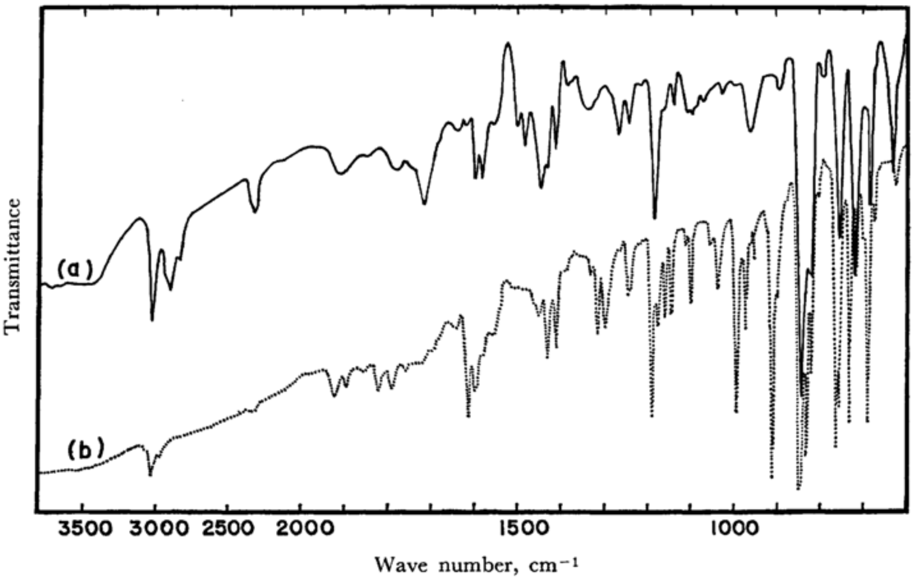

Fig. 1. Infrared spectra of (a) polyvinylpyrene and (b) 3-vinylpyrene in KBr disk.

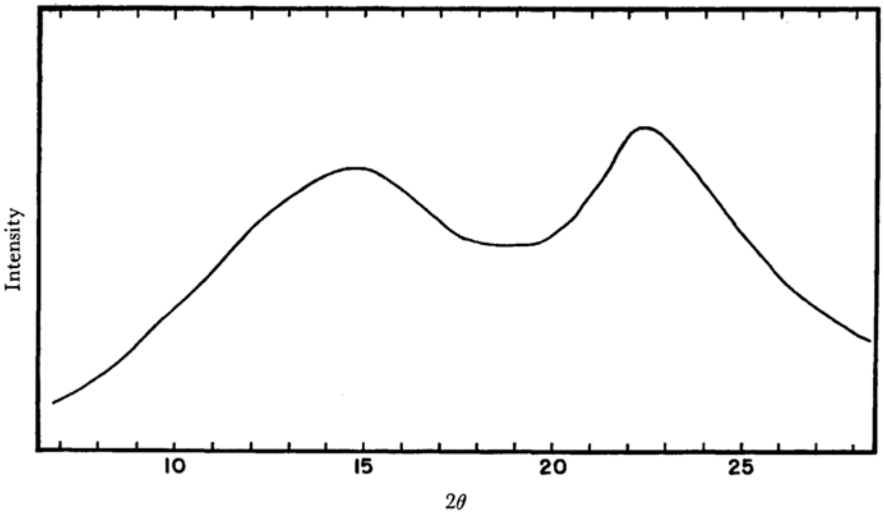

Fig. 2. X-ray diffraction pattern of polyvinylpyrene polymerized by benzoylperoxide catalyst. Rigaku Denki Co.'s X-ray diffractometer, CuK_α (Ni-filtered), 30 kV-20 mA, slit geometry 1°—1°—0.1 mm, scanning speed 1°/min, chart speed 10 mm/min, full scale 400 cps.

of polymerization.

Infrared spectrum of PVP, Fig. 1, shows the disappearance of the absorptions of the end vinyl group (910 and 990 cm^{-1}) in 3-vinylpyrene.

The partially crystalline nature of PVP has been recognized by the examinations with X-ray diffraction and polarizing hot-stage microscope. An X-ray diffraction pattern of PVP polymerized by BPO annealed at 240°C for 4 hr did not show any sharp diffraction peaks as shown in Fig. 2. This X-ray diffraction pattern shows that the polymer is poorly crystallized, if not completely in noncrystalline state.

Examinations of the PVP specimens under the polarizing hot-stage microscope showed the following facts: At room temperature, the polymer powder prepared by precipitation from its solution showed a few birefringent regions as light spots distributed in a dark visual field of crossed Nicols. When this powder is finely powdered in an agate mortar, many light spots appeared along with the considerable amount of weakly light spots. Although the latter weakly light spots may be due to an internal stress *etc.* of PVP sample, the former light spots are believed to be due to the crystalline birefringent regions in the polymer.

TABLE 1. PROPERTIES OF CHARGE TRANSFER COMPLEXES

Charge transfer complexe	Donor : Acceptor	Softening range* °C	ρ Ωcm	ε eV
PVP-iodine	16 : 3	280—290	1.3×10^{8}	0.80
PVP-TCNE	15 : 2	267—280	4.5×10^{12}	1.32
PVP-TCNQ	15 : 2	230—240	1.1×10^{14}	1.34

* Softening range is observed by pressing the polymer between glass plates under microscope.

TABLE 2. POLYMERIZATION OF POLYVINYLPYRENE

	Condition					Product	
	Solvent m*l*	Monomer g	Initiator mg	Time hr	Temp. °C	Softening range, °C	Yield g
1	Benzene 25	2.3	BPO 9.7	22	80	270—295	0.53
2	Toluene 18	1.7	DTBP 11.0	21	110	230—270	0.4
3	Xylene 32	3.2	DTBP 22.0	18	140	235—250	1.0

When PVP sample is heated very slowly, the light spots disappeared completely at about 254°C (PVP polymerized by BPO in benzene), about 198°C (DTBP in toluene), and about 213°C (DTBP in xylene). These temperatures are believed to be the melting points of the polymers.

It is very interesting that PVP prepared by radical polymerization is crystalline. This may be due to the effect of very large pendant pyrene groups. It is observed that *N*-vinylcarbazole having very large carbazyl groups gives highly crystallized polymer even when polymerized by radical process. Detailed results will be published in the near future.[6]

Preparations of the Charge Transfer Complexes. The charge transfer complexes, having PVP as an electron donor, and iodine, tetracyanoethylene (TCNE) or tetracyanoquinodimethane (TCNQ) as an electron acceptor, were prepared.

The absorption spectra of the charge transfer complexes in film show charge transfer bands as shown in Fig. 3. It is known that pyrene-TCNE complex shows charge transfer bands[7] around 500 and 730 mμ in dichloromethane solution, or around 510 and 830 mμ in crystalline state, and pyrene-iodine complex has the charge transfer band[8] around 420 mμ. As shown in Fig. 3, PVP-TCNQ, PVP-TCNE and PVP-iodine complexes exhibit the absorption band due to charge-transfer excitation around 700—900 mμ. The wavelength of the charge transfer band of the PVP-TCNQ complex, 780 mμ, is much longer than that of poly(*N*-vinylcarbazol) - TCNQ complex,[2] around 620 mμ.

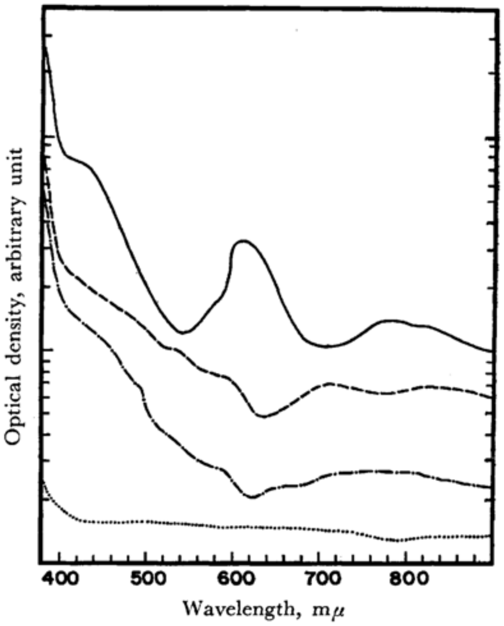

Fig. 3. Absorption spectra of the charge transfer complexes in solid film.
——, PVP-TCNQ; ----, PVP-TCNE;
·—·, PVP-iodine; ……, PVP

From the elementary analyses of iodine and nitrogen, the compositions of the three complexes were found to be pyrene nucleus : acceptor = 16 : 3, 15 : 2, and 15 : 2, respectively (Table 1).

Electrical Properties of the Charge Transfer Complexes. A sample tablet, 12.5 mm diameter and *ca.* 1 mm thick, was made by pressing about 0.3 g of finely powdered samples of charge transfer complexes at 150—200 kg/cm². Silver paste was painted on both sides of the tablet, with a guard ring on one side.

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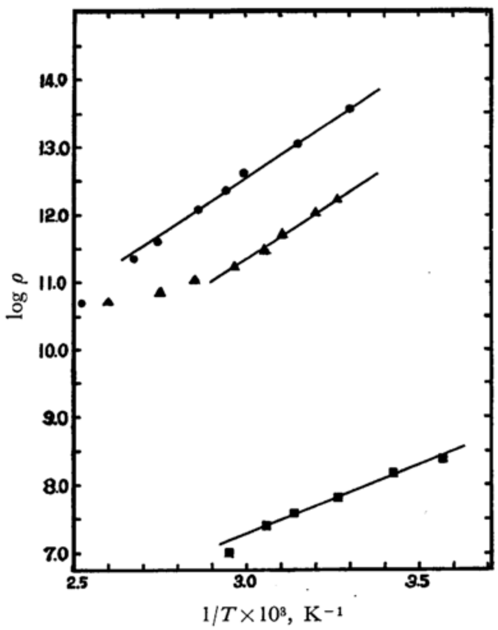

Fig. 4. The relations between resistance and temperature in charge transfer complexes.
—●—, PVP-TCNQ; —▲—, PVP-TCNE;
—■—, PVP-iodine.

The electrical conductivity of the tablet thus prepared was measured by the DC method. The sample was put in a well sealed conductivity cell placed in a thermostat. The current was measured by using a Takeda Riken Vibrating Reed Electrometer.[2,9]

Electrical resistivities of these complexes are fairly low. The relation between applied voltage and current obeys Ohm's law.

Figure 4 shows the relations between resistance and temperature. In PVP-iodine complex, at about 80°C, the curve begins to deviate from an equation $\rho=\rho_0\exp(\varepsilon/2kT)$ (ρ, specific resistance in Ω cm; ρ_0, constant; k, Boltzmann's constant; ε, energy gap of a band model in eV). The deviation may be due to the beginning of decomposition of the complex.

In PVP-TCNE complex, the curve begins to deviate from lineality at about 90°C, showing probably the beginning of decomposition in this case also. PVP-TCNQ complex is most stable to heat.

Among three polymeric charge transfer complexes, PVP-iodine complex has the best electrical conductivity and the smallest band gap energy as shown in Table 1. PVP-TCNQ complex has the best heat stability.

Experimental

Pyrene-3-aldehyde (II).[5] With stirring, 135 g of $POCl_3$ was gradually droped into a mixture of 135 g of *N*-methyl-formanilide and 100 m*l* of *o*-dichlorobenzene during 2 hr at 0—5°C. Into this reaction mixture, 100 g of powdered pyrene was added gradually. After stirring for 3 hr at 90—95°C, the reaction product was decomposed by 1000 m*l* of water containing 480 g of sodium acetate. Both *o*-dichlorobenzene and *N*-methylaniline were steam distilled, and the crude pyrene-3-aldehyde was recrystallized from ethyl alochol. Mp 125—126°C. Yield 56%.

Found: C, 88.67; H, 4.38%. Calcd for $C_{17}H_{10}O$: C, 88.40; H, 4.50%.

3-Vinylpyrene (III). From an injector, ethereal solution (*ca.* 80 m*l*) containing 0.08 mol of phenyllithium[10] was added with stirring into 28.6 g (0.08 mol) of powdered triphenylphosphonium bromide suspended in 250 m*l* of dry ether. The reaction was carried out with stirring in a dry nitrogen stream for about 23 hr at room temperature.[11] After the reaction, 100 m*l* of THF containing 16.1 g (0.07 mol) of pyrene-3-aldehyde was dropped into the reaction solution and 150 m*l* of dry THF was introduced into the solution. After stirring in a dry nitrogen stream at least for about 2 hr at room temperature, ether was removed by distillation and the refluxing of THF was continued for about 24 hr at 65—66°C. THF was distilled and the residue was extracted with benzene, washed by aq. 30% $NaHSO_3$ solution and water. Sometimes triphenylphosphinoxide crystallized out from the solution. 3-Vinylpyrene, showing yellow green fluorescence, was separated from benzene solution by adsorption chromatography (Al_2O_3), 3-vinylpyrene being most weakly adsorbed than the other components. Final recrystallization from ethyl alcohol yielded 3-vinyl pyrene, mp 88—89°C, 76%. 3-Vinylpyrene was stored in nitrogen atmosphere in the dark.

Found: C, 94.69; H, 5.30%. Calcd for $C_{13}H_{12}$: C, 94.20; H, 5.38%.

Polymerization. 3-Vinylpyrene was polymerized by BPO or DTBP in purified benzene, toluene or xylene. The polymerizations were carried out in a dry nitrogen stream under the following conditions (Table 2): The polymer was separated by precipitating with methyl alcohol. The polyvinylpyrene was purified several times by reprecipitation method. $[\eta]$ ~0.1 in THF at 25°C.

Charge Transfer Complexes. Twenty-five milliliters of chloroform containing 0.6 g of sublimed iodine was added into 10 m*l* of chloroform containing 0.5 g of PVP, and the solution was stirred for 5 hr at room temperature, set aside overnight, and poured into petroleum ether, and the very fine precipitate was separated by centrifuge, washed and dried in a desiccator. In the case of both TCNE and TCNQ, the procedures were the same. Found: PVP-iodine, iodine 17.29%; PVP-TCNE, nitrogen 2.93%; PVP-TCNQ, nitrogen 2.89%.

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