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Preparation of an Electrically Conducting Polymer by the Electrolytic Polymerization of 3-Vinylperylene

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An electrically conducting polymer was prepared by the controlled-potential anodic oxidation of 3-vinylperylene in a dichloromethane solution containing tetra-*n*-butylammonium perchlorate as a supporting electrolyte. The electrochemically-doped polymer is a partially oxidized radical-cation salt with ClO_4^- as a dopant; it exhibits a room-temperature conductivity up to 1×10^{-4} S cm $^{-1}$ with an activation energy of ca. 0.3 eV.

INTRODUCTION

Electrically conducting polymers have attracted attention from the viewpoints of both fundamental research and practical applications, and have been a subject of recent extensive studies.[1,2] They seem to be classified mainly into three groups: π-conjugated polymers, non-conjugated polymers containing pendant π-electron systems, and composite systems composed of π-conjugated polymers dispersed in an inert processable polymer. Generally, electrical conductivity in polymers is attained by doping, which has been carried out both chemically and electrochemically.

Linear π-conjugated polymers such as polyacetylene, poly(*p*-phenylene), and poly(*p*-phenylene vinylene), have received attention for their ability to generate high electrical conductivity by doping. It has been shown with polyacetylene that electrical conductivity varies widely in character from insulating to metallic depending upon the doping level.[3,4] It has also been shown that electrolytic polymerizations of pyrrole,[5] thiophene,[6] and aniline[7] produce highly conducting π-conjugated polymers. In these cases, electrochemical doping is achieved at the same time as the polymerization reaction which proceeds via oxidative coupling reactions.

In contrast to π-conjugated polymers, non-conjugated polymers containing pendant π-electron systems are of interest for the following reasons: there are a variety

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of these substances including photoconducting polymers; they are chemically stable and processable; and the standard oxidation-reduction potential is independent irrespective of the doping degree because of weak pendant-pendant interactions. We have been interested in how much conductivity is attained by electrochemical doping of vinyl aromatic polymers and in applications of electrochemically-doped polymers as positive electrode materials for secondary batteries and as photoactive materials for photovoltaic devices. We have reported that insulating vinyl aromatic polymers are transformed into semiconducting polymers by electrochemical doping[8,9] and that electrochemically-doped, semiconducting polymers are also prepared by the electrolytic polymerizations of vinyl monomers such as *N*-vinylcarbazole,[10] 1-vinylpyrene,[11] and 2-*N*-carbazolylethyl vinyl ether.[12] We have shown that electrochemically-doped polymers with aromatic pendants, e.g. poly(N-vinylcarbazole), function as positive electrode materials for rechargeable batteries[13] and as photoactive materials for photovoltaic devices.[14,15]

As a part of a series of our studies on the preparation and properties of electrically conducting polymers containing pendant π-electron systems and on applications of doped polymers as functional materials, we have studied the preparation of electrochemically-doped poly(3-vinylperylene) in light of the following considerations. Perylene-bromine and perylene-iodine charge-transfer complexes are well-known organic conductors from early studies;[16,17] they exhibit rather high electrical conductivities of ca. 10^{-1} S cm^{-1}. Recently a perylene radical-cation salt produced by the electrocrystallization of perylene has been reported to exhibit a room-temperature conductivity as high as 8.6×10^2 S cm^{-1}.[18] This paper deals with the preparation of an electrically conducting polymer by the electrolytic polymerization of 3-vinylperylene, and with characterization and electrical properties of electrochemically-doped polymers.

EXPERIMENTAL

Materials. 3-Vinylperylene was prepared according to the method of Buckley and Teuscher[19] as follows. 3-Perylenecarboxaldehyde was synthesized from perylene by the Vilsmeier reaction, and then converted to 3-vinylperylene using a modification of the Wittig reaction. It was purified twice by silica gel column chromatography, m.p. 154–155°C. Tetra-*n*-butylammonium perchlorate was recrystallized from ethanol three times, dried at 70°C for one day, and redried immediately before use. Dichloromethane was treated with conc. sulfuric acid, water, and then distilled over calcium hydride immediately before use.

Electrochemical measurements. The cyclic voltammetry was carried out for a dichloromethane solution of 3-vinylperylene (1×10^{-3} mol dm^{-3}) containing tetra-*n*-butylammonium perchlorate (0.1 mol dm^{-3}) as a supporting electrolyte with Ag/Ag$^+$ 0.01 mol dm^{-3} Reference electrode at a sweep rate of 100 mV s^{-1}. The electrolytic polymerization was carried out potentiostatically for a dichloromethane solution of 3-vinylperylene (5×10^{-3} mol dm^{-3}) containing tetra-*n*-butylammonium perchlorate (0.1 mol dm^{-3}) in a two-compartment cell with three electrodes at 0.8 V vs. Ag/Ag$^+$ 0.01 mol dm^{-3} reference electrode. Platinum plates ($1.5 \times$

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2.5 cm^2 and 2.0 × 2.0 cm^2) were used as the working and counter electrodes, respectively. When the controlled-potential electrolysis was carried out, green-colored polymers were deposited on the surface of the working electrode. After controlled-potential electrolysis was carried out for an appropriate time, the polymers were washed with purified dichloromethane and dried in vacuo. For example, when the electrolysis of 3-vinylperylene (34.8 mg, 5×10^{-3} mol dm^{-3}) started, a current of ca. 2.5 mA flowed, and it gradually decreased to 0.5 mA during the electrolysis. After electrolysis for 6 hr, during which ca. 18 coulombs of electricity flowed, 30 mg of electrochemically-doped polymers were obtained. The degree of doping for resulting polymers was determined by the analysis of the chlorine content of the dopant.

The electrical conductivity was measured by a two-probe d.c. method for samples of pressed pellets, on which gold was vacuum-deposited to make the electrodes. The activation energy for the electrical conduction was determined from Arrhenius plots of electrical conductivities measured in the temperature range from 20°C to 80°C.

Apparatus. Electrochemical measurements were performed with a Model HA-104 potentiostat (Hokuto Denko, Ltd.), a Model HP-104 function generator (Hokuto Denko, Ltd.), and a Model NP-0361 recorder (Rikadenki). Infrared and electronic absorption spectra were measured with a Model A-102 diffraction grating infrared spectrophotometer (Japan Spectroscopic Co., Ltd.) and a Model U-3200 double beam spectrophotometer (Hitachi, Ltd.), respectively.

RESULTS AND DISCUSSION

Figure 1 shows cyclic voltammograms for the anodic oxidation of 3-vinylperylene in dichloromethane. In the first sweep, the anodic and the corresponding cathodic waves were observed at 0.57 V and 0.47 V, respectively, vs. Ag/Ag^+ 0.01 mol dm^{-3} reference electrode. These waves may be ascribed to the oxidation of 3-vinylperylene and the reduction of the resulting radical cation. The oxidation of 3-vinlyperylene was accompanied by the concurrent anodic polymerization to give electroactive polymers. When the sweep was repeated, the cyclic voltammogram exhibited the anodic waves at a potential more negative than 0.5 V and at 0.86 V vs.
Ag/Ag^+ 0.01 mol dm^{-3} and the corresponding cathodic waves. The gradual increase in the peak currents of the waves at 0.86 V and at 0.68 V, which are due to the oxidation of resulting poly(3-vinylperylene) and the reduction of its oxidized form, respectively, is suggested to result from the accumulation of electroactive polymers on the surface of the electrode. The anodic wave at the potential more negative than 0.5 V and the corresponding cathodic wave, which appear in and after the second sweep with a gradual increase in intensity, are suggested to be due to the oxidation of the biperylene moiety generated by the coupling reaction of the pendant perylene radical cations.

Based on the information obtained from the cyclic voltammetry for the anodic oxidation of 3-vinylperylene, 3-vinylperylene was anodically oxidized by means of controlled-potential electrolysis at 0.8 V vs. Ag/Ag^+ 0.01 mol dm^{-3} reference

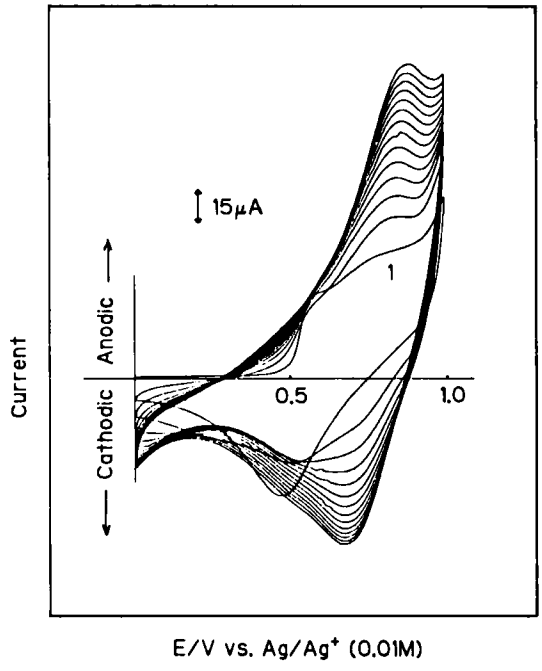

FIGURE 1 Cyclic voltammograms of 3-vinylperylene (1×10^{-3} mol dm^{-3}) in CH_2Cl_2/0.1 mol dm^{-3} Bu_4NClO_4. 1: First sweep. Sweep rate: 100 mV s^{-1}.

electrode. Deep green-colored polymers were deposited on the surface of the working electrode. They were identified as partially oxidized radical-cation salts with ClO_4^- as a counter anion by the electronic and infrared absorption spectra and elemental analysis.

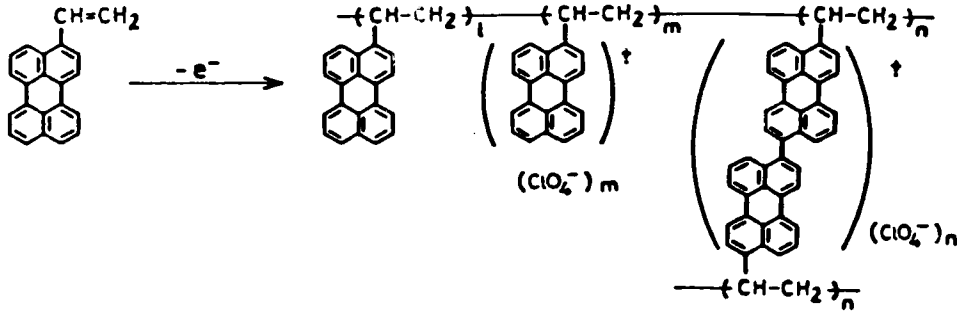

Figure 2 shows the infrared absorption spectra of 3-vinylperylene and electrochemically-doped poly(3-vinylperylene) produced by the electrolytic polymerization of 3-vinylperylene. The characteristic infrared absorption bands at 990 and 910 cm^{-1} observed for 3-vinlyperylene, which is due to the C-H out-of-plane deformation vibration of the vinyl group, were not present in the spectrum of the

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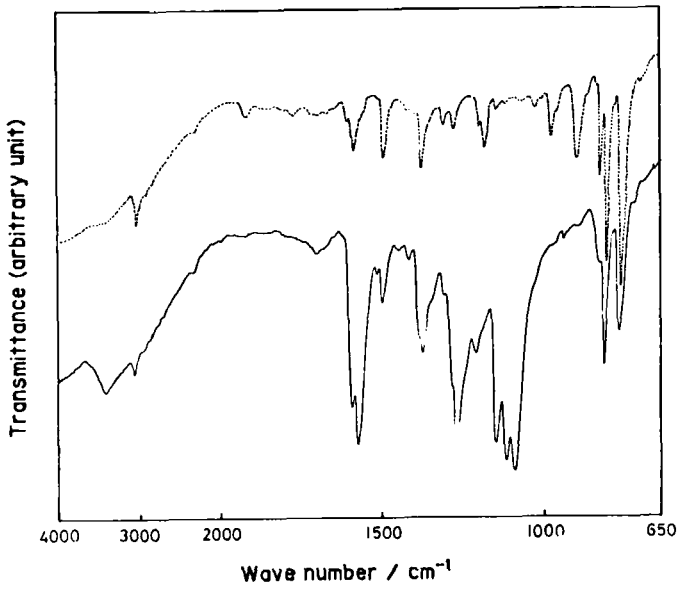

FIGURE 2 Infrared absorption spectra of 3-vinylperylene (-----) and electrochemically-doped poly(3-vinylperylene) produced by the electrolytic polymerization of 3-vinylperylene (——).

resulting polymer. The elctrochemically-doped polymer shows strong infrared absorption bands with peaks at 1140, 1110, and 1080 cm^{-1} due to ClO_4^-. These results indicate that the polymerization takes place at the vinyl group and that the resulting electrochemically-doped polymer contains ClO_4^- as a dopant. It is suggested from the cyclic voltammetry that the pendant perylene rings are partly cross-linked due to the coupling reaction of the pendant perylene radical cations.

Figure 3 shows the electronic absorption spectrum of the electrochemically-doped poly(3-vinylperylene) produced by the electrolytic polymerization of 3-vinylperyl-

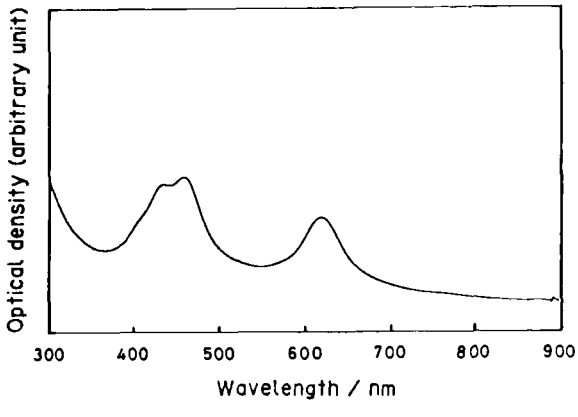

FIGURE 3 Electronic absorption spectrum of electrochemically-doped poly(3-vinylperylene) in the solid state.

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ene. It exhibits a new absorption band with a peak at ca. 620 nm along with the absorption bands characteristic of the neutral perylene chromophore in the wavelength region from 400 nm to 500 nm. The new absorption band with a peak at 620 nm is ascribed to the pendant perylene radical cation. The absorption band observed for the electrochemically-doped poly(3-vinylperylene) in the solid state is red-shifted by ca. 80 nm relative to those reported for perylene radical cations generated by γ-ray irradiation in the sec-butyl chloride matrix solution[20] or by the treatment with antimony pentachloride in chlorobenzene.[21]

Table I lists the room-temperature conductivities and activation energies for conduction for a few samples of the electrochemically-doped poly(3-vinylperylene) prepared by the electrolytic polymerization of 3-vinylperylene. The room-temperature conductivities of electrochemically-doped poly (1-vinylpyrene) prepared by the electrolytic polymerization of 1-vinylpyrene are also listed for comparison. The degree of doping is higher for poly(3-vinylperylene) than for poly(1-vinlypyrene). The electrochemically-doped poly(3-vinylperylene) exhibits higher electrical conductivity than electrochemically-doped poly(1-vinylpyrene); the electrochemically-doped poly(3-vinylperylene) with a doping degree of 71% as determined from the chlorine content exhibits a room-temperature conductivity of ca. 1×10^{-4} S cm^{-1} with an activation energy of 0.28 eV. It is suggested that higher mobilities of charge carriers for poly(3-vinylperylene) than for poly(1-vinylpyrene) as well as higher doping degrees for poly(3-vinlyperylene) are responsible for this. Lower electrical conductivities for the electrochemically-doped poly(3-vinylperylene) relative to the radical cation salts or charge-transfer complexes of low-molecular perylene may be attributed to lower mobilities of charge carriers for the polymers than for the low-molecular materials because of a lower order of the arrangement of pendant perylene chromophores in the polymer.

TABLE I

Electrical Conductivities of Electrochemically-doped Polymers Prepared by Electrolytic Polymerizations of Vinyl Monomers[a)]

Vinyl monomer	Degree of doping[b)](%)	Conductivity σ_{rt} (S cm^{-1})	Activation energy(eV)
VPe[c)]	71	1×10^{-4}	0.28
	64	3×10^{-5}	0.38
VPy[d)]	35	9×10^{-8}	0.41
	24	3×10^{-9}	0.51

[a)]Counter anion: ClO_4^-
[b)]Determined from chlorine analysis
[c)]3-Vinylperylene
[d)]1-Vinylpyrene

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