Polymer Journal, Vol. 19, No. 6, pp 719—725 (1987)

Electronic Conduction in Poly(*p*-phenylene-1,3,4-oxadiazole) Films

Tetsuo TSUTSUI, Yasunori FUKUTA, Takeo HARA,
and Shogo SAITO

*Department of Materials Science and Technology, Graduate School
of Engineering Sciences, Kyushu University,
Kasuga, Fukuoka 816, Japan*

(Received October 16, 1986)

ABSTRACT: Dark conductivity and photoconductivity in poly(*p*-phenylene-1,3,4-oxadiazole) (POD) films were investigated. Above 440 K, ionic conduction was observed. An electronic process which was delicately influenced by the presence of adsorbed oxygen was found below 440 K. Large photoconductivity was observed and its wavelength and temperature dependences were examined. POD films were pyrolyzed at the temperature between 670 and 810 K to give semiconductive polymer films with the conductivity between 10^{-20} and 10^{-5} S cm^{-1}. Variations of dark conductivity, photoconductivity and charge drift mobility with pyrolysis were investigated. Charge drift mobilities of pyrolyzed POD films were around 10^{-7} cm^2 V^{-1} s^{-1} and moderately dependent on the pyrolysis temperature.

KEY WORDS Poly(*p*-phenylene-1,3,4-oxadiazole) / Electrical Conductivity / Photoconductivity / Pyrolysis / Drift Mobility /

Polymers which contain aromatic or heterocyclic rings in their skeletons exhibit minute but distinct and perceptible electronic conduction, although they are known as typical insulating polymers. We have shown the existence of electronic conduction in aromatic polyamides,[1] poly(*p*-phenylene sulfide),[2] poly(ethylene 2,6-naphthalate),[3] and poly(*p*-phenylene).[4] In some cases, electronic conduction is found to be masked by ionic conduction. In some other cases, magnitudes of electronic current are largely affected by several nonsubstantial factors, such as the presence of some kinds of impurities, histories of photoirradiation, and thermal histories.[5] Therefore, we have stressed the importance of elaborate experimental work for the elucidation of the nature of electronic conduction in insulating polymer films.

This paper concerns with the experimental works on dark conductivity and photoconductivity of poly(*p*-phenylene-1,3,4-oxadiazole) (POD). Large photoconductivity in POD films has been known, and patents for electrophotographic use have appeared.[6,7] No detailed study of photoconductivity and dark conductivity, however, has been performed. The recent success of the preparation of conductive films with conductivity as high as 500 S cm^{-1} by pyrolysis of POD has caused renewed interest in the electronic nature of POD films.[8] More recently, a patent claiming the enhancement of conductivity of POD up to 8×10^{-2} S cm^{-1} by AsF$_5$ doping has appeared.[9]

First, dark conduction in POD films was examined while keeping our attention on several small factors that may disturb our understanding of the intrinsic electronic conductivity of POD. Secondly, a photoconductivity of POD was observed. The evaluation of the mobility of charge carriers was also made.

Finally, conductivity and carrier mobility of the POD films pyrolyzed at moderate conditions (670—810 K) were measured. The variation of electronic properties of POD films with pyrolysis gave some important clues for the discussion of electronic properties of POD.

EXPERIMENTAL

POD films of 25 μm thickness were supplied from Furukawa Electric Co. Their elemental analysis and IR spectrum manifested the presumed chemical structure of POD, and no organic additive was detected. By fluorescence X-ray analysis, trace amounts of sulfur, calcium and chlorine atoms assumed to be H_2SO_4 and $CaCl_2$, were detected. Probably, they were left in the films on preparation or processing of the POD films. Low crystallinity of POD films was observed from X-ray diffraction. A polarizing microscopic observation showed the presence of uniaxial orientation.

On both surfaces of cleaned POD films, Au-electrodes were vacuum evaporated; a semitransparent main electrode with 16 mm diameter, a guard electrode, and a counter electrode with an appropriate size were usually used. Dark current and photocurrent were observed under a constant bias voltage between 20 and 200 V by use of a vibrating reed electrometer (Takeda-Riken TR-84M). For photocurrent measurements, the monochromatized light of 440 nm and 200 μW cm^{-2} intensity supplied from 1 kW xenon lamp through IR-cutting and interference filters, irradiated a film surface in a shielded measuring chamber. A 25 cm monochromator was used in place of an interference filter for the measurement of wavelength dependence of photocurrent. Charge drift mobilities of holes in both untreated and pyrolyzed POD films were evaluated by usual time-of-flight techniques. Light pulses with about 5 μs duration from a xenon flush (Sugawara MS230) through a UV-pass filter (Toshiba UV-33S) were used. A thin amorphous selenium layer was inserted between a film surface and a semitransparent Au-electrode for photosensitization if necessary.[10]

POD films sandwiched between pairs of aluminum plates were pyrolyzed at constant temperatures between 670 and 810 K in a flow of N_2 gas for 12 h. Au electrodes with the same configuration as the case of untreated POD films were attached on pyrolyzed POD films.

All the electrical measurements were performed under a vacuum of 10^{-2} Torr, unless otherwise stated.

RESULTS AND DISCUSSION

Dark Conduction

Figure 1 shows the temperature dependence of the conductivity of POD at the temperature region between 350 and 530 K. Three independent measurements were performed: an experiment (A) was done at high temperatures between 470 and 530 K in a flow of nitrogen by using electrodes of the silver electroconducting paint; (B), on a sample with usual Au-electrodes, which had been evacuated at 430 K for an hour, with descending temperature in vacuo; and (C), on the same sample as (b) with descending temperature in dry air.

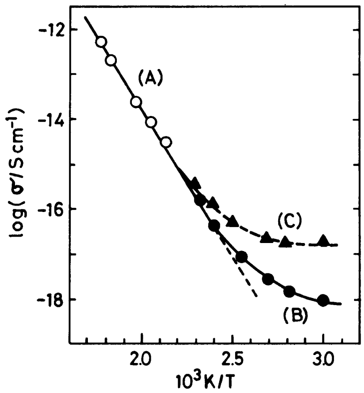

Figure 1. Temperature dependence of dark conductivity in POD films. (A) measured in a flow of nitrogen; (B) measured with descending temperature *in vacuo*; (C) measured in descending temperature in dry air.

Steady state currents could be determined in the case of (A). In the cases of (B) and (C), currents continued to decrease for several hours after the application of a bias voltage. Therefore, we evaluated "apparent conductivities" from the currents at 1000 sec after the application of the bias voltage. All the data points of (A) and two points of (B) fell on a straight line, giving an activation energy of 1.31 eV. The conductivity at room temperature extrapolated from this line is around $10^{-22}\,\mathrm{S\,cm^{-1}}$. This value and the activation energy of conductivity correspond to those of common insulating polymers at their glassy states. In insulating polymers, charge carriers are believed to be trace amounts of ionic impurities. Below 400 K, on the other hand, the conduction process due to electronic carriers occurs.

Figure 2 shows how a trace of oxygen in POD films influences the electronic conduction behavior. When the conductivity of the POD without any particular treatment was measured with ascending temperature *in vacuo*, curve (a) was obtained. This curve was very similar to that observed in dry air with descending temperature from 430 K (Figure 1(c)). From this, however, we should not judge that the effect of adsorbed oxygen on the electronic properties of POD is very little. Another measurement on the sample with descending temperature from 430 K gave the curve (b). This curve was reproducible in other measurements in ascending and descending temperature processes, as long as the sample was not exposed to air. The introduction of air into a measuring chamber caused drastic change in the conductivity of the POD film; curve (c) was obtained with ascending temperature *in vacuo* on the same sample after exposure to air. These observations indicate that oxygen molecules which are firmly adsorbed in the bulk of POD films dominate the electronic properties of POD films. The adsorbed oxygen cannot be eliminated by evacuation at room temperature. Evacuation at 430 K certainly caused partial elimination of oxygen. The decrease of adsorbed oxygen in the films results in decrease of conductivity. Complete elimination of adsorbed oxygen with this procedure should not be postulated. Therefore, one should note that even the conductivities shown in Figure 2(b) do not give the values of completely de-

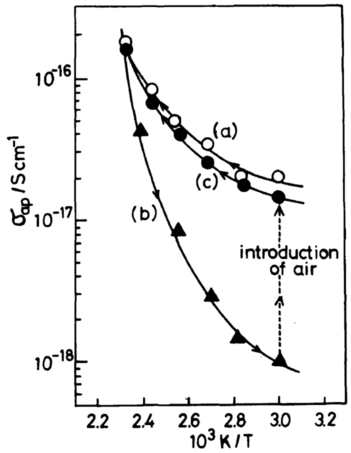

Figure 2. Effect of adsorbed oxygen on dark conductivity of POD. Arrows in the figure indicate the course of measurements. All the measurements were performed under vacuum.

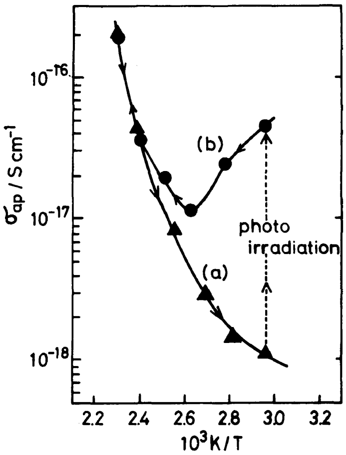

Figure 3. Effect of photo-irradiation on dark conductivity of POD. Arrows in the figure indicate the course of measurements. All the measurements were performed under vacuum.

oxygenated POD. For simplicity, hereafter, we call the sample which was evacuated at 430 K and not exposed to air to be the "deoxygenated sample".

Previously, we reported that adsorbed oxygen greatly enhanced the conductivity of poly(*p*-phenylene sulfide) (PPS).[2] This report gives another example of the function of oxygen as electron acceptors for insulating polymers.

As we reported before, a pre-photoirradiation history was another major factor that dominated dark conduction in PPS.[2] We thus investigated the pre-irradiation effect in POD films (Figure 3). A deoxygenated sample was irradiated with 440 nm light for 10 min at 330 K, and immediately its apparent conductivity was measured. Certainly, the pre-irradiation caused a temporary increase of an apparent dark conductivity. But the apparent conductivity values rapidly decreased, as measurments were repeated in an ascending temperature process. The values before photoirradiation were restored soon. The history of photo-irradiation in POD is very temporary. This observation is in a marked contrast with the case of PPS. PPS exhibits a large long-lasting (more than several ten hours) photoirradiation effect on dark conduction, and the photoirradiation history could be eliminated by annealing at a temperature above the T_g of PPS.

The increase of apparent dark conductivities with the preirradiation originates from the slow thermal release of trapped carriers. The dissimilarity of the pre-irradiation effect in POD and PPS may reflect the differences of the depth and distribution of trapping sites.

Photoconduction

POD exhibits a large photoconductivity. Figure 4 shows the wavelength dependence of photocurrent in POD measured at 330 K at the applied field of 4×10^4 V cm^{-1}. In the same figure, optical transmission of the film is also shown. The peak was observed at 420 nm. The peak well corresponds to the edge of the optical transmission. At the wavelength region where carrier generation takes place at a skin-layer of a film (<400 nm), $J_p^{\oplus}$, the photocurrent when an irradiated electrode is positively biased, was about 1 decade larger than $J_p^{\ominus}$, that when negatively biased. This clearly indicates that positively charged carriers (holes) are predominant in the photoconduction in POD.

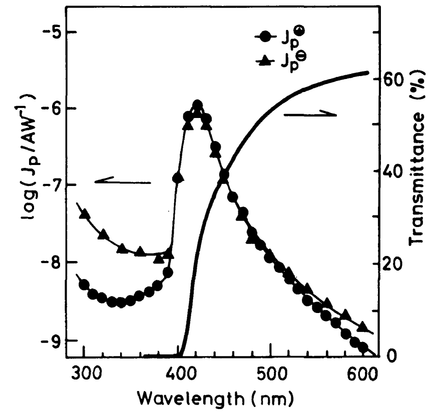

Figure 4. Wavelength dependence of photocurrent. $J_p^{\oplus}$, an illuminated electrode was biased positive; $J_p^{\ominus}$, an illuminated electrode was biased negative.

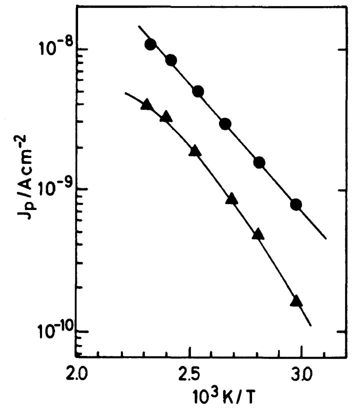

Figure 5. Temperature dependence of photocurrent. The 440 nm light with 200 μW cm^{-2} intensity was used. (●), measured under vacuum with descending temperature from 430 K (deoxygenated); (▲), measured in dry air.

Figure 5 shows the temperature dependence of photocurrents in deoxygenated POD and POD in dry air. The 440 nm light with *ca.* 200 μW cm^{-2} intensity was used because of the homogeneous bulk generation of carriers. The photocurrent of deoxygenated POD falls on a straight line, which gives an activation energy of photoconduction, 0.37 eV. The photocurrent of POD with adsorbed oxygen turned out to be 1/3—1/5 the deoxygenated one. Oxygen incorporated in POD caused enhancement of the dark conductivity but a suppression of the photoconductivity. This observation can be rationalized in terms of the carrier generation efficiency and carrier mobility. Oxygen may assist the carrier generation in dark and contribute to the enhancement of dark conductivity. On the other hand, it may provide carrier traps which cause decrease of carrier mobility. Decrease of carrier mobility serves to suppress both dark conductivity and photoconductivity.

Figure 6 compares the photocurrent of deoxygenated POD film with its dark current. One can recognize photocurrents more than five thousand times as large as dark currents at the lower temperature region where ionic conduction does not appear. Here, we give a rough comparison of the photoconductivity of POD with those of other photoconductive polymers. The photoconductivity of POD is much larger than those of polymers with aromatic or heterocyclic rings in their skeletons, such as PPS, aromatic polyamides and polyimide, and as large as that of a typical photoconductive polymer, polyvinylcarbazole.

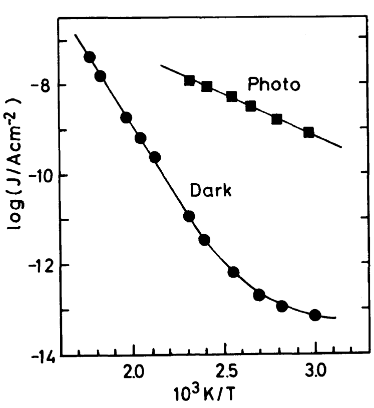

Figure 6. Comparison of photocurrent with dark current in deoxygenated POD.

Estimation of charge drift mobility in POD films was made. Below 370 K, we failed to find any sign of carrier transit across a film. Transits of holes were observable at temperature between 370—430 K, although the precise estimation of temperature dependence and applied field dependence of transit times was quite difficult. The estimated drift mobility of holes at 370—430 K was 6×10^{-8}—2×10^{-7} cm^2 V^{-1} s^{-1}.

Variation of Electronic Conduction with Pyrolysis

Figure 7 shows the variation of dark conductivity σ_{rt} and photoconductivity J_{p} (at room temperature) with pyrolysis temperature. With the pyrolysis at temperatures below 600 K, no detectable chemical reaction took place, and no change of σ_{rt} and J_{p} was observed. The pyrolysis at above 670 K brought about rapid decomposition of POD chains accompanied by weight loss, and σ_{rt} rapidly increased with increase of pyrolysis tempera-

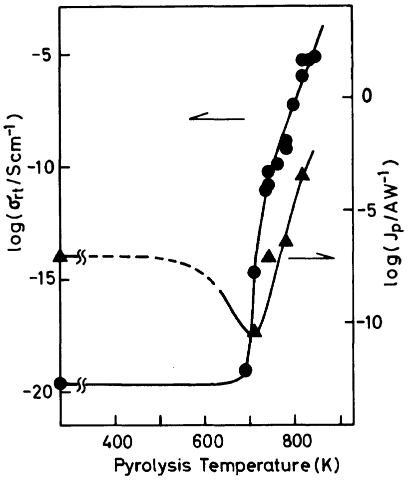

Figure 7. Dark conductivity and photoconductivity of pyrolyzed POD plotted against pyrolysis temperature.

ture.[8] In contrast, the J_p value did not show monotonous increase. It once decreased and started moderately increasing at the pyrolysis temperature above 770 K. The decrease of J_p at an early stage of pyrolysis can be ascribed to the cleavage of oxadiazole rings in POD skeleton, which is one of the most essential components for large photoconductivity in untreated POD. The increase of J_p with pyrolysis at higher temperatures is considered related to the development of conjugated network structures.

Fortunately, the evaluation of charge drift mobility was possible in several POD films pyrolyzed under moderate conditions. A more sophisticated discussion on electronic conduction is expected, when both conductivity and carrier mobility can be determined on the same polymer films.

Figure 8 shows a typical example of transient photocurrents plotted in double logarithmic scales (Scher–Montroll plot). The transit times of holes indicated by arrows in the figure shifted to shorter times with increase of applied voltages. From the observed dependence of transit times of holes on applied fields, charge drift mobilities of holes, μ_d, were evaluated.

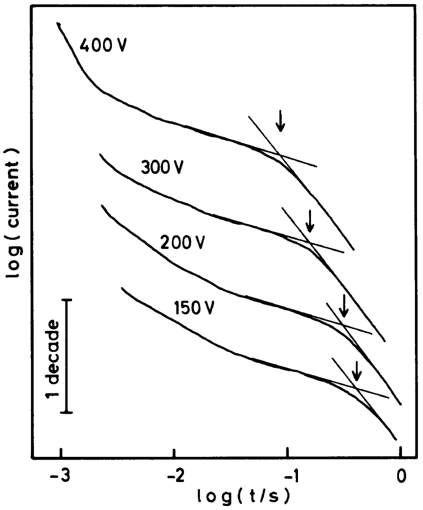

Figure 8. Double logarithmic plots of transient photocurrents (holes) in the POD pyrolyzed at 728 K. Numerals in the figure express applied voltages. Arrows indicate transit times of carriers.

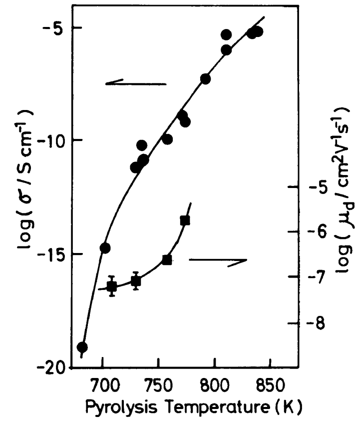

Figure 9. Conductivity and drift mobility of holes plotted against pyrolysis temperature. Note that vertical logarithmic scales for conductivity and mobility are different.

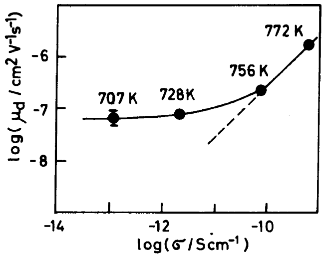

Figure 10. Drift mobility of holes plotted against conductivity in pyrolyzed POD films. Numerals in the figure express pyrolysis temperature.

In Figure 9, σ_{rt} and drift mobility of holes μ_d are plotted against pyrolysis temperature. One notices that μ_d shows very slow increase with the increase of pyrolysis temperature. To examine the relation between μ_d and σ_{rt} in detail, μ_d is plotted against σ_{rt} in Figure 10. When σ_{rt} is lower than $10^{-12}\,\mathrm{S\,cm^{-1}}$, μ_d is little dependent on σ_{rt}. In other words, pyrolysis seems to cause to increase the number of carriers which concern charge transport. We mentioned that μ_d of untreated POD ranges around $10^{-7}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at around 400 K before. This estimation corresponds well with the μ_d values moderately dependent on pyrolysis temperature.

Notwithstanding the pyrolysis at 670—730 K brings about drastic chemical changes in POD accompanied by about 50% weight loss and cleavage of oxadiazole rings, the variation of drift mobility with pyrolysis is rather moderate. Probable interpretation of this observation is that the type of charge transport, *i.e.*, hopping among localized sites, is in common among these samples. Carrier traps may control hopping processes and bring about low mobility values which are not so sensitive to the chemical structures of polymers. The increase of μ_d with pyrolysis at the temperatures above 730 K suggests the development of large conjugated ring structures which serve to delocalize hopping sites.

CONCLUSIONS

Electronic conduction behavior in both untreated and pyrolyzed POD films has been studied. The summary for the dark conduction and photoconduction in untreated POD films is as follows.

(1) Above 440 K, ionic conduction with an activation energy of 1.31 eV was observed. Below 440 K, electronic conduction which was affected by a trace of adsorbed oxygen was found to exist.

(2) Oxygen incorporated within POD films was suggested to act as an electron acceptor and contribute to enhance the dark conductivity of POD.

(3) Large photoconductivity with a peak at 420 nm, which corresponded to the absorption edge of the 25μm-thick POD films, was observed.

(4) Drift mobility of holes at arond 400 K was estimated to be 10^{-7} cm^2 V^{-1} s^{-1}.

The variation of electronic properties of POD with pyrolysis was examined. The following novel findings should be pointed out.

(5) At the early stage of pyrolysis, the photoconductivity decreases with the progress of pyrolysis, giving a clear contrast with the monotonous increase of the dark conductivity.

(6) The relation between charge drift mobility and dark conductivity was investigated in the pyrolyzed POD films. In the pyrolyzed POD with the conductivity smaller than 10^{-12} S cm^{-1}, the charge mobility was almost independent of conductivity. On the other hand, in the pyrolyzed POD with the conductivity larger than 10^{-10} S cm^{-1}, the mobility changed at the same rate as that of the conductivity.

Acknowledgment. The authors wish to thank Furukawa Electric Co. for kindly supplying the POD films.

REFERENCES

1. T. Hara, T. Tsutsui, and S. Saito, *Nippon Kagaku Kaishi*, 1431 (1984).
2. T. Tsutsui, N. Nitta, and S. Saito, *J. Appl. Phys.*, **57**, 5367 (1985).
3. M. Ishiharada, S. Hayashi, and S. Saito, *Polymer*, **27**, 349 (1986).
4. H. T. Chiu, T. Tsutsui, and S. Saito, *Polym. Commun.*, **26**, 61 (1985).
5. S. Saito, T. Tsutsui, S. Tokito, T. Hara, and H. T. Chiu, *Polym. J.*, **17**, 209 (1985).
6. M. Manilio and K. Franko, French Patent, Fr. 1,493,172 (1967).
7. K. Morimoto, Japanese Patent, 43-26709 (1967).
8. H. Murakami, H. Yasujima, Y. Yumoto, S. Mizogami, and S. Yoshimura, *Solid State Commun.*, **45**, 1085 (1983).
9. K. Shinozuka, Y. Tomizuka, and A. Nojiri, Japan-Kokai, 60-44550 (1985).
10. T. Hara, T. Tsutsui, and S. Saito, *Jpn. J. Appl. Phys.*, **24**, 970 (1985).