Electrical Conductivity of Plasma-Treated Poly(p-Phenylene Sulfide) Doped with Iodine

D. M. TU,[1] G. P. ZHUANG,[1] and K. C. KAO[2]*

[1]Department of Electrical Engineering, Xi'an Jiaotong University, Xi'an, China and
[2]Materials and Devices Research Laboratory, Department of Electrical and Computer Engineering, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

SYNOPSIS

Plasma treatment of poly(p-phenylene sulfide) (PPS) doped with I_2 is found to increase both the electrical conductivity and the stability of the material. The average conductivity of plasma-treated samples reaches an apparently saturated value of 1.7×10^{-3} s cm^{-1}, which is about six orders of magnitude higher than that of the same material without plasma treatment, and this conductivity remains practically unchanged under exposure to ambient environment for 10 days. Infrared and secondary ion mass spectra of the samples before and after plasma treatment suggest that the charge-transfer complexes are formed in PPS doped with I_2 after plasma treatment. This is also consistent with the temperature dependence of conductivity results which show that the activation energy for electrical conduction decreases from 2.0 eV for pure PPS to 0.2 eV for plasma-treated I_2-doped PPS. Using isothermal potential and current decay techniques, we have also measured the trap density distribution. Plasma treatment, on the one hand, does create more traps in PPS, but, on the other hand, it enhances conductivity. The mechanism of electrical conduction is briefly discussed.

INTRODUCTION

In the past, polymers were generally regarded as good insulators. Since the discovery of conducting polyacetylene,[1,2] many conducting polymers, and, in particular, those with π conjugated structures in their skeletal chains,[3-7] have been actively studied because they exhibit metallic properties when they are doped with strong acceptors or donors[7] and have the potential for practical applications. Of many polymers of this kind, poly(p-phenylene sulfide) (PPS) is one which is melt-, solution-, and machine-processable. This advantage makes its industrial applications feasible. However, PPS has no π conjugation along the skeletal chains, and the neighboring phenyl rings are inclined by alternating angles ($+45°$ and $-45°$) with respect to the planar zig-zag chain of the sulfur atoms.[8] This disadvantageous structure results in a low conductivity of pure PPS, which is of the order of 10^{-20} s cm^{-1} belonging to an excellent insulator. Pure PPS also has a high ionization potential (~ 6.3 eV). Thus, in order to transform this material into a good conductor, it is necessary to heavily dope this material with strong acceptors such as AsF_5 and SbF_5. X-ray photoelectron spectroscopy (XPS) spectra[9] have shown that for SbF_5-doped PPS, charge-transfer complexes are formed as $(PPS)^+ (SbF_6)^-$, whereas for I_2-doped PPS, iodine acts as weak acceptors and does not contribute to the formation of a charge-transfer structure in the PPS chains. Up to the present, many dopants are known to be capable of increasing the conductivity of PPS to high levels, but the increase is generally unstable, decaying with time under exposure to ambient environment. The conductivity of SbF_5- or SO_3-doped PPS could drop to 10^{-3} times its initial value and that of I_2-doped PPS could reduce to a value lower than 10^{-12} s cm^{-1} after exposure to air for a short period.[9]

The instability of the doped PPS is the major obstacle hindering its use for practical applications. Several investigators have reported that high conductivity and high stability of doped polymers can be achieved by ion implantation.[10,11] However, after ion implantation, the material usually becomes brittle, losing its original processability.[12] Thus, this method has its limitations for impurity doping into polymers. Recently, low-temperature plasma processing has been widely used for film deposition, impurity doping, etching, and surface treatment.[13,14] In this paper, we present our plasma treatment technique for improving both the conductivity and the stability of I_2-doped PPS, as well as our analysis of the structure of this material based on the infrared and the secondary ion mass spectra. The mechanism responsible for electrical conduction is also discussed.

EXPERIMENTAL

PPS samples were produced by molding. PPS powder was first melted and then molded at 310°C to form a sheet of 150 μm in thickness and 6 cm in diameter. The chamber for I_2-doping is made of glass. PPS sheet and iodine were placed inside the gap between two parallel aluminum electrodes in the chamber, the electrodes being 15 cm in diameter and their separation being 5 cm. The chamber was then pumped down to a vacuum of 10^{-1} Torr and, at about the same time, put into a large oven that was maintained at a constant temperature of 100°C. The doping concentration was controlled simply by the doping time. After the doping process for a predetermined doping concentration (or a predetermined doping time) had been completed, the doped sample was then subjected to plasma treatment in the same chamber by applying a high-frequency voltage of 1 kV at 2.4 MHz to the aluminum electrodes to create a uniform plasma of I_2 vapor/air gas mixture in the gap, the operating gas pressure being 10^{-1} Torr. The average conductivity was measured using a two-point probe technique to avoid the effect of contact resistance between the electrode and the sample. The average conductivity was calculated using the following relation:

$$\sigma_{av} = \frac{IL}{Vwd} \qquad (1)$$

where I is the current through the sample; V is the voltage between two point probes whose separation is L; w and d are, respectively, the width and the thickness of the sample. For secondary ion mass spectra (SIMS) measurements we used the Escalab MKII spectrometer. For both the SIMS and infrared absorption measurements, specially made specimens were used, which were produced by molding of doped PPS powder mixed with KBr powder. We have also measured the trap distribution using the isothermal potential and current decay methods.[15,16] For untreated PPS samples, since the current is low, we measured the potential decay with time; whereas for plasma-treated I-doped PPS samples, since the current is high, we measured the current decay with time. For current decay measurements, aluminum electrodes were vacuum deposited on both sample surfaces to form a sandwich electrode configuration with a guard electrode to divert the unwanted surface leakage current to ground, the diameter of the guarded electrode being 2.5 cm. After the sample had been subjected to a dc prestressing voltage of 2 kV for 30 min, the voltage source was removed and the sample was immediately short-circuited for 10 s. After that, the sample was connected in series to a resistor of 100 MΩ and a picoammeter, and the current decay with time was immediately measured using a high-speed recorder. Based on the current, I, as a function of time, t, the trap distribution can be determined from the following relations[16]:

$$N(E) = \frac{4It}{qkTAd} \qquad (2)$$

and

$$E = kT \ln (\nu t) \qquad (3)$$

where $N(E)$ is the trap concentration at the energy level E, A is the guarded electrode area, q is the electronic charge, k is the Boltzmann constant, T is the absolute temperature, and ν is the attempt-to-escape frequency which is 10^{-12} s^{-1}. For potential decay measurements, the same sandwich electrode configuration and prestressing procedure were used. But in this case, the surface potential decay of the sample was measured using a potentiometer in conjunction with a sensor probe placed near the sample surface. This method is based on the induction of the static electric charge on the sample surface to the sensor probe without direct contact to the sample surface. Based on the surface potential V_s as a function of time t, the trap distribution can be determined from the following relation[15]:

$$N(E) = -\frac{4\epsilon t}{qkTd^2}\frac{dV_s}{dt} \qquad (4)$$

and eq. (3) where ϵ is the permittivity of the sample.

There are many factors that may affect the efficiency of the plasma treatment such as gas pressure, high-frequency voltage, plasma treatment time, etc. For a fixed gas pressure of 10^{-1} Torr and a fixed high-frequency voltage of 1 kV, the conductivity of I_2-doped PPS depends on plasma treatment time as shown in Figure 1. The optimal plasma treatment time for the doped sample that had undergone the I_2-doping process for 3 h was 3 min. Therefore, for all experimental results being reported, we used 3 min for plasma treatment time at a gas pressure of 10^{-1} Torr and a high-frequency voltage of 1 kV. It should be noted that for a fixed gas pressure and a fixed plasma treatment time the conductivity of doped PPS depends on applied high-frequency voltage in a manner similar to the conductivity–plasma treatment time characteristic shown in Figure 1.

RESULTS AND DISCUSSION

The average electrical conductivity of plasma-treated I_2-doped PPS, σ_{av}, as a function of doping time, t_d, is shown in Figure 2. σ_{av} increases with t_d, reaches a peak value for t_d of 5 h, and then starts to decay with t_d. The I_2 content is directly related to t_d. The I_2 contents of 10% and 15% in PPS by weight correspond to t_d of 3 h and 5 h, respectively. For t_d of 5 h, σ_{av} of plasma-treated I_2-doped PPS reaches

Figure 2 The average electrical conductivity of plasma-treated I_2-doped PPS as a function of doping time.

a peak value of 1.7×10^{-3} s cm^{-1}, whereas σ_{av} for the doped PPS with the same doping time but without plasma treatment is 4.3×10^{-9} s cm^{-1}, indicating that plasma treatment increases the conductivity by six orders of magnitude.

When a doped sample is exposed to ambient environment, its conductivity decays with time, indicating its instability. Figure 3 shows clearly that σ_{av} of I_2-doped PPS without plasma treatment drops by four orders of magnitude after only 10 min of exposure, whereas that of plasma-treated I_2-doped PPS with the same doping time of 5 h remains practically unchanged after 10 days of exposure and drops by one order of magnitude after 100 days of exposure, indicating that plasma treatment increases also the stability of the material.

Figure 4 shows the infrared (IR) absorption spectra for three cases: (A) pure PPS without doping and without plasma treatment, (B) plasma-treated I_2-doped PPS with doping time of 4 h, and (C) I_2-doped PPS with the same doping time but without plasma treatment. In Figure 4(A), the peaks at 1570.7, 1468.7, and 1384.4 cm^{-1} are due to the C—C bond stretching vibration of benzyl; the peaks at 1089.1, 1071.5, and 1008.2 cm^{-1} correspond to the sulfide bond absorption; and the peaks at 807.81, 741.02, and 702.30 cm^{-1} are related to the C—H bond out-of-plane bent vibration of 1.4-substituted
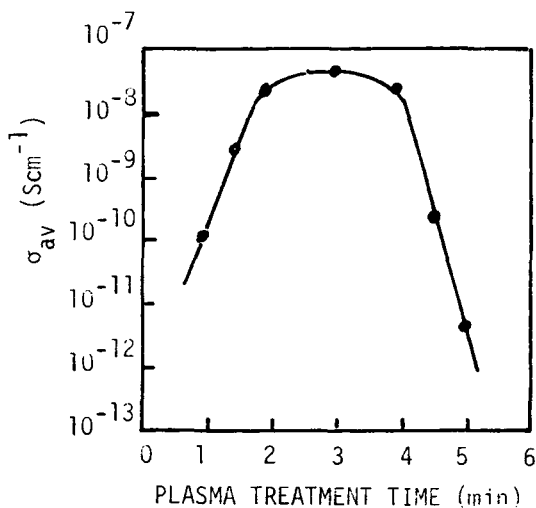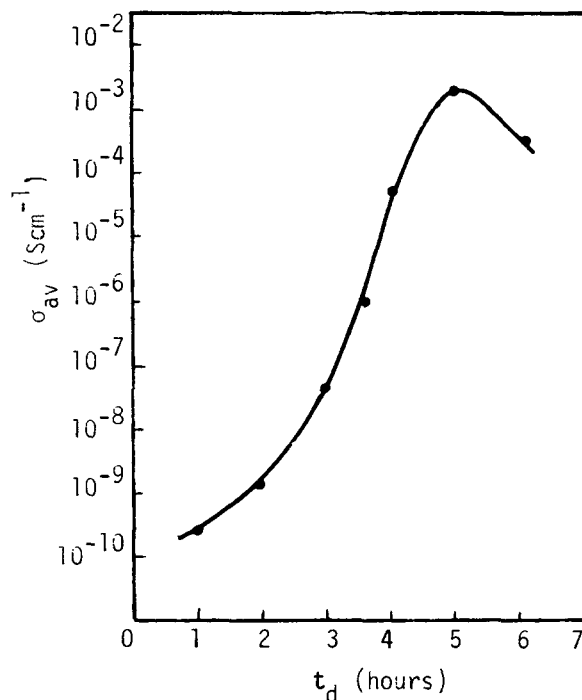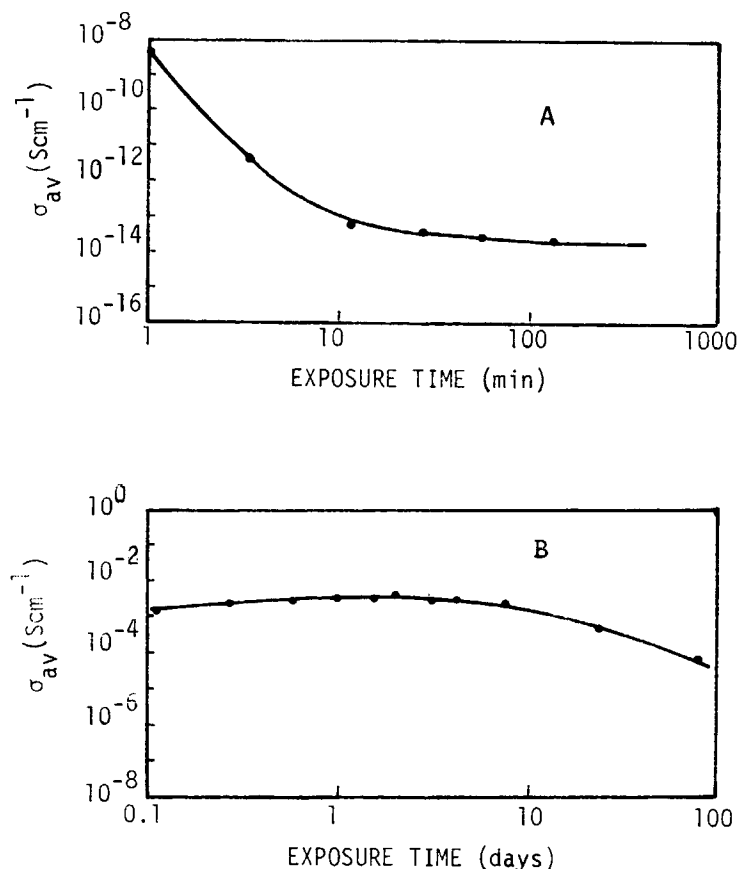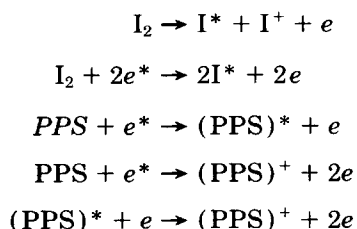

Figure 1 The average electrical conductivity of I_2-doped PPS as a function of plasma treatment time. Doping time: 3 h.

Figure 3   The decay of the average electrical conductivity of I_2-doped PPS with time of exposure to ambient air environment: (A) without plasma treatment; (B) with plasma treatment. Doping time: 5 h.

benzyl. By comparing these spectra for these three cases, it can be seen that the difference between case (A) and case (C) is very little, but there is a significant difference between case (A) and case (B). The two peaks at 1089.1 and 1071.5 cm^{-1} occurring in (A) are merged into one peak at 1092.6 cm^{-1} in (B), indicating that the sulfide-bonding structure has undergone a change after plasma treatment. Furthermore, the peak at 807.81 cm^{-1} occurring in (A) has been shifted to a larger wavenumber at 818.36 and becomes larger in (B) after plasma treatment. Iodine and other gases under low-temperature plasma will be dissociated into activated atoms, ions, and electrons. Iodine and PPS will react as follows:

$$I_2 \rightarrow I^* + I^+ + e$$

$$I_2 + 2e^* \rightarrow 2I^* + 2e$$

$$PPS + e^* \rightarrow (PPS)^* + e$$

$$PPS + e^* \rightarrow (PPS)^+ + 2e$$

$$(PPS)^* + e \rightarrow (PPS)^+ + 2e$$

where e denotes electron and $*$ denotes the activated state. These reactions will transform weak acceptors to strong acceptors, leading to the formation of charge-transfer complexes:

$$(PPS) + I^* \rightarrow (PPS)^+ I^-$$

$$(PPS)^+ + 2I_2 \rightarrow (PPS)^+ I^- + I_3^+$$
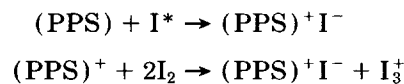
Iodine has a strong electron affinity, which tends to reduce the electron cloud density around the benzene ring and, hence, causes the absorption peak due to the C—H bond out-of-plane bent vibrations to shift to a larger wavenumber. The activated I atoms will form chemical bonds with the PPS molecules with the following possible structures:
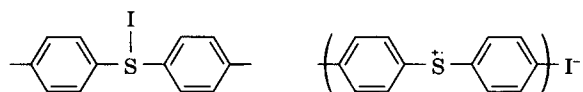
The IR absorption spectrum of the I_2-doped PPS without plasma treatment is similar to that of pure
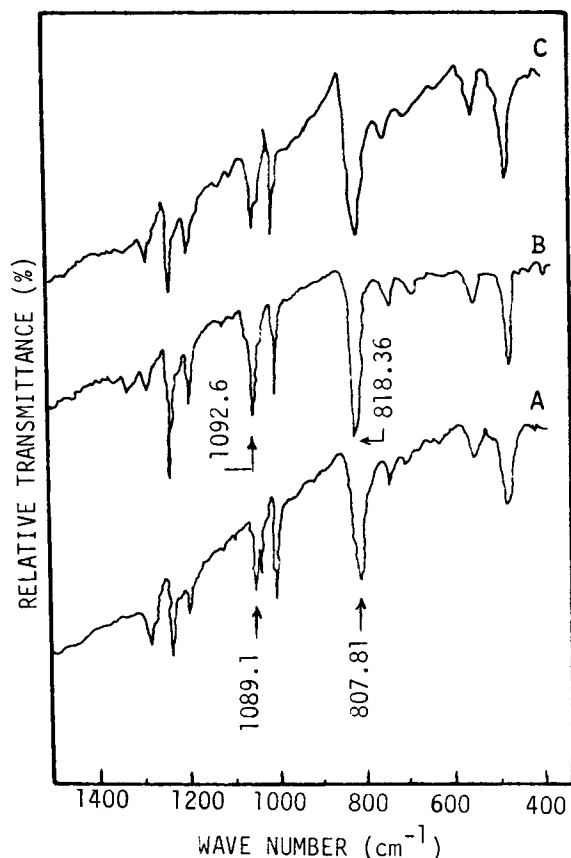
Figure 4 The infrared absorption spectra for (A) pure PPS without doping and without plasma treatment; (B) plasma-treated I_2-doped PPS with doping time of 4 h; and (C) I_2-doped PPS with the same doping time of 4 h but without plasma treatment.

PPS, indicating that I_2 molecules doped in PPS behave as entities penetrating into PPS by diffusion without chemical reaction with PPS molecules. This explains why the conductivity stability is so poor, because I_2 molecules can easily evolve from the material. However, plasma treatment dissociates I_2 into I^* or I^+, which becomes chemically active to react with PPS to form a charge-transfer complex.

The analysis of the secondary ion mass spectra for the same three cases (A), (B), and (C) shows that plasma treatment creates two new groups, $(C_3H_2S)^+$ and $(CHSI)^+$, corresponding to ion masses of 70 and 172, respectively, and that the concentration of I^- corresponding to an ion mass of 127 is much larger for plasma-treated I_2-doped PPS than that without plasma treatment. Some of the ions detected by SIMS are listed in Table I for comparison purposes. The SIMS results are consistent with the IR absorption spectra in support of the chemical reaction of I^* with PPS in plasma-treated samples.
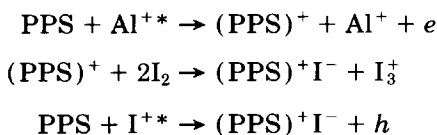
Three basic parameters that are characteristic of the material structure control the electrical conductivity, and they are the ionization potential, I_c; the π electron bandwidth, W_p; and the forbidden energy gap, E_g. For polyacetylene, the values of I_c, W_p, and E_g are 4.7, 6.5, and 1.4 eV, respectively,[7] whereas for PPS, these corresponding values are 6.3, 1.2, and 3.9 eV, respectively.[17,18] Since polyacetylene has small I_c and E_g, and large W_p, even the doping with weak acceptors like I_2 can enhance its conductivity to 10^2 s cm^{-1}. PPS has a high ionization potential; the doping of I_2 can increase the conductivity to only

Table I   Some Ions and Their Relative Concentrations Detected by SIMS in Plasma-Treated I_2-Doped PPS

| Mass | Ion | Normalized Relative Concentration | | |
		Pure PPS	Plasma-Treated I_2-Doped PPS	I_2-Doped PPS without Plasma Treatment
12	C_1^+	1.00	1.00	1.00
27	Al^+	4.54	692.00	14.40
32	S^+	0.28	0.15	0.16
46	CH_2S^+	0.18	2.77	0.25
70	$C_3H_2S^+$	—	0.85	—
172	$HCIS^+$	—	4.77	—
12	C_1^-	1.00	1.00	1.00
16	O^-	0.38	5.56	0.55
32	S^-	1.57	0.72	2.14
127	I^-	0.38	2.22	0.64

The values for positive ions are normalized to the value for C_1^+. The values for negative ions are normalized to the value for C_1^-.

10^{-9} s cm^{-1}. Plasma treatment of I_2-doped PPS can increase its average conductivity to 1.7×10^{-3} cm^{-1}. Apart from the charge-transfer complexes created by the bonding of I and PPS, Al$^+$ ions knocked out from the electrodes by ionic bombardment and I$^+$ ions created during plasma treatment can also penetrate into PPS. Al$^+$ and I$^+$ may react with PPS as follows:

$$PPS + Al^{+*} \rightarrow (PPS)^+ + Al^+ + e$$

$$(PPS)^+ + 2I_2 \rightarrow (PPS)^+ I^- + I_3^+$$

$$PPS + I^{+*} \rightarrow (PPS)^+ I^- + h$$

where h is the hole. The concentration of Al$^+$ in plasma-treated I_2-doped PPS is quite high, as shown in Table I. To find out whether Al$^+$ would play a role in the increase of the conductivity, we have produced some plasma-treated undoped PPS sample (under the same plasma treatment as that for I_2-doped PPS) and measured the Al$^+$ content using SIMS. The results show that the relative concentration of Al$^+$ in these plasma-treated undoped PPS samples is about 880 (relative to C$^+$ concentration), which is even higher than 690 for plasma-treated I_2-doped PPS (Table I), but their conductivity is only 2×10^{-11} s cm^{-1}. This indicates clearly that it is not the Al$^+$ content, but the formation of $(PPS)^+ I^-$ charge-transfer complexes that enhances the electric conductivity.

The intensity of one peak for one particular mass in the SIMS measurements can be recorded as a function of sputtering time as the sample is sputtered, yielding a depth profile. By measuring the sputtered depth with sputtering time, we have depicted the relative concentration of (HCIS)$^+$ and Al$^+$ in plasma-treated I_2-doped PPS as functions of the depth measured from the surface exposing to the plasma. Both the (HCIS)$^+$ and Al$^+$ concentrations decrease rapidly with the depth, and they become negligibly small at the depths larger than 700 Å from the surface. For the average conductivity measurements using a two-point probe technique, we used the thickness of 150 μm for the calculation of the cross-section area A. This may be valid for the I_2-doped samples without plasma treatment. For plasma-treated I_2-doped samples, the effective cross-section area may be much smaller because the high conductivity path is limited to the narrow layers close to both sample surfaces. Supposing that the effective thickness of the layer is 700 Å, equal to the depth experiencing the influence of the plasma treatment, the total effective thickness for the calculation of the cross-section area should be 2×700

$= 1400$ Å instead of 150 μm. In this case, the calculated conductivity should be $1.7 \times 10^{-3} \times [(150 \times 10^{-4})/(1400 \times 10^{-8})] \approx 1.7$ s cm^{-1}, rather than 1.7×10^{-3} s cm^{-1}.

Several investigators have reported that the temperature dependence of the conductivity of AsF$_5$-doped PPS (Ref. 5) and TaF$_5$-doped PPS (Ref. 19) follows the relation $\sigma_{av} \propto \exp(-aT^{-1/2})$, where a is a constant. The $\exp(-aT^{-1/2})$ dependence has been attributed to the carrier transport due either to a hopping process[20,21] or to a tunneling process.[22,23] However, for PPS doped with TCNE, DDQ, chloranil, and TNF, the conductivity does not have the $\exp(-aT^{-1/2})$ dependence, but follows[24] $\sigma \propto \exp(-\Delta E/kT)$, where ΔE is the apparent activation energy. The pure PPS also follows this relation[25] with an activation energy of 2.0 eV. Our plasma-treated I_2-doped PPS also follows this relation, as shown in Figure 5, which gives $\Delta E = 0.2$ eV, implying that plasma treatment of the doped samples reduces the activation energy for electrical conduction.

We have also measured the isothermal surface potential decay with time for pure PPS samples and the isothermal current decay with time for plasma-treated I_2-doped PPS samples. The results are shown in Figure 6. From eqs. (2)–(4) and Figure 6 we have calculated the trap distribution in pure PPS and plasma-treated I_2-doped PPS samples. The results are shown in Figure 7. It can be seen that for pure PPS the major traps are located at 0.78, 0.82, and 0.89 eV, whose trap density is of the order of 10^{13} cm^{-3} eV^{-1}, whereas for plasma-treated I_2-doped PPS, the major traps are located at 0.83, 0.89, and
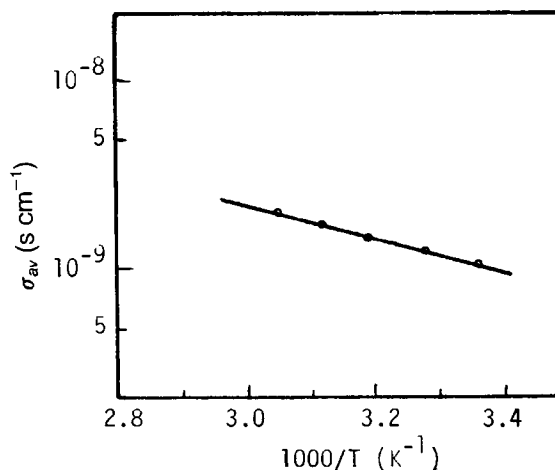

Figure 5 The average electrical conductivity of plasma-treated I_2-doped PPS as a function of temperature. Doping time: 3 h.
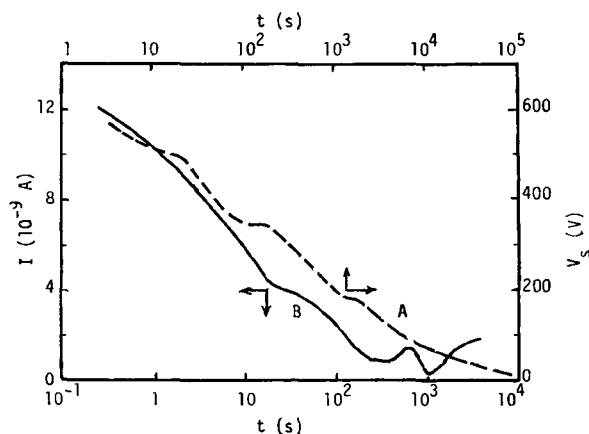
Figure 6 (A) The surface potential decay with time for pure PPS without doping and without plasma treatment; (B) the current decay with time for plasma-treated I_2-doped PPS with doping time of 3 h.

at $E > 0.91$ eV, where E is measured from the band edge. The traps at 0.83 and 0.89 eV for the plasma-treated I_2-doped samples correspond to those at 0.82 and 0.89 eV for pure PPS, but their density is much larger, in the order of 10^{16} cm^{-3} eV $^{-1}$. Iodine doping with subsequent plasma treatment increases the formation of $(PPS)^+I^-$ charge-transfer complexes and also increases the density of traps. The $(PPS)^+I^-$ and I_2 always tend to increase the conductivity, but the traps tend to decrease the conductivity. This is why the conductivity increases

with increasing doping concentration, reaches a peak at an optimal doping concentration, and then decreases with further increase in doping concentration. A similar trend would also be expected for the variation of the conductivity with plasma treatment time for a fixed doping concentration, as shown in Figure 1.

CONCLUSIONS

On the basis of the experimental results described above, the following conclusions are drawn:

1. Iodine doping into PPS and subsequent plasma treatment increase both the average electrical conductivity and the stability of the material.
2. The analysis of both the infrared absorption and the secondary ion mass spectra shows that plasma treatment creates $(C_3H_2S)^+$ and $(HCIS)^+$ groups, indicating its action in promoting the chemical reaction between I and PPS.
3. Plasma treatment, on the one hand, creates more traps in PPS, but, on the other hand, it promotes the formation of $(PPS)^+I^-$ charge-transfer complexes enhancing the electrical conductivity.
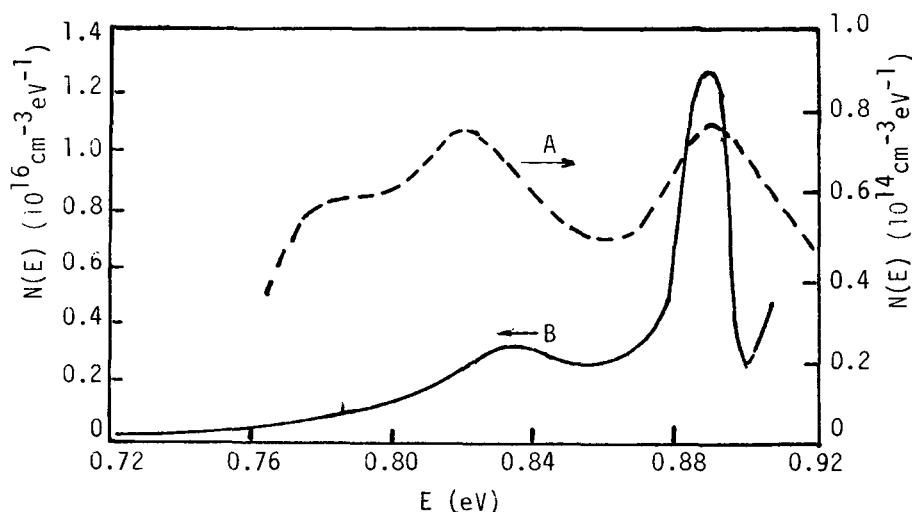

Figure 7 The density of trapping states as a function of energy E measured from the conduction band edge (A) pure PPS without doping and without plasma treatment; (B) plasma-treated I_2-doped PPS with doping time of 3 h.

4. Both the pure PPS and the plasma-treated I_2-doped PPS follow the relation $\sigma_{av} \propto \exp(-\Delta E/kT)$, implying that the carrier transport is a thermally activated process.

REFERENCES

1. J. C. W. Chien, *Polyacetylene—Chemistry, Physics and Material Science,* Academic Press, New York, 1984.
2. C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, *Phys. Rev. Lett.,* **39,** 1098 (1977).
3. D. M. Ivory, G. G. Miller, J. M. Sawa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, *J. Chem. Phys.,* **71,** 1506 (1979).
4. L. W. Shacklette, H. Eckhardt, R. R. Chance, G. G. Miller, D. M. Ivory, and R. H. Baughman, *J. Chem. Phys.,* **73,** 4098 (1980).
5. L. W. Shacklette, R. L. Elsenbaumer, R. R. Chance, H. Eckhardt, J. E. Frommer, and R. H. Baughman, *J. Chem. Phys.,* **75,** 1919 (1981).
6. J. F. Rabolt, J. C. Clarke, K. K. Kanazawa, J. R. Reynolds, and G. B. Street, *Org. Coat. Plast. Chem.,* **43,** 772 (1980).
7. R. H. Baughman, J. L. Bredas, R. R. Chance, R. L. Elsenbaumer, and L. W. Shacklette, *Chem. Rev.,* **82,** 209 (1982).
8. B. J. Tabor, E. P. Mayre, and J. Boon, *Eur. Polym. J.,* **7,** 1127 (1971).
9. H. Shinizu, Y. Tanabe, and H. Kanetsuna, *Polym. J.,* **18,** 367 (1986).
10. D. C. Weber, P. Brant, C. Carosella, and L. G. Benski, *J. Chem. Soc. Chem. Commun.,* 522 (1981).
11. T. Venkatesan, S. R. Forrest, M. L. Kaplan, C. A. Murray, P. H. Schmidt, and B. J. Wilkens, *J. Appl. Phys.,* **54,** 3150 (1983).
12. H. V. Boening, *Plasma Science and Technology,* Carl-Hansen Verlarg, Munich, Vienna, 1982.
13. F. Y. Liu, S. H. Kim, D. Liu, and K. C. Kao, *Rev. Sci. Instrum.* **57,** 986 (1986).
14. H. Z. Zhao, D. M. Tu, L. Y. Gao, Y. N. Liu, and K. C. Kao, in *Proceedings of the 6th International Symposium on Electret, Oxford, Sept. 1-3, 1988.*
15. J. C. Simmons and M. C. Tam, *Phys. Rev.,* **B7,** 3706 (1973).
16. P. K. Watson, *IEEE Trans. Elect. Insul.,* **EI-22,** 129 (1987).
17. J. L. Bredas, R. R. Chance, R. Silbey, G. Nicolas, and P. Durand, *J. Chem. Phys.,* **77,** 371 (1982).
18. R. H. Friend and J. R. M. Giles, *J. Chem. Soc. Chem. Commun.,* 1101 (1984).
19. J. Tsukamoto and K. Matsumura, *Jpn. J. Appl. Phys.,* **23,** 1584 (1984).
20. B. Wasserman, G. Braustein, M. S. Dresselhaus, and G. E. Week, *Mat. Res. Soc. Symp. Proc.,* **27,** 423 (1984).
21. B. S. Elmen, M. K. Thakur, D. J. Sandman, and M. A. Mewkirk, *J. Appl. Phys.,* **57,** 4996 (1985).
22. M. L. Kaplan, S. R. Forrest, R. H. Schmidt, and T. Venkatesan, *J. Appl. Phys.,* **55,** 732 (1984).
23. P. Sheng, *Phys. Rev.,* **B21,** 2180 (1980).
24. S. Tokito, T. Tsutsui, and S. Saito, *Polym. J.,* **17,** 959 (1985).
25. T. Tsutsui, N. Nitta, and S. Saito, *J. Appl. Phys.,* **57,** 5367 (1985).