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13. ABSTRACT *(Maximum 200 words)*

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Statistical Report for AFOSR Contract No. F49620-90-C0072

Arthur J. Epstein

Principal Investigator

a) I. <u>Publications in Reviewed Journals</u>

1. A. Burns, Z.H. Wang, G. Du, J. Joo, A.J. Epstein, J.A. Osaheni, S.A Jenekhe and C.S. Wang, *Ion Implantation of Conducting Ladder and Rigid-Rod Polymers*, **Proceedings of the Materials Research Society 247, Symposium N on Electrical, Materials 247,** 2-6 December 1991, (Boston, Massachusetts) 735-740, eds. L.Y. Chiang, A.G. Garito, and D.J. Sandman (published by Materials Research Society, Pittsburgh, PA, 1992).

2. J. A. Osaheni, S.A. Jenekhe, A. Burns, G. Du, J. Joo, Z.H. Wang, A.J. Epstein, H Song, and C.S. Wang, *Spectroscopic and Morphological Studies of Highly Conducting Ion-Implanted Rigid-Rod and Ladder Polymers*, **Macromolecules 25,** 5828-5835(1992).

II. <u>Submitted Publications</u>

1. G. Du, Z.H. Wang, J. Joo A. Burns, S. Jasty, P. Zhou, A.J. Epstein, J.A. Osaheni, S.A. Jenekhe, C.S. Wang, *Weak Localization, Electron-Electron Interaction, and Metal-Insulator Transition in Ion-Implanted Polymers*, **Synthetic Metals** xx, xxx (1992).

2. G. Du, Z.H. Wang, A. Burns, J.Joo, J.A. Osaheni, S.A. Jenekhe, and and A.J. Epstein, *Coulomb Gap and Metal-Insulator Transition in Ion-Implanted Polymers*, **Phys. Rev. Lett.** xx, xxx (1992).

b) <u>Books</u>

S.A. Jenekhe, ed., **Macromolecular Host-Guest Complexes: Optical, Optoelectronic, and Photorefractive Properties and Applications** (published by Materials Research Society, Pittsburgh, PA, 1992).

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4. John A. Osaheni (Department of Chemistry, University of Rochester, Rochester, NY) - 50%

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1. Andrew Burns - (Wright Patterson Air Force Base, Dayton, Ohio) - 100%

2. K.S. Narayan (Wright Patterson Air Force Base, Dayton, Ohio) - 100%

External Honors

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1. Fellow, American Physical Society
2. Distinguished Scholar, The Ohio State University, 1991
3. A.J. Epstein, *New Frontiers in Electronic and Magnetic Polymers*, US-India Workshop on Frontiers of Research in Polymers and Advanced Materials, Goa, India, January 5-10, 1992.

Jenekhe

2. Invited Lecture at the China-U.S. Binational Workshop on Photoinduced Charge Transfer in Polymers, Beijing, China, August 30-September 3, 1992.

f) Presentations

1. G. Du, A. Burns, Z.H. Wang, A.J. Epstein, D.B. Swanson, N. Theophilou, E.M. Scherr, A.G. MacDiarmid, F. Arnold, C.Y.C. Lee, R. Spry, and C.S. Wang, *Anisotropic AC Transport of Oriented, Undoped Polymers*, **American Physical Society 1991 March Meeting**, Cincinnati, Ohio, 18-22 March 1991 [Bulletin of the American Physical Society 36, 427-428 (1991)].

2. Z.H. Wang, A. Burns, J.S. Joo, A.J. Epstein, C.S. Wang, J.A. Osaheni, and S.A. Jenekhe, *Transport Properties of Ion-Implanted Ladder and Rigid Rod Conducting Polymers*, **Materials Research Society Fall Meeting**, Boston, Massachusetts, 2-6 December 1991 (Paper N11.36).

3. A. Burns, R. P. McCall, G. Du, J. Joo, A.J. Epstein, C.S. Wang, *Infrared and Photoinduced Infrared Studies of Rigid Rod and Ladder Polymers*, **American Physical Society 1992 March Meeting**, Indianapolis, Indiana, 16-20 March 1992.

4. Wang, *Charge Transport in Ion-Implanted Polymers*, **American Physical Society 1992 March Meeting**, Indianapolis, Indiana, 16-20 March 1992.

5. J. Joo, Z.H. Wang, G. Du, A. Burns, A.J. Epstein, J.A. Osaheni, S.A. Jenekhe, C.S. Wang, *High Microwave Dielectric Constants of Ion-Implanted Polymers*, **American Physical Society 1992 March Meeting**, Indianapolis, Indiana, 16-20 March 1992.

6. G. Du, J. Joo, A. Burns, Z. Wang, S. Jasti, P. Zhou, S.A. Jenekhe, J.A. Osaheni, C.S. Wang, and A.J. Epstein, *Weak Localization, Electron-Electron Interaction, and Metal-Insulator Transition in Ion-Implanted Polymers*, **International Conference on Science and Technology of Synthetic Metals**, Goteborg, Sweden, 12-18 August 1992.

7. J.A. Osaheni, S.A. Jenekhe, A. Burns, G. Du, J. Joo, Z.H. Wang, A.J. Epstein, C-S Wang, *Spectroscopic and Morphological Studies of Highly Conductivting Ion-Implanted Rigid-Rod and Ladder Polymers*, **Macromolecules 25**, 5828-5835(1992).

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FINAL TECHNICAL REPORT FOR
AFOSR CONTRACT F49620-90-C-0072
1 SEPTEMBER 1990 - 31 OCTOBER 1991

1. INTRODUCTION

1.1 Background

Aromatic heterocyclic ordered rigid rod, ladder, and semi-ladder polymers, exemplified by poly(1,4-phenylene-2, 6-benzobisthiazole) (PBT), poly(1,4-phenylene-2, 6-benzobisoxazole) (PBO), poly(2,5-dihydroxy-1,4-phenylene-2, 6-benzobisthiazole) (DHPBT), poly (2,5-dihydroxy-1, 4-phenylene-2, 6-benzobisoxazole) (DHPBO), benzimidazobenzophenanthroline-type ladder (BBL) and semi-ladder (BBB) polymers, combine exceptional high temperature stability (500-700°C) with excellent mechanical properties and environmental (chemical and photochemical) resistance [1-12]. This combination of properties makes these polymers suitable for many applications, including aircraft and aerospace, high strength fibers, molecular composites, engineering structures, and heat-resistance coatings [8-11]. This class of high performance organic materials has emerged from many years of work under the Air Force Ordered Polymer research program [8-9].

Recently, interesting electrical properties have been discovered in the same ordered rigid rod and ladder polymers [13-17], suggesting their potential for further development as electronic materials for solid state devices [18]. Both p-type and n-type chemical doping of BBB and BBL to high conductivity (~2 S/cm) has been reported [13,16]. Electrochemical p-type and n-type doping to conductivities as high as 5-20 S/cm was achieved in uniaxially oriented BBL films [16]. An equally high (~20 S/cm) electronic conductivity was found in an electrochemically n-type doped PBT [17]. Ion implantation of boron, argon, and krypton in BBL films at moderate ion energies (200 keV) and fluences (4×10^{16} ions/cm^2) was found to increase the room temperature conductivity of the ladder polymer to as high as 220 S/cm [15].

The results of these initial studies [13-17] of the electrical properties of ordered rigid rod and ladder polymers suggest that this class of polymers represents a promising new direction for research in synthetic metals. The successful combination of high electronic conductivity with the high thermal stability and excellent mechanical properties of ordered rigid rod and ladder polymers could result in technologically useful high temperature electronic materials. However, among the fundamental questions that must first be addressed is the nature of electronic transport in the materials.

There are many mechanisms for charge conduction present in electronic polymers [19-21]. The strong electron-phonon interaction in polymers often leads to the formation of polarons, bipolarons or solitons which have a major effect on the electronic states accessible to electrons traversing a sample. The details of the charge transport are very much dependent upon crystallinity, coherence length, and local order determining the degree of localization of the electrons in a solid. Conductivities less than 10 S/cm at room temperature may be representative of thermal activation to extended states, thermally activated hopping in energy band tails, polaron hopping, variable range hopping (with 1-, 2-, or 3 dimensional preferred hops) or more exotic mechanisms. For example, mobile neutral solitons have been proposed to have a central role in *trans*-$(CH)_x$ [22], while variable range hopping is proposed to be the transport mechanism for iodine doped Shirakawa polyacetylene [23]. More highly conducting samples (up to the range of 10^5 S/cm) may be representative of true metallic conduction with conductivity limited by barriers. The conductivity may then be determined by the relative size of the metallic islands and the exact mechanisms for tunneling through or activation across the barriers between the metallic regions. For example, the metallic regions are large for highly conducting Naarmann polyacetylene [24] and small for emeraldine hydrochloride [25].

It is necessary to carry out a correlated array of probes to distinguish among these charge conduction mechanisms. In addition to the temperature dependence of dc conductivity to low temperatures, the electric field dependence of the conductivity, magnetoresistance, and thermoelectric power give direct insight into the conduction mechanism. A measure of the density of states at the Fermi energy is obtained through magnetic susceptibility and/or electron spin resonance. Measurements of the frequency dependence of the conductivity are particularly useful for the less conductive samples, while Kramers-Kronig analysis of reflectance for the highly conducting systems give insight into the conductivity for that case.

The high conductivity σ, up to 224 $ohm^{-1}\,cm^{-1}$, with ion implantation of BBL is at first sight surprising. Implantation of polyacetylene [26] and poly(p-phenylene sulfide) [27] with similar fluences yielded very much lower increases in σ and saturated σ of only 10^{-5} $ohm^{-1}\,cm^{-1}$ or less. These saturated σ's are many orders of magnitude below that which doping yields in those materials. One may speculate that the ladder structure is much more favorable for getting high conductivity through ion implantation. If bonds are broken in one strand of the ladder there would still be a complete conduction path in the other strand. The BBL structure may be particularly favorable in this regard because there are two adjacent rings or more transverse to the chain direction in portions of the monomer. Also, the more rigid structure of the ladder polymers would be helpful in reducing scattering of electrons due to oscillations of the rings.

It is also striking that ion implantation produces σ in BBL an order of magnitude larger than obtained by electrochemical doping of that material. The most likely explanation of this observation is that the carrier concentration resulting from ion implantation is larger. It may not be possible to get a stable phase chemically or electrochemically with the ions as close as required to achieve such high carrier concentration. For the case of Ar^+ implantation with a fluence of $4.0\times10^{16}/cm^2$ and a range of 0.36 μm [15], if every ion accepts an electron from the polymer chain the number of holes would be $1\times10^{21}/cm^3$. It is noteworthy that this is of the order of the concentration of electrons added to polyacetylene chains due to the *maximum* doping seen with K^+ ions, 16.67% [28]. Of course not all of these holes may contribute to conduction; some of them may be trapped. On the other hand, if such high doping wipes out the gap present in undoped material, as is found in polyacetylene [29], the conduction electron density could be higher than $1\times10^{21}/cm^3$. Another possible reason why σ in implanted BBL is greater than σ of electrochemically or chemically doped BBL is that the ordered structure of the implanted polymer is probably different, as pointed out by Jenekhe and Tibbetts [15], the ordered structure resulting from implantation may favor higher electron mobility.

It is significant that, in addition to having high conductivity, the Ar^+ and Kr^+ implanted BBL have a slow decrease of σ with decreasing temperature T, the former losing only ~half of this conductivity between 300K and low temperature. These two features are also observed for high-quality polyacetylene heavily doped with K, I, AsF_5 or several other dopants. The combination of these two features suggests that, rather than be semiconducting, the material consists of metallic regions separated by barriers, consisting of less conducting regions, through which the electrons can tunnel [30]. In the case of ion-implanted material the barriers are likely to be disordered regions. To verify that the Ar^+ implanted material (and perhaps also the Kr^+ implanted material) consists of metallic regions separated by barriers it would be important to measure σ vs T to lower temperatures, 4K at least. Both σ for a metal and the tunneling probability should be independent of T in the low temperature limit. Above that σ may increase with T due to thermal fluctuations, specifically due to the decrease of the effective barrier width due to increased thermal motion of the carriers from the metallic regions [30], or to phonon-assisted tunneling. The explanation for the increase in σ with T has not yet been established for high conductivity polyacetylene. More careful studies should also be done for the B+ implanted material to probe the origin of its lower conductivity. In all cases, surface chemical composition studies are necessary to verify that the ion-implanted regions are not simply graphitized.

In sum, the rigid rod nature and essentially planar conformation of conjugated ladder polymers, such as BBL, suggest that higher electronic charge mobilities may be achievable compared to the more structurally disordered single-stranded quasi-one-dimensional conjugated polymers such as polyacetylene, poly p-phenylene, or polypyrrole. The conductivities achieved to date in BBL and BBB by electrochemical and chemical doping are however, far less than in polyacetylene. It is also of critical importance to determine the true maximum conductivity achievable in these polymers by ion implantation.

1.2 Ion Implantation of Polymers

The general subject of ion implantation of polymers is covered in a recent review paper [31]. Our focus here is on ion implantation as a means of enhancing the electrical conductivity of polymers and the nature of electronic charge transport in such ion-implanted materials. The technique of ion implantation which is widely used in the electronic industry [32-36], has been used to produce conducting materials from *both conjugated and nonconjugated polymers* [31, 37-45]. Starting with nonconjugated polymers, conductivities as high as 10^3 S/cm have been demonstrated [40, 41]. Nearly all the conjugated polymers that have previously been made conductive by chemical and electrochemical doping methods have also been rendered highly conductive ($\sim 10^{-8}$ to 10 S/cm) by ion implantation, including [19, 26, 37-39, 42-45]: polyacetylene, poly(sulfurnitride), poly(p-phenylene), poly(p-phenylenesulfide), polythiophenes, polydiacetylenes, polyquinolines, and polyphthalocyanines. Of particular relevance is the recent study of the electrical properties of ion-implanted BBL films [14, 15]. The room temperature saturation conductivity of such irradiated BBL films was found to be as high as 220 S/cm and to depend on the beam current density (J_b, μA/cm^2).

The growing interest in the electrical properties of ion-implanted polymers is a recognition of the many attractive features of ion implantation as a method of enhancing the electrical conductivity of organic polymers. Ion-implanted conducting polymers are generally more stable in air compared to similar chemically and electrochemically doped materials. Ion implantation allows the precise control of the concentration of "dopants" and hence electrical and physical properties. Furthermore, virtually any element of the periodic table can be implanted. The high spatial resolution of ion implantation techniques, when combined with photolithographic techniques allow high resolution *spatially selective* enhancement of the conductivity of polymer thin films that is very difficult to achieve by chemical and electrochemical doping methods. In fact, the approach of high resolution selective implantation "doping" of conjugated polymer thin films has already been demonstrated and used to fabricate microelectronic device structures [14, 15, 45]. Thus, ion implantation is an ideal technique for fabricating microelectronic and electro-optic devices from semiconducting and metallic polymer thin films.

Unfortunately the nature of electronic conduction in ion-implanted polymers is not yet understood. A number of apparently conflicting models have been proposed to explain the high conductivity of ion-implanted polymers including a conducting grain model [40, 41], one-dimensional variable range hopping model [36], and an application of fractal concepts [44]. The problem of elucidating electronic transport in ion-implanted polymers is compounded by the poor understanding of the molecular structure and morphology of the materials. Among the many implantation-induced changes in molecular structure and morphology of polymers that have been documented in the literature [31] are: increase in the number of double bonds and the degree of conjugation, increase of the carbon content, loss of low molecular weight volatiles such as H_2, H_2O, O_2, CO, CO_2, etc., increase in the amount of free radicals or number of spins; increase in the extent of ionization, change in degree of crystallinity, chain cross-linking or chain scission; and densification. It follows, therefore, that any attempt at a complete understanding of the conduction mechanism in ion-implanted polymers must be based on a detailed picture of the molecular and morphological structures of the materials.

As described below in more detail, we have addressed these basic issues of the molecular structure, morphology, electronic structure and electrical transport mechanism in ion-implanted polymers.

2. RESULTS OF CONTRACT (SEPT 1990 - 31 OCT 1991)

The objective behind this ladder and semi-ladder polymer project project is the characterization of highly conducting ion implanted ladder polymers that are both mechanically and environmentally stable and determination of their conduction mechanism Such ion implanted polymers have previously reported to have conductivities as high as 220 S/cm [15]. The results of the current contract are described below.

The strategy of understanding the conducting mechanism involves a process of obtaining a broad base of information. The first step is to develop insight into the electronic structure of the pristine polymers. This is done through spectroscopy (infrared into the ultraviolet), photoinduced spectroscopy (infrared into the ultraviolet), and transport studies. With these techniques, the basis for determination of structure property relationships is accomplished. The second phase involves ion implantation of selected polymers under controlled conditions. Knowing the conditions establishes the dosage and bombarding energies to be used when formulating models and conductivity values. After implantation, the assessment in change in chemical and electronic structure is to be accomplished, as well as conductivities and related transport properties. This is done in order to understand the material and its physical and structural characteristics. Methods of chemical and physical characterization include SEM, XPS, Raman, diffuse and specular (when possible) reflectance, ooptical absorption, conductivity, magneto-transport, thermopower and others. With the gathering of all this information, a model to understand the conductivity and predict methods to control and improve it can be developed and continuously refined

The results for the pristine materials will be discussed first, due to their place with respect to our strategy. Optical absorption studies of BBL, PBT, PBO, DPBT, DPBO, and DPBI films in the infrared were carried out using KBr pellets; the data agree with the published data [3,46]. Two representative infrared absorption spectra are shown in Fig. 1. The UV-VIS-Near IR absorption spectrum of spin coated BBL was reported (Fig. 2), and agrees with the published data [47]. After the optical studies were completed, photoinduced absorption studies were undertaken. BBL, PBT, PBO, DPBT, DPBO, and DPBI were studied in the infrared and BBL was studied in the UV-VIS-Near IR region. The results showed that only the rigid rod samples show any photoinduced absorption. This agrees with the model of Ginder and Epstein [48] developed through the study of polyaniline and polyphenylene-sulfide of the essential role of ring rotations in stabilizing long lived photoinduced charges, since of the polymers studies, only in the rigid rod systems do the rings have an ability to rotate [6]. PBT's photoinduced spectrum is shown in Fig. 3 as a representative of the rigid rod polymers. The broad electronic transitions centered at about 1100cm^{-1} and >2300 cm^{-1} are indicative of self-localization of charge [48].

Transport data were also obtained. No DC or thermopower studies were possible on the pristine films due to the high resistivities ($\rho_{DC} > 10^{-10}$ ohm-cm; with sample resistance >100 GΩ for the configuration used). AC transport studies were possible and performed on BBL, DPBT, and PBO aggregate film samples. The results indicate a variable range hopping conductivity and provide estimates of room temperature DC conductivity values of approximately 10^{-10} S/cm. Some results are shown in Figs. 4-6.

We now focus on the results of the ion implanted samples. All samples were implanted at Honeywell Corp. (Minneapolis, MN) under Professor Jenekhe's

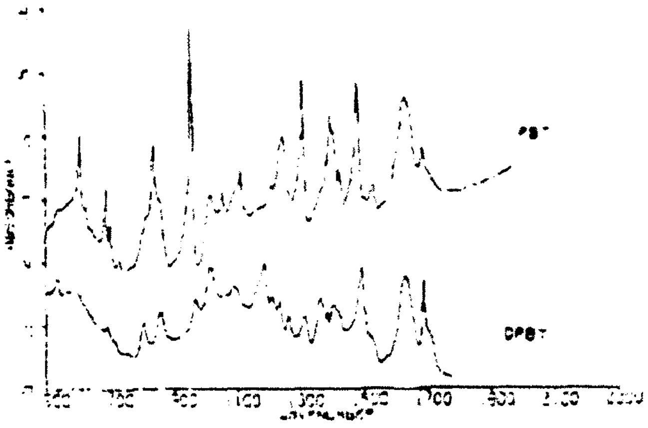

Fig. 1. Infrared absorbance for PBT and DPBT in KBr pellets.

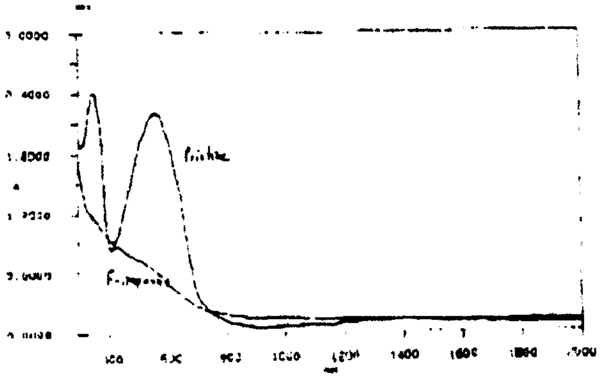

Fig. 2. UV/VIS/Near IR absorbance of spin coated BBL.

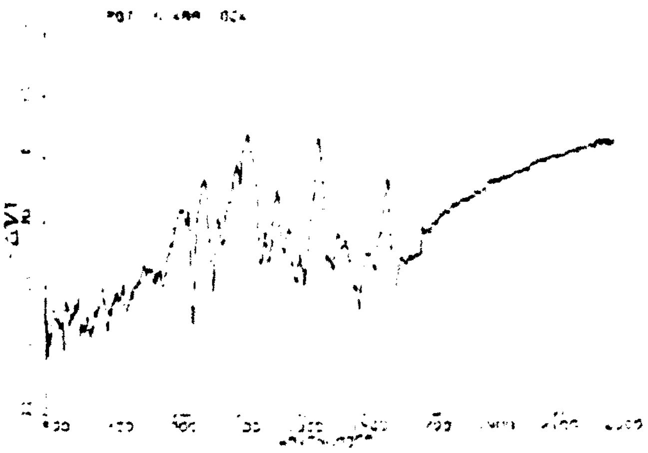

Fig. 3. Photoinduced absorption spectrum of PBT.

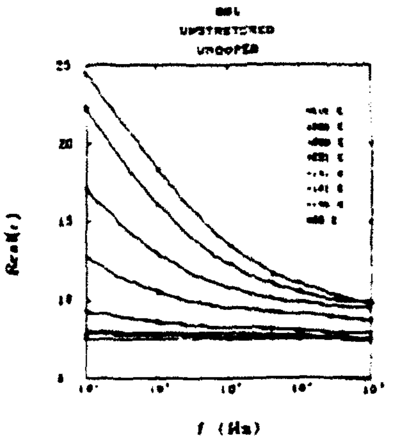

Fig. 4. Dielectric constant as a function of frequency for unstretched, undoped BBL.

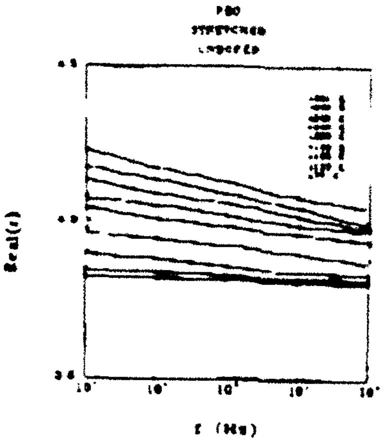

Fig. 5 Frequency dependent dielectric constant for stretched, doped PBO.

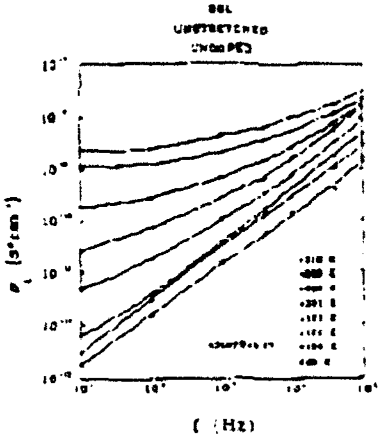

Fig. 6. Frequency dependent conductivity for unstretched, undoped BBL.

direction using 200 keV krypton beam at a dosage of 4 x 10^{16} ions/cm^2 and a dose rate of 2 µA/cm^2.

In order to investigate the physical properties and probe the conducting mechanism, temperature dependent DC conductivity, microwave frequency conductivity, magnetoresistance, and thermopower studies were performed. BBL, PBO, FMPBT, PBT, and DPBT aggregate free standing films implanted at Honeywell were studied as well as the UES implanted aggregate BBL sample. Room temperature conductivities as high as 180 S/cm were obtained based on an assumed implanted layer thicknesses of 0.35 x 10^{-4} cm. The implanted layer thicknesses were determined from SEM measurements performed at Wright Patterson Air Force Base. The conductivity and measured thickness are shown in Table I. Resistances up to 250 Ω/square were determined. The temperature dependence for the Honeywell implanted films from 4 K to 300 K is weak and is reminiscent of that of a disordered metal [49,50]. Results of all free standing films implanted at Honeywell are shown in Figs. 7-8. Microwave conductivities and dielectric constant measurements were made on PBO, PBT, and DPBT, including temperature dependences. The results agree with the DC conductivity measurements, showing a weak temperature dependence, as shown in Figs. 9-10. In addition, based on an analysis using the slopes of the DC and microwave conductivity vs temperature curves, some localization features are present. Magnetoresistance measurements were performed with current parallel/pendicular to the magnetic field on ion implanted PBO at 4.2K using magnetic fields as high as 8 Tesla. The data , Figs. 11-12, show a positive magnetoresistance, typical of 3-D metallic behavior. Preliminary thermopower measurements show a small thermopower, which indicated the material is metal-like, and positive, indicating hole-like carriers.

Table I

Films implanted at Honeywell

Films	PBT aggregate	DPBT aggregate	PBO aggregate	FMPBT extruded
thickness x 10^{-6} meters	70	17-21	18	10
thickness of implanted layer x 10^{-6} meters	0.3-0.4	0.3-0.4	0.3-0.4	0.3-0.5
pristine surface	rough	rough	rough	smooth
implanted surface	network	holes	network	network
room temperature conductivity S/cm	72.4	0.88	80.6	0.98

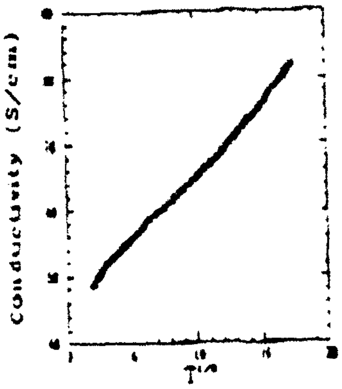

Fig. 7. Temperature dependent conductivity of PBO.

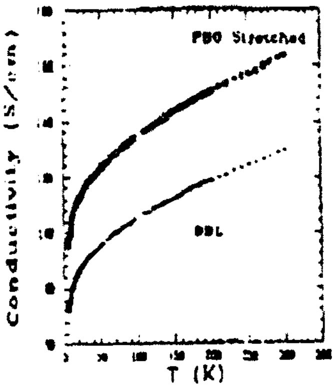

Fig. 8. Temperature dependent conductivity of BBL and stretched PBO.

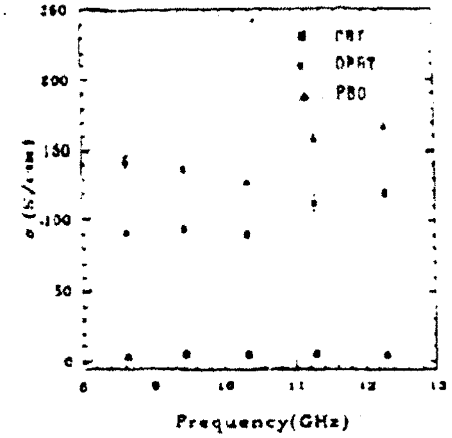

Fig. 9. Microwave conductivity for PBT, DPBT, and PBO.

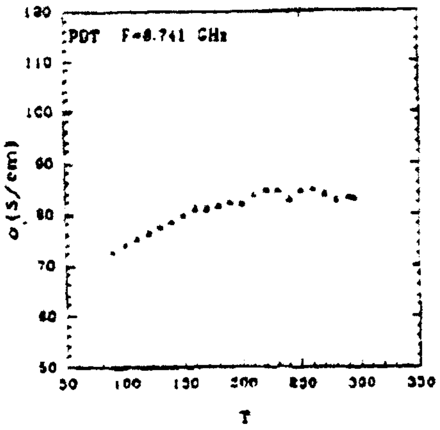

Fig. 10. Temperature dependent microwave conductivity for PBT.

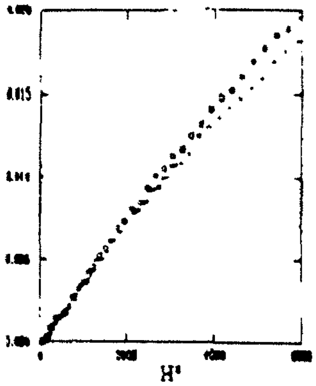

Fig. 11. Magnetoresistance of PBO.

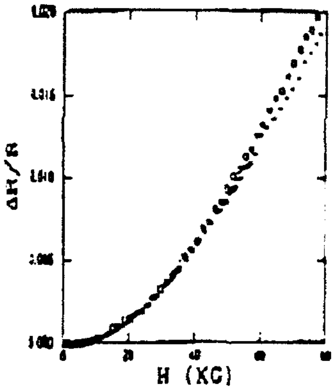

Fig. 12. Magnetoresistance of PBO with linear field dependence.

To determine the chemical structure and content of the implanted samples, XPS was performed. XPS is a surface technique, investigating the composition to a depth of approximately 100 Å. The XPS apparatus is an OSU Chemistry Department shared analytical instrument. The samples studied were spin coated BBL and BBB, and aggregate BBL, PBO, PBT, and DPBT films. All films show a depletion of S and N after ion implantation. However, all films implanted at Honeywell show impurities, most notably fluorine. The BBL sample implanted by UES showed no fluorine, but it did show a small impurity consisting of tantalum. Highlights of the XPS results are summarized in Table II. After discovering this fluorine anomaly, both Professor Jenekhe and Honeywell were contacted to try and deduce its origin. At OSU, the pristine samples and nonimplanted sides of the implanted samples were studied to understand the origin of the contamination. Though fluorine was absent from the pristine aggregate and spin coated BBL films, DPBT, PBT, and PBO aggregate films showed a presence of fluorine. A recent paper by Nawal [51] on XPS work on pristine BBL shows data which agrees with our results having F and other impurities. His interpretation is that the F, P and Si impurities are due to contamination by the polyphosphoric acid solvent or the glass substrate (for the case of spin coated samples). In addition, Nawal's work describes the lineshape analysis of the carbon and nitrogen peaks, showing 3 and 2 inequivalent C and N atoms, respectively. We have begun a similar lineshape analysis, and our results agree with those of Nawal. In addition, we are examining the implanted C and N lineshapes in order to deduce the effect of implantation on structure.

Optical studies on the implanted samples have taken place both at the University of Rochester and at OSU. Professor Jenekhe has studied the spin coated BBL and BBB samples in both the pristine and implanted forms in the UV-VIS-Near IR. He has observed a broad metal-like absorption for the implanted forms. Our results at OSU agree with Professor Jenekhe's results. In addition, at OSU we have performed diffuse and specular (where possible) reflectance infrared and Raman spectroscopies on selected samples. Using a Chemistry Department infrared spectrometer we collaborated with Professor McCreery of the Chemistry Department for the Raman work. Results from the diffuse reflectance experiments are shown in Figs. 13-14 for the pristine and implanted sides of PBT, respectively. The results indicate a loss of H and shows spectral broadening, implying a disordered material. Raman results for both pristine and ion implanted PBO show fluorescence in the blue and green spectral regions and that no graphitic structure is present, as indicated by no absorption bands at 1360 or 1580 cm^{-1}. To reduce or eliminate fluorescence, work is planned with Professor McCreery using an infrared diode laser. In addition, one sample was sent to Perkin Elmer (free of charge) to be examined by their new FT-Raman system, again operating with a diode (near IR) laser.

Present activities are concentrating on reproducing and confirming our preliminary results, as well as initiating experiments using other techniques such as EPR and electric and magnetic field dependent conductivity. Given the base of information developed during the first year of the contract, we have begun to consider the mechanism for conductivity in a thin disordered carbon film generated on a surface of the ladder, pseudoladder, and rigid-rod polymers by the ion implantation process. The full development of a microscopic model for the charge conduction in ion implanted polymers is a goal to follow during the second contract year.

Table II

Highlights of the XPS DATA

Polymer	sample number	selection	dominate elements	weak elements
PBT	PS01018/A90701A	implanted side	F, C	S
PBT	PS01018/A90701A	nonimplanted side	F, C, N, S	P, Si
PBT	PS02028	pristine	C, S, N	P, Si
DPBT	PS01004/A00607	implanted side	F, C	S, P, N
DPBT	PS01004/A00607	nonimplanted side	C, N, S	P, Si
DPBT	PS01004	pristine	C, N, S	P, Si
PBO	PS01018A/A00525	implanted side	F, C	
PBO	PS01018A/A00525	nonimplanted side	F, C, O, N	
PBO	PS01018A	pristine	C, O, N	F
BBL	spin coated 2.8	implanted	C, F, Na	N
BBL	spin coated 8.2	pristine	C, N, O	
BBL	aggregate	implanted side	C	N, Ta
BBL	aggregate	nonimplanted side	C, N, O	

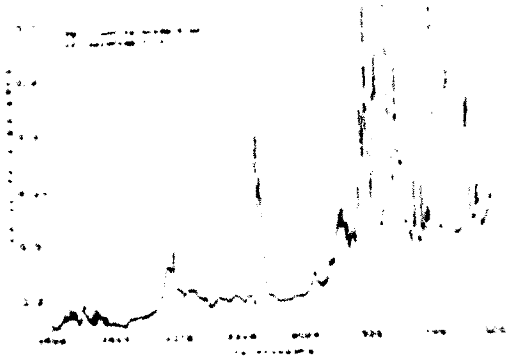

Fig. 13. Diffuse reflectance spectrum of pristine PBT.

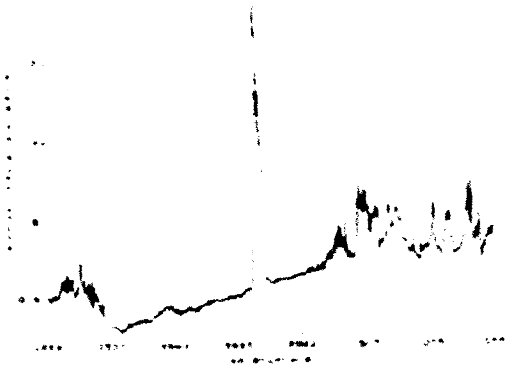

Fig. 14. Diffuse reflectance spectrum of implanted PBT.

3.0 REFERENCES

1. R.L. Van Duesen, *J. Polym. Sci. Polym. Lett.* B14, 211 (1966).
2. F.E. Arnold and R.L. Van Duesen, *Macromolecules* **2**, 49 (1969).
3. F.E. Arnold and R.L. Van Duesen, *J. Appl. Polym. Sci.* **15**, 2035 (1971).
4. F.E. Arnold, *J. Poly. Sci. Part A-1* 8, 2079 (1970).
5. A.J. Sicree, F.E. Arnold, and R.L. Van Duesen, *J. Polym. Sci.: Polym. Chem. Ed.* **12**, 265 (1974).
6. J.F. Wolfe in: *"Encyclopedia of Polymer Science and Engineering,"* 11, 2nd ed., John Wiley: New York, pp. 601, (1988).
7. (a) J.F. Wolfe and F.E. Arnold, *Macromolecules* 14, 909 (1981); (b) J.F. Wolfe, B.H. Boo, and F.E. Arnold, *Macromolecules* 14, 915 (1981).
8. (a) T.E. Helminiak, Preprints, *Am. Chem. Soc. Div. Org. Coat. Plast.* 40, 475 (1979); (b) T.E. Helminiak and F.E. Arnold, C.L. Benner, *Polym. Preprints* 16 (2), 659, (1975).
9. D.R. Ulrich, *Polymer* **28**, 533 (1987).
10. P.M. Hergenrother, *"Heat-Resistant Polymers"* in: "Encyclopedia of Polymer Science and Engineering," 7, 2nd ed., John Wiley: New York, pp. 639 (1985).
11. P.E. Cassidy, *"Thermally Stable Polymers"*, Marcel Dekker: New York, (1980).
12. T.D. Dang, L.S. Tan, K.H. Wei, H.H. Chuah, and F.E. Arnold, *Polym. Mater. Sci. Eng.* **60**, 424 (1989).
13. (a) O.K. Kim, J. *Polym. Sci. Polym. Lett.* 20, 662 (1982). (b) O.K. Kim, *Mol. Crys. Liq. Cryst.* 1055, 161 (1984); (c) O.K. Kim, *J. Polym. Sci. Polym. Lett.* **23**, 137 (1985).
14. S.A. Jenekhe, *Chem. and Eng. News*, pp 27 (May 4, 1987).
15. S.A. Jenekhe and S.J. Tibbetts, *J. Polym. Sci: Polym. Phys. Ed.* **26**, 201 (1988).
16. S.A. Jenekhe, *Polym. Mater. Sci. Eng.* **60**, 412 (1989).

17. P.A. Depra, J.G. Gaudiello, and T.J. Marks, *Macromolecules* 21, 2295 (1988).

18. (a) J.H. Lai, S.A. Jenekhe, and R.J. Jensen, and M. Royer, *Solid State Technology* 27 (11), 165 (1984); (b) ibid, 27 (12), 149.

19. A.J. Epstein, *Handbook of Conducting Polymers* 2, edited by T.A. Skotheim, Marcel Dekker, Inc., New York, 1041 (1986).

20. N.F. Mott, and E.A. Davis, *Electronic Processes in Non-crystalline Materials*, Clarendon Press, Oxford, (1979).

21. P. Nagels, *Top. Appl. Phys.* 36, 114 (1979).

22. S. Kivelson, *Phys. Rev. B* 25, 3798 (1982); *Mol. Cryst. Liq. Cryst.* 77, 65 (1983); *Phys. Rev. Lett.* 46, 1344 (1981).; A.J. Epstein, H. Rommelmann, M. Abkowitz, and H.W. Gibson, *Phys. Rev. Lett.* 47, 1549 (1981).

23. A.J. Epstein, H. Rommelmann, R. Bigelow, H.W. Gibson, D. Hoffman, and D.B. Tanner, *Phys. Rev. Lett.* 50, 1866, (1983); 51, 2020 (1983).

24. Th. Schwimmel, W. Reiss, J. Gimeiner, G. Denninger, M. Schwoerer, H. Naarmann, and N. Theophilou, *Solid State Commun.* 65, 1311 (1988); N. Theophilou, D.B. Swanson, A.G. MacDiarmid, A. Chakraborty, H.H.S. Javadi, R.P. McCall, S.P. Treat, F. Zuo, and A.J. Epstein, *Synth. Met.* 28, D35 (1989).

25. F. Zuo, M. Angelopoulos, A.G. MacDiarmid, and A.J. Epstein, *Phys. Rev. B* 36, 3475 (1987).

26. W.N. All[illegible] C.A. Carosella, J.J. DeCorpo, C.T. Ewing, F.E. Saalfeld, and D.C. We[illegible] [illegible]th. Met. 1, 151 (1979/80)

27. H. Mazurek, D.R. Day, E.W. Maby, J.S. Abel, S.D. Senturia and M.S. Dresselhaus, *J. Polymer Science: Polymer Physics Ed.* 21, 537 (1983).

28. R.H. Baughman, N.S. Murthy, and G.G. Miller, *J. Chem. Phys.* 79, 515 (1983).

29. E.M. Conwell, H.A. Mizes, and S. Jeyadev, *Phys. Rev. B*, in press.

30. P. Sheng, *Phys. Rev. B* 21, 2180 (1980).

31. S.A. Jenekhe, in *"Encyclopedia of Polymer Science and Engineering"* Supplement Vol. 2nd ed., John Wiley: New York, pp. 352 (1989), and references therein.

32. H. Ryssel and I. Ruge, *Ion Implantation*, John Wiley, New York (1986).

33. J.W. Mayer, L. Eriksson, and J.A. Davies, *Ion Implantation of Semiconductors*, Academic Press, New York (1970).

34. G. Carter and W.A. Grant, *Ion Implantation of Semiconductors*, Wiley, New York (1976).

35. W.K. Hofker and J. Politiek, *Phillips Tech. Rev.* 39, 1 (1980).

36. G.K. Hubler and O.W. Holland, C.R. Clayton, and C.W. White, eds.. *Ion Implantation and Ion Beam Processing of Materials*, Materials Research Society Symp. Proc. 27, North-Holland, New York (1984).

37. M.S. Dresselhaus, B. Wasserman, and G.E. Wnek, in: ref. 36, pp. 413.

38. H. Mazurek, D.R. Day, E.W. Maby, J.S. Abel, S.D. Senturia, M.S. Dresselhaus, and G.Dresselhaus, *J. Polym. Sci. Polym. Phys. Ed.* 21, 537 (1983).

39. G.E. Wnek, B. Wasserman, M.S. Dresselhaus, S.E. Tunney, and J.K. Stille, *J. Polm. Sci.: Polym. Lett. Ed.* 23, 609 (1985).

40. T. Venkatesan, S.R. Forrest, M.L. Kaplan, C.A. Murray, P.H. Schmidt, and B.J. Wilkens, *J. Appl. Phys.* 54, 3150 (1983).

41. M. L. Kaplan, S.R. Forrest, P.H. Schmidt, and T. Venkatesan, *J. Appl. Phys.* 55, 732 (1984).

42. J. Bartko, B.O. Hall, and K. F. Schoch, Jr., *J. Appl. Phys.* 59, 1111 (1986).

43. B.S. Elman, D.J. Sandman, and M.A. Newkirk, *Appl. Phys. Lett.* 46, 100 (1985).

44. B. Wasserman, *Phys. Rev. B* 34, 1926 (1986).

45. N. Koshida and Y. Suzuki, *J. Appl. Phys.* 61, 5487.

46. D.Y. Shen and S.L. Hsu, *Polymer* 23, 969 (1982).

47. S.A. Jenekhe and P.O. Johnson, *Macromolecules* 23, 4419 (1990).

48. J.M. Ginder and A.J. Epstein, *Phys. Rev B* 41, 10674 (1990).

49. A.B. Kaiser in *Electronic Properties of Conjugated Polymers*, edited by H. Kuzmany, M. Mehring, and S. Roth (Springer-Verlag, Berlin Heidelberg, 1987), p. 2.

50. C.C. Tsuei, *Phys. Rev. Lett.* 57, 1943 (1986).

51. H.S. Nawal, *Polymer* 32, 802 (1991).

4. TRANSITION OF ACCOMPLISHMENTS TO INDUSTRY AND AIR FORCE

The Principal Investigator, Arthur J. Epstein of The Ohio State University and Samson Jenehke of the University of Rochester have worked closely with researchers at Wright Patterson Air Force Base work as well as closely with the researchers of the University of Dayton Research Institute associated with the Wright Patterson Air Force Base to share openly all the information gained in this research. This technology transfer is facilitated by the presence of an Ohio State University postdoctoral fellow, Dr. Andrew Burns, in residence at Wright-Patterson Air Force Base. Also Drs. Jenehke and Epstein have worked closely with scientists at Xerox Webster Research Center in Webster, New York (especially M. Abkowitz and E. Conwell respectively) to transfer information to that company.

5. GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS SPONSORED BY AIR FORCE CONTRACT

The Ohio State University

Postdoctoral Fellow

Andrew Burns (Fulltime at Wright Patterson Air Force Base)

Graduate Students

Gang Du (50%)
Jinsoo Joo (50%)

University of Rochester

Graduate Students

John A. Osaheni (50%)
Micheal F. Roberts (~50%)

6. CUMULATIVE LIST OF PAPERS PREPARED, SUBMITTED, AND PUBLISHED

None published for 1990-1991

7. EXTERNAL HONORS

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1. Fellow, American Physical Society, 1981.
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