

ELECTRONIC CONDUCTION IN POLYMERS

III. ELECTRONIC PROPERTIES OF POLYPYRROLE

By B. A. BOLTO,* R. McNEILL,* and D. E. WEISS*

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Summary

The electron spin resonance absorption and electrical resistivity have been measured under rigorous conditions for a series of polypyrroles prepared over the temperature range 120–500°. When plotted as a function of pyrolysis temperature the resistivity shows a maximum in the region 200–300°. Although the resistivity of the polymers prepared at 120° and 500° is roughly similar, their e.s.r. behaviour is quite different. The low-temperature polymer, containing much complexed iodine, shows a very broad signal arising from an excited state probably associated with a polypyrrole–iodine charge-transfer complex; the high temperature polymer, containing no iodine, shows a strong narrow signal arising from the ground state of the polymer.

The changes in conductivity of the polymers following the adsorption of electron acceptor or donor molecules have been measured. It is concluded that, depending on the relative amounts of electron donating or attracting chemisorbed species in relation to the concentration of donor nitrogen atoms in the polypyrrole, the polymer may behave as an intrinsic or extrinsic semiconductor with *n*- or *p*-type characteristics. Charge-transfer complexes of strength sufficient to cause partial ionization induce extrinsic behaviour by changing the ratio of the number of electrons to the number of holes. Substituent groups such as the hetero atoms which interact with the π -electron system inductively or through resonance affect only the relative mobility of the charge carriers and induce intrinsic behaviour.

I. INTRODUCTION

Part I of this series¹ described a chemical examination of polypyrrole which suggested that it may be regarded as a three-dimensional network of pyrrole rings interconnected by direct carbon to carbon linkages. For polymers prepared below 250° iodine was present as iodine of substitution and as molecular iodine. When the polymers were prepared at higher temperatures iodine was present as the molecular form only for pyrolysis temperatures of up to about 500°. Above this there was no iodine detected at all. Part II of this series² has shown that the molecular iodine is present as a charge-transfer complex, some of which is so weakly held that it can be considered to be only physically adsorbed. The present paper describes further experiments which establish the influence of charge-transfer complexes of polypyrrole on its electronic properties. A study has also been made of its electron spin resonance (e.s.r.) absorption.

* Division of Physical Chemistry, C.S.I.R.O. Chemical Research Laboratories, Melbourne.

¹ McNeill, R., Siudak, R., Wardlaw, J. H., and Weiss, D. E., *Aust. J. Chem.*, 1963, **16**, 1056.

² Bolto, B. A., and Weiss, D. E., *Aust. J. Chem.*, 1963, **16**, 1076.

II. ELECTRICAL RESISTIVITY

The resistivity R of the polymers at 25° was found by measuring the resistance of a plug of the polymer in a stream of nitrogen whilst compressed to 8400 p.s.i. Details of the procedure are given in Part I of this series. The plug had been previously dried whilst under pressure in a stream of nitrogen at 150° . The results, given in Table I of Part I, show only the order of the resistivity since owing to the instability of the

TABLE I

Temperature	150°	175°	200°	250°	300°
R at 25° (ohm cm)	44	49	67	82	138

polymers their resistance depends on their age and the atmosphere to which they have been exposed, and it was not always possible to measure the resistance immediately after preparation. However it is apparent that the polymers are relatively good conductors of electricity. Since no polarization was observed during the measurement of the electrical resistance, even over substantial periods of time, it is assumed that the conductivity is of electronic origin.

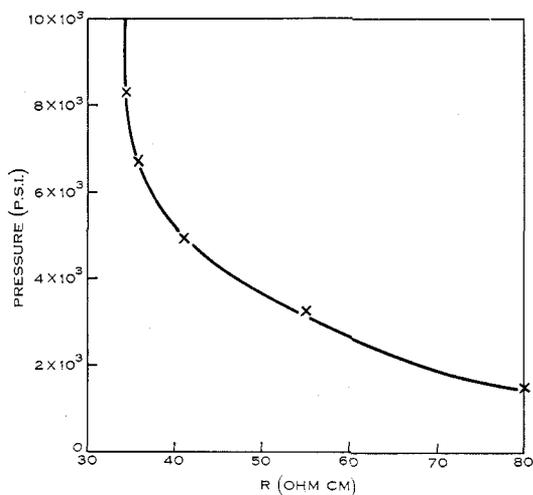


Fig. 1.—Plot of resistivity *versus* pressure applied to sample.

The effect of pressure on the resistivity of the plug is given in Figure 1. A pressure of 8400 p.s.i. was chosen for routine tests. Higher pressures were undesirable because of the possibility of fracturing the Alundum cylinder containing the polymer.

The logarithm of the resistivity of the polymers prepared below 550° varied linearly with the reciprocal of the absolute temperature when plotted over the temperature range of 25 – 150° , as shown in Figure 2. However a change in slope appears to occur for the polymers prepared at the higher temperatures.

The effect of drying on the electrical resistivity of the plug was determined by drying the plug for 5 hr in a flow of 43 ml/min of nitrogen containing less than 10 p.p.m. of oxygen before measuring R at 25° (Table 1). It was found that R increased with increase in the temperature of drying. Since physically adsorbed gases and water should be removed at 150° this temperature was arbitrarily chosen for routine measurements of R .

The effect of degassing polymer No. 20/25 was studied in more detail using the vacuum valance illustrated in Figure 3. A 0.2 g sample of polymer was suspended from a quartz-fibre spring balance in an enclosed vessel which was heated by a

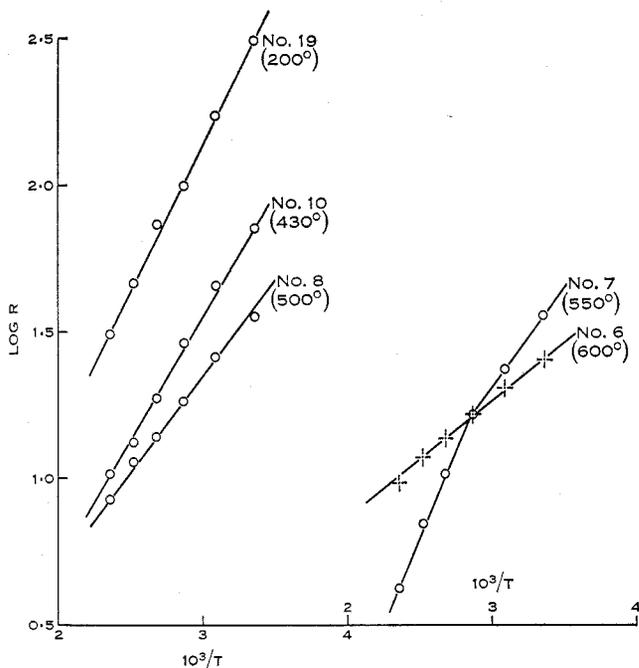


Fig. 2.—Plot of log resistivity *versus* the reciprocal of the absolute temperature for polymers prepared at various temperatures.

thermostatically controlled air-bath. Nearby, a similar quantity of polymer was packed between platinum plates connected to a resistance bridge. The geometry of both samples was the same. The weight loss and electrical resistivity of the samples could be simultaneously followed during outgassing at various temperatures in a vacuum better than 10^{-3} mmHg.* Detachable cold traps in the vacuum system enabled desorbed substances to be collected for examination.

A considerable amount of water was removed by outgassing at 25° for 26 hr. The resistivity R_1 of the polymer at 25° was then measured. Heating to 150° for 112 hr resulted in the evolution of further water and considerable amounts of iodine, but

* The vacuum was measured by an ionization gauge since a Pirani vacuum gauge was not available.

evolution of the latter was not complete until the temperature was raised to 180° for 408 hr. On heating at 250° for 120 hr further water but only a very small amount of iodine was evolved. The resistivity R_2 was measured at the end of each stage in the procedure after cooling to 25°. The changes observed, expressed as the ratio R_1/R_2 , are shown in Table 2.

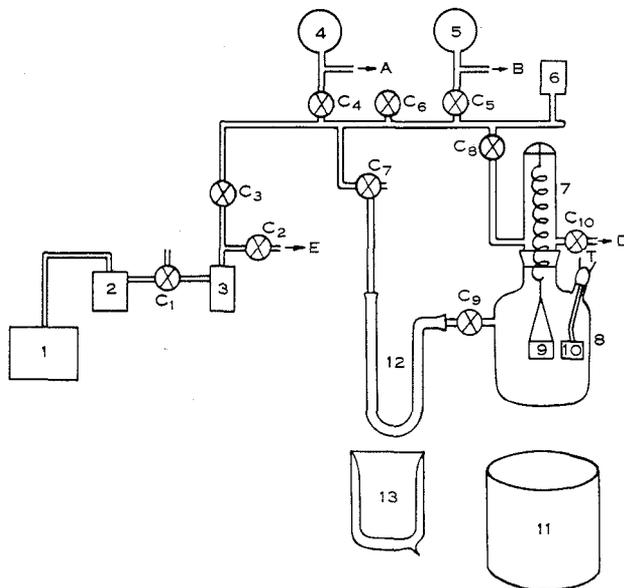


Fig. 3.—Diagram of vacuum-balance apparatus.

1, Rotary vacuum pump; 2, mercury diffusion pump; 3, liquid air cold trap; 4, oxygen reservoir; 5, ethylene reservoir; 6, Penning gauge; 7, fixed section of vessel containing silica spiral; 8, detachable section of vessel containing sample holders of identical size for gravimetric work (9) and resistivity measurements (10); 11, ring furnace for heating samples; 12, detachable liquid air cold trap.

C_1 to C_{10} stopcocks; C_1 to air; C_2 to mercury manometer E ; C_3 main valve; C_4, C_5 reservoir isolators; C_6 for introduction of gases to reservoirs; C_7 three-way valve for introduction of air to the trap 12 to allow its removal (C_{10} closed); C_8, C_9 adsorption vessel isolators; C_{10} to mercury manometer D . Difference in levels of D and E gives gas pressure in adsorption vessel; A, B , mercury manometers for reservoirs, to assist in control of gas addition to the system; T , terminals for resistivity measurements. Gravimetric measurements and manometer levels were read using a cathetometer.

The fact that outgassing influences the resistivity of the polymer suggests that chemisorbed species were present in the original polymer. Since adsorbates held by weak physical forces would have little influence on the electrical properties it is probable that chemisorption occurs involving a charge-transfer between the adsorbate and the polymer. The process would be related to that observed in molecular charge-transfer complexes, for example, perylene-iodine. The electrochemical study of polypyrrole presented in Part II of this series also provides good evidence for the presence of strongly complexed molecular iodine.

On admission of oxygen at the conclusion of the run R_1/R_2 dropped steadily to a value of 0.85 after 4.5 hr, although after 2 hr the weight increased by only 1.4% of that after outgassing at 250° and then remained steady. This behaviour suggests that the bonding of the adsorbed oxygen may be slowly changing with time. The weak adsorption of oxygen relative to iodine is possibly due to the fact that molecular oxygen is a very much weaker electron acceptor than molecular iodine and does not therefore form very stable charge-transfer complexes.³

TABLE 2

Temperature of Outgassing	Time (hr)	Weight Loss (%)	R_1/R_2 at 25°
150°	112	34.7	2.76
180°	408	44.9	2.09
250°	120	50.2	1.70

The first two stages of the outgassing when both water and iodine were evolved resulted in a lowering of the resistivity of the polymer which increased, but was still lower than that of the original, when essentially only water was evolved at 250°. The desorption of iodine and water hence appear to have an opposing influence on the resistivity. However, in view of the prolonged time at the relatively high temperatures used in the experiment it cannot be certain that the observed changes in resistivity were due only to desorption phenomena since some structural change may also have occurred.

TABLE 3

Treatment	Time (hr)	Weight Change (mg)	Weight Change (mmole/g)	Resistivity* R_1/R_2
Outgassed at 250° under vacuum	72	24.4	—	—
O ₂ admitted at 27 cmHg	116	7.7	1.36	0.79
O ₂ pumped off	48	7.3	1.30	1.0
C ₂ H ₄ admitted at 50 cmHg	3	13.6	2.76	3.32
C ₂ H ₄ pumped off	24	13.6	2.76	0.93

* R_1 taken as the resistivity in the outgassed state.

The adsorption of ethylene on a polypyrrole prepared at 400° (No. 73/74) was examined in the vacuum balance apparatus. This material had a low concentration of adsorbed iodine and could be outgassed with less danger of structural damage than the polymers prepared at lower temperatures. The sample was initially outgassed under vacuum for 3 days at 250°. Oxygen was then admitted at 25° and the adsorption

³ Tsubomura, H., and Mulliken, R. S., *J. Amer. Chem. Soc.*, 1960, **82**, 5966.

isotherm plotted. The sample was again outgassed at 25° under vacuum and ethylene was admitted. The adsorption isotherm was again plotted and the ethylene was then pumped off. At each stage the resistivity of an equal weight of sample, subjected to the same conditions was measured. The results are tabulated in Table 3.

It was found that the adsorption of oxygen at 25° was slow and was accompanied by a rise in resistivity. Most of the adsorbed oxygen could be removed by prolonged evacuation, during which the resistivity dropped to its original value. However the adsorption of ethylene was fast and was accompanied by a steep drop in resistivity. The ethylene could be removed easily by evacuation after which the resistivity rose to its original value. The mole ratio of ethylene adsorbed to oxygen adsorbed at equilibrium was approximately 2:1, which may indicate that one oxygen molecule occupied two donor sites. Sample No. 73/74 contained approximately 12 mg-atoms of nitrogen per gram of dry polymer. Thus if adsorption was associated with the nitrogen sites only about a quarter of these sites were active or accessible to ethylene.

An attempt to improve the technique of measuring the resistivity of the polymer by forming a compressed plug at high pressures failed.

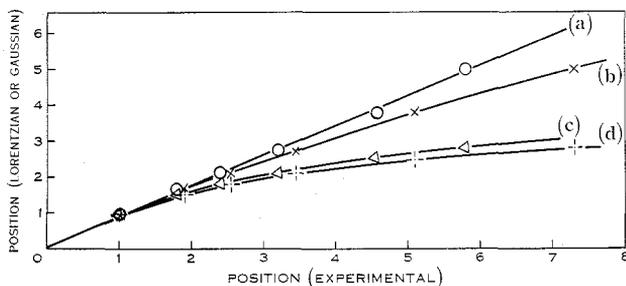


Fig. 4.—Line shape analysis curves for polypyrrole prepared at 160°.

(a) Lorentzian plot for 11.9% polymer in alumina; (b) Lorentzian plot for undiluted polymer; (c) Gaussian plot for 11.9% polymer in alumina; (d) Gaussian plot for undiluted polymer.

III. ELECTRON SPIN RESONANCE

Electron spin resonance experiments were performed on a special series of polypyrrole samples, prepared and measured under carefully controlled conditions. The sample preparation equipment consisted of a furnace linked to a nitrogen-filled glove box, as described by Singer *et al.*⁴ Tetraiodopyrrole was loaded in the furnace, pyrolysed for 24 hr under a stream of oxygen-free nitrogen, and removed to the glove box for the preparation of samples, without exposing them to air. It was also possible to load a resistance cell under these conditions, so that measurements could be made of the electrical conductivity of samples which had not been exposed to the air.

Since the polymers were good electrical conductors, a decrease in the e.s.r. signal and change in line shape would occur if the dimensions of the sample were of the

⁴ Singer, L. S., Spry, W. J., and Smith, W. H., "Proceedings of the Third Conference on Carbon." p. 121. (Pergamon Press: New York 1959.)

order of or greater than the microwave skin depth. As has been pointed out by Singer and Kommandeur,⁵ materials having a resistivity of about 10 ohm cm have skin depths of the order of 1 mm. In order to overcome this problem and avoid complicated line shapes the polymer was dispersed in alumina, an insulator.

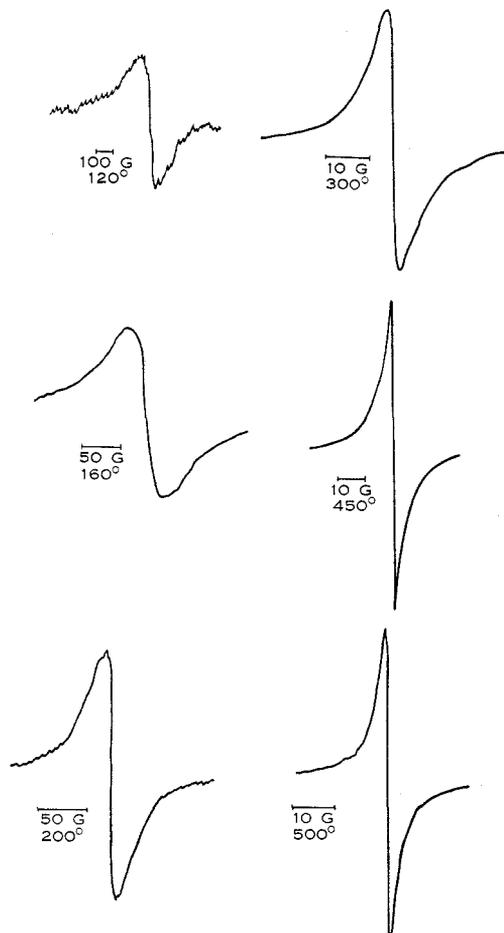


Fig. 5.—Examples of e.s.r. signals obtained for alumina mixtures of polypyrroles prepared at various temperatures.

Measurements were performed at 9500 Mc/s on a Varian V4500 spectrometer with 100 Kc/s field modulation. Line shape analyses were carried out using the method described by Hyde.⁶ An example of the effect of dispersing the polymer in alumina is shown in Figure 4. The line shape of the undiluted polymer was neither Lorentzian nor Gaussian, but the straight line obtained for the diluted sample showed that the

⁵ Singer, L. S., and Kommandeur, J., *J. Chem. Phys.*, 1961, **34**, 133.

⁶ Hyde, J. S., "Fourth Annual NMR/ESR Workshop." (Varian Associates: Palo Alto, Calif. 1960.)

experimental line shape could be accepted as closely Lorentzian. This allowed estimation of the spin concentration by comparing the integrated absorption, which is proportional to hw^2 (where h and w are the peak-to-peak height and width of the signal respectively), with that obtained similarly from the Lorentz-shaped curve for a standard sample of known spin concentration. The material selected for use as a standard was $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in single crystal form. After being weighed on a micro-balance it was embedded in paraffin wax in a silica tube.

TABLE 4

Pyrolysis Temperature	Spins/g of Iodine-free Polypyrrole at 25°	Peak-to-peak Line Width (gauss)	Resistivity at 25° (ohm cm)	I/N Ratio
120°	86 $\times 10^{18}$	120	11	2.94
160°	32	57	59	0.55
200°	18	16	140	0.44
300°	7.6	4	200	0.12
450°	4	2	67	0.03
500°	5	2	32	0.01

Examples of the e.s.r. signals obtained from alumina mixtures of polypyrroles prepared over a range of pyrolysis temperatures are shown in Figure 5. All the signals occurred in the $g = 2$ region. The results obtained, together with the resistivity measurements, are shown in Table 4. Variation of the microwave power level in the case of the polypyrroles prepared at 120° and 500° at the lowest temperature at which e.s.r. temperatures were made (-100°) indicated that saturation effects were absent when the lowest available microwave power was employed.

TABLE 5

Polymer No.	Pyrolysis Temperature	R at 25° (ohm cm)	Polymer No.	Pyrolysis Temperature	R at 25° (ohm cm)
64	120°	35	67	240°	171
71	120°	2160	75	240°	77
70	160°	21	63	300°	44
68	190°	86	72	390°	38
14	200°	93	65	400°	32
15	200°	117	80	450°	29
16	200°	182	78	500°	10
20/25	200°	171	76	600°	3
62	200°	268	77	700°	1

The spin concentration was greatest at the lower preparation temperatures, when there was a greater proportion of molecular iodine present. That the number of spins and the line width decreased markedly as iodine was removed can be seen from

the plots of these values versus pyrolysis temperature, shown in Figure 6. Little iodine was left on the polymer when the treatment temperature reached 300°, and this was the region in which the spin concentration and line width levelled off. It would appear that up to this stage the paramagnetic species included contributions arising from a charge-transfer interaction between polypyrrole and iodine. The line width diminished

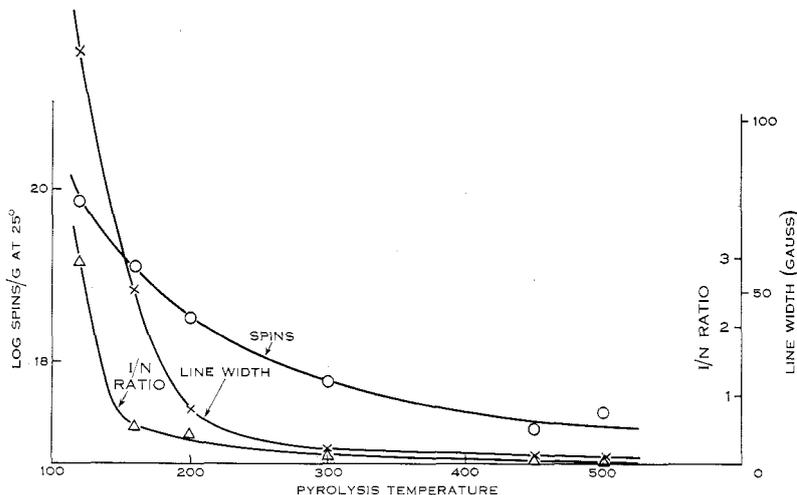


Fig. 6.—Variation of spin concentration, line width, and iodine content with the polypyrrole preparation temperature.

from an initially very broad signal, probably associated with the polypyrrole-iodine complex, to a very narrow signal when there was negligible iodine content. The continued narrowing of the resonance line may be due to increasing exchange interactions resulting from an increase in the size of the conjugate macromolecule.

TABLE 6

Pyrolysis Temperature	Spins/g of Iodine-free Polypyrrole		Peak-to-peak Line Width		I/N Ratio
	At 25°	At -100°	At 25° (gauss)	At -100° (gauss)	
120°	86 × 10 ¹⁸	43 × 10 ¹⁸	120	48	2.94
300°	7.6	7.6	4	1	0.12
450°	4	8	2	3	0.03
500°	5	29	2	3	0.01

It is interesting that over the range where the above pronounced changes occurred there was an increase in the resistivity, reaching a maximum in the 200–300° pyrolysis temperature region as shown in Table 4. The present results confirm the

earlier resistivity data obtained with samples ground in the presence of air, when a similar maximum in the 200–300° heat-treatment region was found as shown in Table 5.

Measurement of the spin concentration at -100° revealed a variation in the behaviour of the samples, indicated in Table 6. For the iodine-free polypyrroles the number of spins increased on cooling the sample, by a factor up to 5.8 for the polymer prepared at 500°. At the same time there was little change in the line width.

In the case of the polypyrrole prepared at 120° and containing about 3 atoms of iodine, mainly complexed, per pyrrole ring, there was a change in the thermal dependence of the spins. At -100° the spin concentration was half that at 25°, while the line width also decreased by a factor of 2.5. This result suggests that the *main* contribution to the paramagnetic species in this polymer arises from a polypyrrole–iodine charge-transfer complex.

On exposure of the polypyrrole samples to air the e.s.r. signal broadened most markedly for the polymer prepared at 500°, and containing essentially no complexed iodine. Only a small effect was observed with the polymer prepared at 160°; this material had an I/N ratio of 0.55.

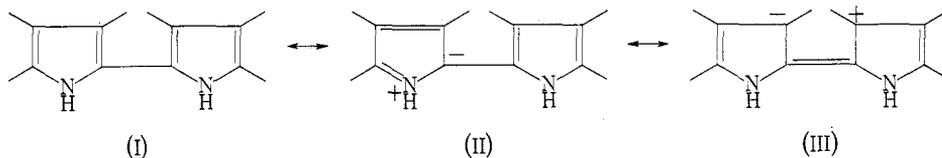
Pyrolysis temperature:	500°	160°
Line width broadened by factor of	90	2

Since negligible effects were obtained when the same two polymers were exposed instead to wet nitrogen, the above results can be attributed to the influence of oxygen rather than water. They suggest that in the absence of iodine the polymer forms a charge-transfer complex with oxygen. The slow adsorption of oxygen on outgassed polypyrrole prepared at 400° and containing little iodine, described above in the vacuum balance experiments, and the fact that molecular oxygen is a much weaker electron acceptor than molecular iodine indicate that oxygen cannot compete effectively with iodine in chemisorption.

IV. DISCUSSION

The data obtained may be interpreted as indicating that polypyrrole and probably other organic polymers may, according to circumstances, behave as either intrinsic or extrinsic semiconductors possessing *n*- or *p*-type characteristics.

Secondary amino groups in the pyrrole rings of polypyrrole tend, as in pyrrole itself, to donate π -electrons to the giant aromatic network of the polymer and themselves become partially deficient in electrons. It is possible to write many resonance structures of the following type:



Such amino groups and any other substituents which are capable of resonance interaction with the main aromatic system of the polymer, or which result in only a

partial withdrawal or donation of electrons by an inductive mechanism, will alter the conductivity by changing the relative mobility of the electrons and holes. However, since the concentration of both carriers is the same the polymers can be considered to be "intrinsic" semiconductors with *n*- or *p*-type properties depending on the actual structure.

Whilst forms such as (II) are the most stable, other charged forms such as (III) can also exist which carry no positive charge on the nitrogen and thus provide a means for the delocalization of any positive charge tending to accumulate on the nitrogen atoms. Hence even if complete ionization were possible the ratio of the number of electrons to the number of holes would be unaffected. Substituents which participate in resonance therefore cannot completely localize a charge but only influence its mobility relative to the other type of carrier.

The mobility of the carriers will also be preferentially affected by the presence of chemisorbed electron donating or accepting species which result in transfer of electrons either to or from the adsorbate. With increase in the strength of the charge-transfer process the ionic fraction will become greater, with a parallel increase in the e.s.r. signal. In the ion radicals thus produced the charge is localized by the adsorbate, with the result that the conductivity is also affected because of a change in the number of charge carriers. The extent of this change will depend on the strength of the charge-transfer interaction. The polymer will then display *n*- or *p*-type "extrinsic" behaviour.

The existence of two distinct types of electronic structures in polypyrroles is shown by the e.s.r. data reported above. The polymers prepared at 450° or 500° and free of iodine show a strong e.s.r. absorption with a narrow line width. In these polymers the resonance signal results from the ground state of the polymers and is in accord with observations of Berlin and co-workers^{7,8} for several other conjugated macromolecules. However the polymer prepared at 120°, and which contains a large amount of chemisorbed iodine, gives a very broad e.s.r. signal in which the paramagnetic species arise from an excited state probably due to the presence of a polypyrrole-iodine charge-transfer complex. This is indicated by the fact that on cooling from 25° to -100° the number of spins was halved while the line width also decreased, by a factor of 2.5. Both these changes are in the direction observed by Singer and Kommandeur⁵ for complexes of perylene and pyrene with iodine, and by Smaller *et al.*⁹ for indole-iodine complexes.

The electrical resistivity of the polymers prepared at 120° and 500° are roughly similar but polymers prepared at intermediate temperatures show a resistivity which is considerably higher. This possibly results from a transition from an extrinsic *p*-type behaviour for the polymer prepared at 120° to an intrinsic *n*-type behaviour for the polymers prepared at 400-500°.

There is, however, no decisive evidence for a *p*-type extrinsic structure in the polymers prepared at low temperatures. The lines in Figure 2 show no change in

⁷ Berlin, A. A., Blumenfeld, L. A., Cherkashen, M. I., Kalmonson, A. E., and Selskayer, O. G., *High Mol. Cpds. USSR*, 1959, **1**, 1361.

⁸ Berlin, A. A., Blumenfeld, L. A., Matveeva, N. G., and Kalmonson, A. E., *High Mol. Cpds. USSR*, 1959, **1**, 1647.

⁹ Smaller, B., Isenberg, I., and Baird, S. L., *Nature*, 1961, **191**, 168.

slope for the plot of resistivity versus the reciprocal of the absolute temperature of the sample for a polymer prepared at 200° which might indicate a transition from extrinsic to intrinsic conduction at higher sample temperatures. The temperatures at which resistivity measurements were made were in the limited range of 25 to 150°. However, such a change is suggested for the polymers prepared at 550° and 600°, although these polymers are free of complexed iodine.

The vacuum balance studies of the adsorption of ethylene and oxygen on a polypyrrole prepared at 400° indicate *n*-type behaviour for this polymer. Thus adsorption of the electron donor, ethylene, on the outgassed polymer enhanced the conductivity whilst the adsorption of the electron acceptor, oxygen, decreased the conductivity. When a polymer prepared at 200°, and containing therefore considerable amounts of chemisorbed molecular iodine, was outgassed in the vacuum balance both molecular iodine (electron acceptor) and water (electron donor) were evolved, the latter being the more tenaciously held. The results given in Table 2 indicate that whereas the chemisorption of iodine tends to reduce the conductivity, the chemisorption of water enhances it, so that the influence of the two adsorbates is competitive. As with the polymer prepared at 400°, admission of oxygen to the outgassed 200° polymer reduced the conductivity.

TABLE 7*

Polymer No.	Temperature of Preparation	Molecular I ₂ (m-equiv/g)	Molecular I ₂ Removed by		Relative Increase in <i>R</i> after Extraction with	
			Alcohol (%)	Benzene (%)	Alcohol	Benzene
64	120°	3.69	63	59	18	6
70	160°	3.39	63	60	18	7
68	190°	3.06	65	55	9	3
67	250°	1.97	43	29	2	1.5
63	300°	1.49	49	11	5	2.6

* Dry basis.

These results thus suggest that the tendency of the secondary amino groups to donate electrons to the π -electron system of the polymer creates electron-deficient sites at the nitrogen atoms, where electron-donor molecules can chemisorb, and electron-rich carbon sites where electron-acceptor molecules such as iodine can chemisorb. Chemisorbed molecular iodine could also be an electron-rich site for the chemisorption of water but sterically this process might be difficult. The relative electron transfer effect of these chemisorbed species, together with that of the polymer itself should decide whether the polymer-adsorbate system shows *n*- or *p*-type properties.

These competitive effects make it difficult to interpret unambiguously experiments where the electrical resistance of the polymer was measured before and after treatment with chemicals. For instance, the effect of removing iodine by solvent extraction on the resistivity of polypyrroles is given in Table 7.

The values in the last columns indicate the ratios of the resistivities of the extracted polymer and of the original. It will be seen that the presence of the chemisorbed molecular iodine has seemingly enhanced the conductivity and that the increase is much greater at the lower pyrolysis temperatures. However interpretation of these results is complicated by the possible chemisorption of the solvent and by reaction of the polymer with oxygen whilst removing the iodine over a period of weeks.

The electrochemical reduction of the chemisorbed iodine also resulted in an increase in the resistivity of the polymer as reported in Part II, but it cannot be certain in these experiments that some reduction of the polymer itself did not occur. The large rise in resistivity observed also suggests that some such reduction did occur since a lowering of the degree of conjugation considerably affects the resistivity. This factor is discussed below.

There are therefore conflicting data on the influence of iodine on the conductivity of polypyrrole. Whereas removal of iodine by evacuation caused a decrease in resistance, its removal by solvents or electrochemical reduction increased the resistance of all the polymers studied but this may have been due to other factors. Since removal of iodine by evacuation should not be accompanied by side effects, the conclusions derived from these studies, particularly those with the polymer prepared at 400°, are probably the more reliable. However these do not exclude the likely possibility indicated above that if the concentration of acceptor iodine sites becomes sufficiently great the behaviour of the polymer will change from *n*- to *p*-type. In the latter range, partial removal of iodine will increase the resistivity.

Substituent iodine atoms will presumably function as electron acceptors tending to localize π -electrons. This behaviour should influence the basicity of the polymers, although the sharp division into two categories observed with the H^+/N ratios as a function of the amount of iodine of substitution is surprising and cannot be fully accounted for (see Part I). Because of their electron withdrawing inductive effect iodo substituents in polypyrrole will have a particularly high electron density and may serve as donor sites for the chemisorption of at least some of the molecular iodine.

The electrical resistance of the polymer will depend on that of the polymer chain itself (the chemical factor) and that of the boundary regions between adjacent polymer chains. The chemical factor is primarily dependent on the length of the conjugated chain within the polymer molecules. Since the polymeric network is completely insoluble its molecular weight is unknown so the extent of the conjugation cannot be ascertained. An interesting feature of the postulated polypyrrole structure is that every bond provides a conjugated link since, being composed of five-membered rings, there is no position equivalent to the *meta*-position in a benzene derivative. The introduction of the pyrrole secondary nitrogen atoms does not reduce the conjugation but rather enhances it because of their participation in the aromatic type resonance of the system. However the orbital overlap between the rings must be severely curtailed since the structure being heavily cross-linked in three dimensions is out of plane, so that the electrical resistance of this network is probably not negligible. This resistance most likely resides at the bonds connecting the nonplanar rings. However, there is little doubt that a major resistance occurs also at the boundary regions between the polymer chains. Since the molecular weight is unknown it is difficult to assess

this factor. It is possible that since the formation of a charge-transfer complex in a molecular crystal enormously reduces its resistance a donor-acceptor interaction between neighbouring chains of polypyrrole may possibly also reduce the inter-boundary resistance in polypyrrole.

The results show also that the chemisorption of iodine and water has only a small influence on the electrical conductivity of the polymer although much bigger effects had been expected. The resistance does not alter greatly when the pyrolysis temperature varies from 160° to 400° although the iodine content of the polymers varies considerably. Likewise outgassing has only a comparatively small effect on the resistivity. A similar insensitivity to impurity centres has been observed in polymer carbons¹⁰ and molecular complexes.¹¹ The effect is undoubtedly due to the presence of a large number of current carriers whose numbers can be affected significantly only by the presence of a very large number of electron donor or acceptor sites.

V. CONCLUSIONS

Despite their nonplanarity, orbital overlap between adjacent pyrrole rings in polypyrrole suffices to impart a relatively high level of conductivity. It is therefore possible to synthesize *n*- and *p*-type polymers having a high internal surface area and composed of small aromatic or hetero rings which permit the introduction of functional groups at concentrations of at least 4 m-equiv/g. Whilst activated carbons possess a high internal surface area, the size of the aromatic units is usually large so that few peripheral sites are available for the introduction of functional groups. Consequently development of the poly-aromatic polymer concept offers wide scope for the synthesis of many semiconducting polymers containing a wide variety of functional groups.

It has been established that the predominant factor for good conductivity is extensive conjugation, since the breaking of the path of through conjugation in the polymers as in carbinol formation with alkali or reduction of double bonds by prolonged electrochemical treatment results in over a thousandfold decrease in conductivity. The introduction of electron donating or accepting sites into such a system, either as substituents or as adsorbates, does not alter the magnitude of the conductivity greatly.

In view of the comparatively good conductivity of polypyrrole and the small role that seems to be played by the amino groups, it is surprising that the polymer prepared by Gibson *et al.*¹² by the reaction of sodium with hexachlorobenzene has been reported not to conduct electricity. The electrical properties of this polymer require reinvestigation.

VI. ACKNOWLEDGMENTS

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¹⁰ Pohl, H. A., "Proceedings of the Fourth Conference on Carbon." p. 241. (Pergamon Press: London 1960.)

¹¹ Sehr, R., Labes, M. M., Bose, M., Ur, M., and Wilhelm, F., "Conference on Electronic Conductivity in Organic Solids." (Duke Univ. Press 1960.)

¹² Gibson, J., Holohan, M., and Riley, H. L., *J. Chem. Soc.*, 1956, 456.