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⁶ Electrical Properties of Pyrrole
and its Copolymers

by

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Chemistry

ELECTRICAL PROPERTIES OF PYRROLE AND ITS COPOLYMERS

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ABSTRACT: Electrochemically prepared polypyrrole film have metallic conductivities in the range 40-100 Scm^{-1} whereas poly-N-methyl pyrrole films have conductivities more typical of a semiconductor $\sim 10^{-3} \text{Scm}^{-1}$. Films made by the electrochemical polymerization of mixtures of pyrrole and N-methylpyrrole have redox potentials intermediate between those of either monomer indicating that they are in fact random copolymers. The electrical conductivity and thermopower measured as a function of copolymer composition show no evidence for an abrupt metal-semiconductor transition. All these polymers are stable in air to temperatures in excess of 100°C.

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With the sole exception of $(\text{SN})_x$,¹ neutral polymers are poor conductors of electricity. However, many conjugated polymers can be made to show substantial conductivity by chemical oxidation or less frequently reduction of the polymer backbone.² Conducting polymers can also be prepared by electrochemical polymerization accompanied by simultaneous oxidation. This technique has been used successfully for the preparation of conducting films of polymers derived from pyrroles.³ Films prepared by the stoichiometric electropolymerization of pyrrole itself in the presence of an electrolyte solution of tetraethyl ammonium tetrafluoroborate have metallic conductivity in the range 40-100 Scm^{-1} .⁴ Dall'Olio⁵ has reported similar but more brittle films also obtained by the anodic oxidation of pyrrole, in this case in dilute sulfuric acid. From a combination of chemical and electrochemical analysis the ionic structure shown below has been proposed for oxidized pyrrole,⁶ however, the exact chemical composition depends on the preparation conditions.³ The evidence that the polymerization occurs at the α carbons comes primarily from the oxidative degradation studies of chemically prepared polypyrroles or pyrrole blacks, which lead predominantly to pyrrole-2,5-dicarboxylic acid. Also, α -substituted pyrroles do not undergo this type of polymerization but β -substituted pyrroles do, suggesting that α -substitution blocks the polymerization process.⁷

The uniqueness of the electrochemically prepared conducting polymers lies in the fact that the oxidation of the polymer is not achieved by a chemical oxidizing agent but is achieved electrochemically simultaneous with the polymerization. This process is analogous to the spontaneous polymerization and oxidation which occurs when solid S_4N_4 is reacted with bromine vapor to give $(\text{SNBr}_4)_x$,^{8,9} when solid terphenyl is reacted with AsF_5 ¹⁰ to give hexafluoroarsenate derivatives of polyphenylene or when solid acetylene reacts with AsF_5 to give conducting polyacetylene.¹¹ However, in contrast to both these reactions the electrochemical process avoids the use of strong oxidizing agents such as halogens or AsF_5 . Other polymers not produced electrochemically, for example, $(\text{CH})_x$ can also be oxidized electrochemically.^{12,13} The electrochemical oxidation of polypyrrole and $(\text{CH})_x$ is reversible enabling thin films of the polymers to be readily switched between the neutral insulating state and the oxidized conducting state.¹⁴ These redox reactions are

accompanied by color changes. Although thin films of pyrrole can be reversibly oxidized and reduced in the absence of air, exposure to air results in a blue black film which is no longer electrochemically reducible.¹⁵ After this initial reaction with air the films appear to be stable to further reaction in air. It is these electrochemically oxidized pyrrole films after exposure to air which have been used for chemical and electrical characterization. Electron diffraction data shows diffuse halos corresponding to an interplanar separation of $3.4\text{\AA}$ which is consistent with the separation of planar chains of pyrrole rings.⁶ Comparison of λ_{max} of reduced polypyrrole (410μ) with that of known oligomers suggests a conjugation length of $\sim 4\text{--}10$ pyrrole units.¹⁶ From the λ_{max} of oxidized polypyrrole (430μ) a similar relatively short conjugation length would be predicted.

Though electropolymerization of pyrrole itself leads to metallic films, polymerization of the corresponding N-methyl pyrrole leads to films of much lower conductivity $\sim 10^{-3} \text{ Scm}^{-1}$ despite the fact that chemical analysis and electrochemical analysis indicate only a slightly smaller degree of oxidation for this polymer.¹⁴ This lower conductivity may be due to the lack of planarity or to the increased chain separation in the polymer resulting from the increased size of the methyl group relative to hydrogen. Preparation of random copolymer films of pyrrole and N-methyl pyrrole gives rise to films of intermediate conductivity depending on the copolymer composition.⁶ In this paper we report an analysis of the properties of these copolymer films together with a study of their stability and that of polypyrrole itself.

FILM PREPARATION

All the films were prepared in essentially the same manner. The working electrodes were $1'' \times 3''$ glass slides on which a $300\text{\AA}$ layer of chromium overcoated with $2000\text{\AA}$ of platinum had been vacuum deposited. The counter electrodes were also constructed from $1'' \times 3''$ glass slides, wound with $0.025''$ diameter gold wire to form a planar net, having a surface area of $\sim 15 \text{ cm}^2$. The two planar electrodes were inserted into a cell containing a 0.1 molar solution of the tetraethylammonium tetrafluoroborate electrolyte in acetonitrile to which was added 1% by volume of water. Studies on

the preparation of polypyrrole films have shown that this addition of water leads to smoother films which adhere more strongly to the platinum electrode, however, the presence of water is not essential for the production of conducting films. The requisite mixture of pyrroles was added to the electrolyte solution to give a total molarity of 0.1. A potential of 2.2 volts was applied across the cell, with the platinum acting as the anode. The film growth proceeded at a rate of $\sim 10 \mu\text{m}$ per hour.

Because of the similar composition of the two monomers it is difficult to determine the relative contribution of the two monomers to the polymer from the results of chemical analysis. Accordingly we have characterized each copolymer film by the relative composition of the two monomers in the initial cell solution. Figure 1 shows a cyclic voltammogram of a copolymer film designated a 1:1 film. The measured peak heights scale linearly with the sweep rate indicative of a surface localized oxidation/reduction process as opposed to one taking place in the bulk of the solution. The process is obviously not simple. The separation and different shapes of the forward and reverse waves show that the process is not strictly electrochemically reversible, however, the voltammogram can be repeatedly cycled indicating chemical reversibility. The broad reduction peak occurs at potentials anodic of the pronounced oxidation peak suggesting that further oxidation has taken place. Comparison of this first oxidative peak with those of polypyrrole and poly N-methyl pyrrole taken under similar conditions indicates that the oxidation potential of the copolymer lies between them. This suggests that the films prepared by this procedure are indeed copolymers and not just simple mixtures of polypyrrole and poly N-methyl pyrrole; the voltammograms show no signs of the redox peaks of either of these components.

ELECTRICAL CONDUCTIVITY

The four probe electrical conductivity of copolymers of pyrrole and N-methyl pyrrole as a function of copolymer composition is shown in Figure 2. The films are prepared by the electrochemical polymerization of mixtures of the two pyrroles in acetonitrile using tetraethyl ammonium tetrafluoroborate as the electrolyte, and platinum or nesa glass anodes with a gold cathode.

The compositions quoted in the data are those of the starting mixture and are not necessarily the film composition. The metallic nature of the conductivity in polypyrrole has been inferred from the magnitude and temperature dependence of its thermopower.⁶ Further evidence comes from thermal conductivity measurements which give a room temperature value of $9 \times 10^{-3} \text{ cal sec}^{-1} \text{ K}^{-1}$. This value is intermediate between that of metals and insulating polymers indicating that in these conducting polymers there is a substantial electronic contribution to the thermal transport. The poly N-methyl pyrrole films have conductivities $\sim 10^{-3} \text{ Scm}^{-1}$, more typical of a semiconductor than a metal. However, the conductivity versus composition data for the copolymers show no abrupt change indicative of an identifiable transition from semiconducting to metallic behavior. Such a transition is evident, for instance, in the conductivity of polyacetylene as a function of degree of oxidation.¹⁷

THERMOPOWER

The thermopower as a function of temperature for polypyrrole, poly N-methyl pyrrole and two copolymers is shown in Figure 3. The room temperature electrical conductivity of each sample is also indicated. The polypyrrole and the 1:1 copolymer samples have similar thermopowers both in magnitude and temperature dependence; their thermopower is appropriate for a metal and consistent with their high conductivities. The more insulating poly N-methyl pyrrole and the 1:3 pyrrole. N-methyl pyrrole copolymer have much larger thermopowers which do not extrapolate to zero at low temperatures, more suggestive of semiconducting behavior. Figure 4 shows the thermopower at 300°K as a function of copolymer composition. As we observed for the corresponding conductivity data there is no discontinuity in the thermopower data which might be expected to accompany the metal semiconductor transition.

OPTICAL SPECTRA

The absorption spectrum of polypyrrole tetrafluoroborate is shown in Figure 5a. The strongest absorption at 1.2 eV has an absorption coefficient of $\sim 8 \times 10^4 \text{ cm}^{-1}$ and is quite broad with a tail extending throughout the IR region, characteristic of the free carrier absorption of a metal. The small

band at ~ 2.9 eV is presumably an interband transition. The 1:1 copolymer has a similar spectrum (Figure 5b) with a broad peak ~ 1.2 eV and a tail extending into the IR. This metallic absorption is consistent with both the thermopower and the conductivity measurements on this copolymer. Again the peak around 3.2 eV may be associated with an interband transition. The absorption spectrum of the poly N-methyl pyrrole was measured in the absence of the monomer using a sealed electrochemical cell consisting of parallel nesatron plate electrodes sandwiching the tetraethyl ammonium tetrafluoroborate/acetonitrile electrolyte solution. On one of the nesatron plates was a $1000\text{\AA}$ film of the polymer which had been deposited in a separate apparatus and then incorporated into the optical cell containing electrolyte solution but no N-methyl pyrrole. This cell was placed in the sample beam of the spectrometer and a similar cell with no polymer film was inserted in the reference beam. The spectra of freshly prepared films, measured with no applied voltage across the plates, were found to change with time. Initially a rather strong absorption was observed ~ 1.0 eV (Figure 5a) consistent with the semiconducting properties of these oxidized polymer films. However, over a period of several days this free carrier absorption decreases and the spectra shown in Figure 6b are obtained. This spectra is very similar to that of the neutral polymer (Figure 6c) obtained by electrochemically reducing the oxidized polymer. Thus in the absence of an applied voltage these oxidized films appear to slowly revert to the neutral state in the presence of the electrolyte solution. This is consistent with the observation that the oxidation reaction occurs at a positive potential of +0.5V relative to SSCE. The free electron absorption could be regenerated by oxidizing the film, in fact spectra were taken under alternating bias conditions with ± 3 volts across the cell. In the insulating neutral state with the N-methyl pyrrole electrode negative, the near IR absorption was not present (Figure 6c) but on reversing the potential and oxidizing the film the strong absorption in the near IR was again observed (Figure 6d). Both the wavelength and the magnitude of this absorption appear to depend on the degree of oxidation as can be seen by comparing the spectra in Figure 6a and 6d.

The results of Raman and IR studies are shown in Figure 7. The Raman of both polypyrrole and poly N-methyl pyrrole show similar bands which arise from the pyrrole moiety. The bands are

broadened as a result of the poor crystallinity of the material. Transmission of the IR spectra of these metallic films, were obtained using very thin free standing films prepared by floating the films off the substrate. This was achieved by soaking the films in inert solvents, e.g., acetone, methylene chloride or coater. The FTIR transmission data for polypyrrole show peaks similar to those observed in the Raman except for slight shifts in intensity and peak position. This similarity between the FTIR and Raman data is also consistent with the high degree of disorder in these films. A complete understanding of the details of these spectra must await data on the air sensitive neutral polypyrrole. The absence of obvious BF_4^- stretching frequencies for all these polymers is surprising. The NH stretching frequencies are of very low intensity and also quite broad. Three peaks in Figure 8 can be assigned to NH stretching in the region above 3000 cm^{-1} . The reasons for their broad shape and low intensity is unknown but may be related to hydrogen bonding effects. The $(\text{CH})_x$ stretching region $\sim 2900\text{ cm}^{-1}$ is quite sharp and straightforward.

STABILITY OF POLYPYRROLES

All of other presently known conducting polymer systems are reactive to various degrees in ambient atmosphere. However, polypyrrole BF_4^- after its initial reaction with air is remarkably stable. The N-methyl pyrrole polymer appears less sensitive to air exposure and unlike polypyrrole itself can be reversibly electrochemically oxidized and reduced even after exposure to air. The stability of these two polymers and their copolymers have been examined by thermal analysis as well as conductivity measurements as a function of temperature.

The thermogravimetric analysis results are shown in Figure 9. The heating rate was $10^\circ\text{C}/\text{minute}$ and the atmosphere was helium, though the results were very similar for heating in air. Both the pyrrole and the N-methyl pyrrole polymer undergo slow loss of weight below 250°C . For polypyrrole the rate of weight loss increases significantly above 300°C . The brittleness of both polymers becomes marked after heating to these temperatures. Heating to 580°C in helium caused the polypyrrole to lose 60% in weight and become grey-black rather than blue-black. By this

temperature the polymer was very brittle and significantly less conducting. In the case of the poly N-methyl pyrrole a conducting residue remained even after heating to 850°C in helium. Though the nature of the residue was not determined it was probably graphitic. The 1:1 copolymer shows stability similar to the homopolymers at temperatures up to 250°C after which it begins to lose weight rather more rapidly.

The relative stability of these polymers below 150°C in air or helium is also illustrated by the conductivity data in Figure 10. As reported previously the temperature dependence of the conductivity of polypyrrole is that of a semiconductor but thermopower measurements show the films to be metallic. The conductivity varies reversibly with temperature for temperatures below 150°C. Heating beyond 150°C in air or helium causes the conductivity to start to decrease irreversibly. The amount of this decrease depends both on the ultimate temperature and on the time the films spend above 150°C. On cooling to room temperature the films can again be cycled reversibly below 150°C with no indication of further deterioration. The third heating cycle shows that even after two excursions above 150°C the film can still be cycled reversibly below ~150°. Figure 11 shows similar conductivity versus temperature data for the 1:1 copolymer for heating in both air and vacuum. The copolymer is somewhat less stable than polypyrrole itself. Its conductivity can be reversibly cycled to temperatures as high as 100°C but irreversible decreases in conductivity occur if the films are heated beyond 100°C.

CONCLUSION

Electrochemically prepared films of copolymers of pyrrole and N-methyl pyrrole have redox potentials intermediate between those of polypyrrole and poly N-methyl pyrrole. The electrical conductivity of these copolymer films is intermediate between the metallic conductivity of polypyrrole and the semiconducting value of poly N-methyl pyrrole. Neither thermopower nor conductivity measurements show any evidence of an identifiable semiconductor-metal transition as a function of copolymer composition. The conductivity in all of these polymers arises only when they are partially

electrochemically oxidized. In experiments described in this paper the counter anion is tetrafluoroborate. Absorption experiments on the poly N-methyl pyrrole have confirmed that the broad ~ 1 eV peak common to all conducting polypyrroles is in fact associated with the free carrier absorption and is absent in neutral nonconducting films. These copolymers provide a practical route to stable polymers with a wide range of conductivities. The stability of these copolymers as well as that of polypyrrole has been monitored by measuring the conductivity as a function of temperature. All the systems show remarkable stability in air at room temperature compared to other conducting polymers. The conductivity of polypyrrole can be reversibly cycled to 150°C in air or helium. Above these temperatures irreversible decreases in the conductivity take place even in helium. Though the copolymers show similar room temperature stability irreversible changes in conductivity take place if heated beyond 100°C .

ACKNOWLEDGMENTS

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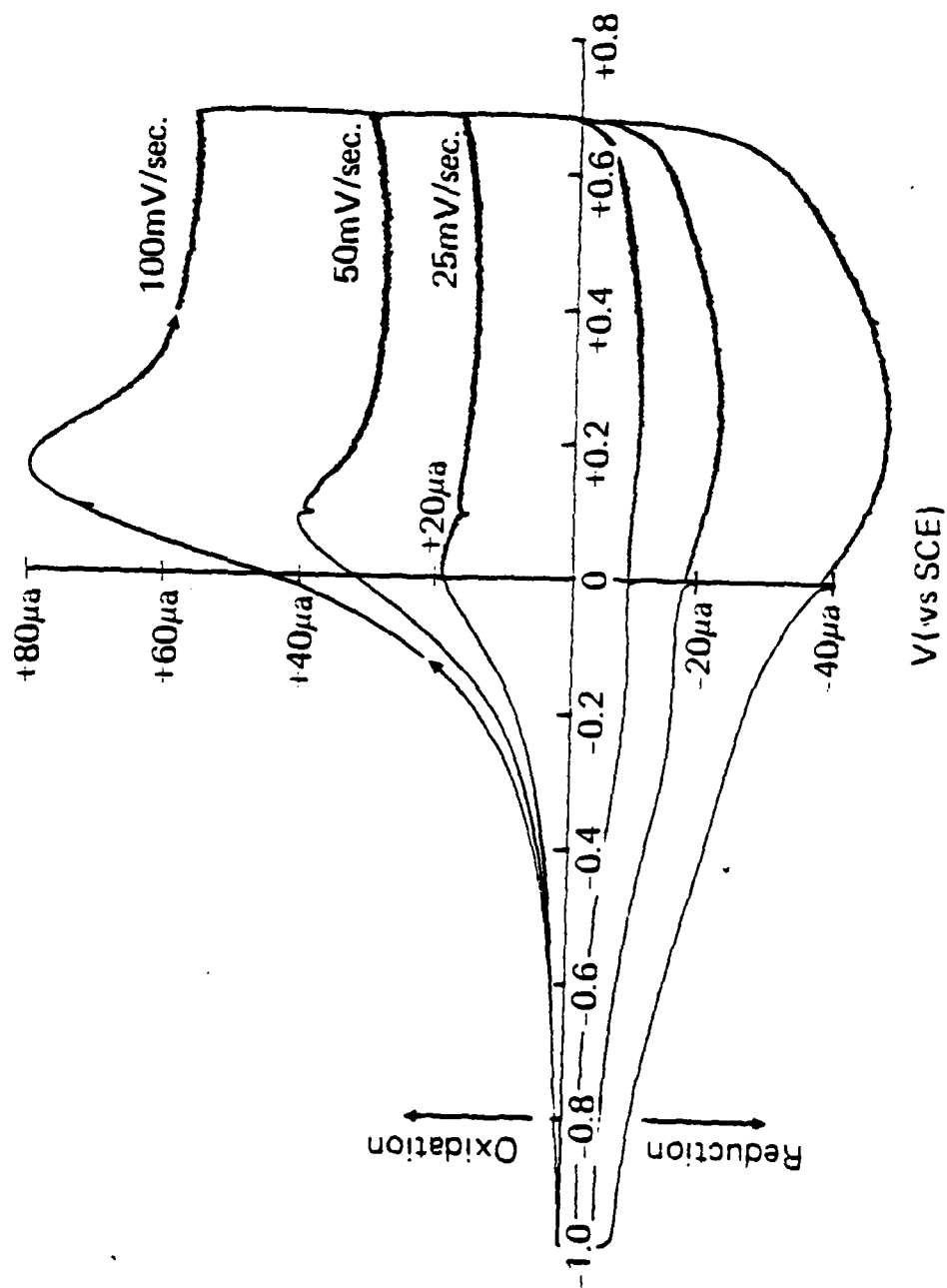


Figure 1. Voltammograms of $\sim 700\text{\AA}$ 1:1 copolymer film grown on a 0.2 cm^2 platinum button electrode immersed in a 0.1 M tetraethylammonium tetrafluoroborate, acetonitrile solution. Scan rates 100 mV sec^{-1} , 50 mV sec^{-1} , 25 mV sec^{-1} .

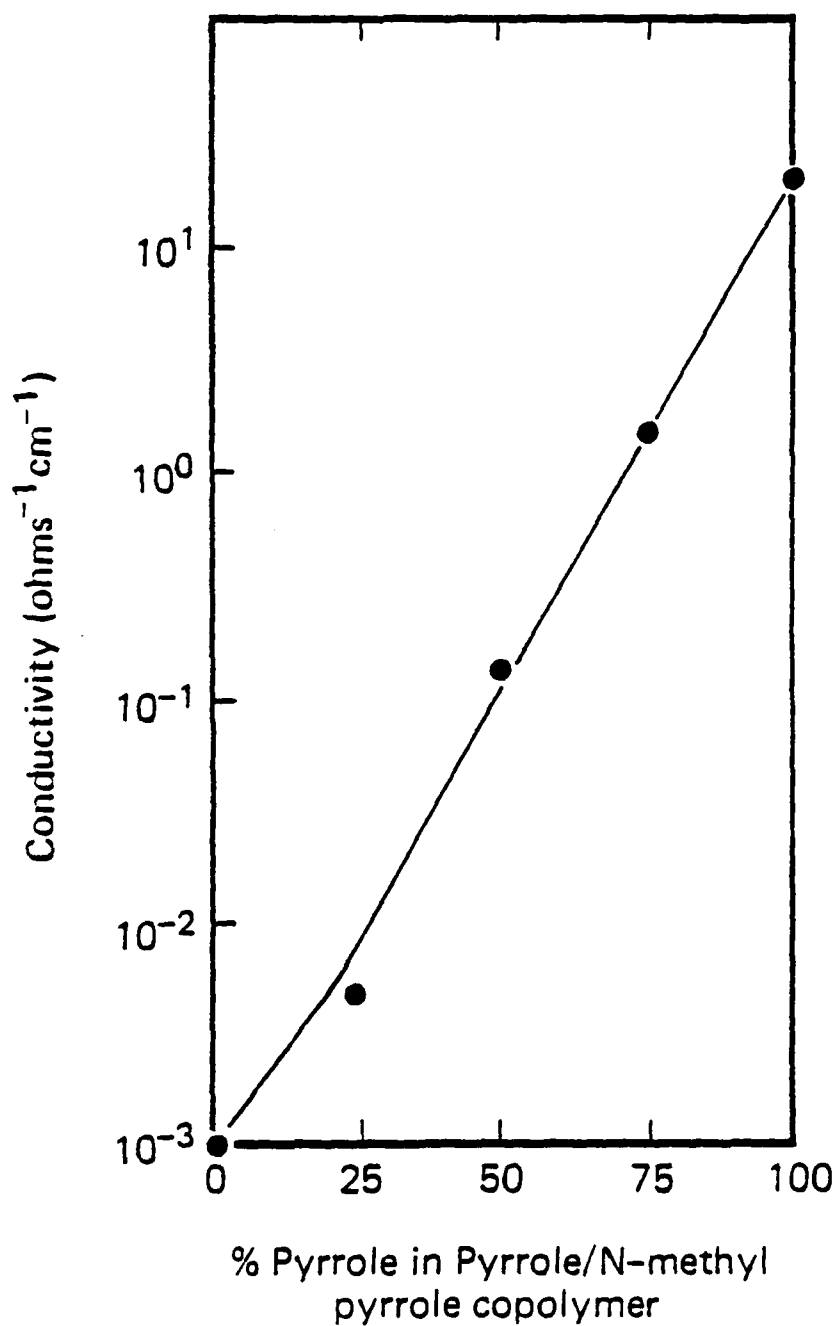


Figure 2. The four probe electrical conductivity of copolymers of pyrrole and N-methyl pyrrole as a function of copolymer composition.

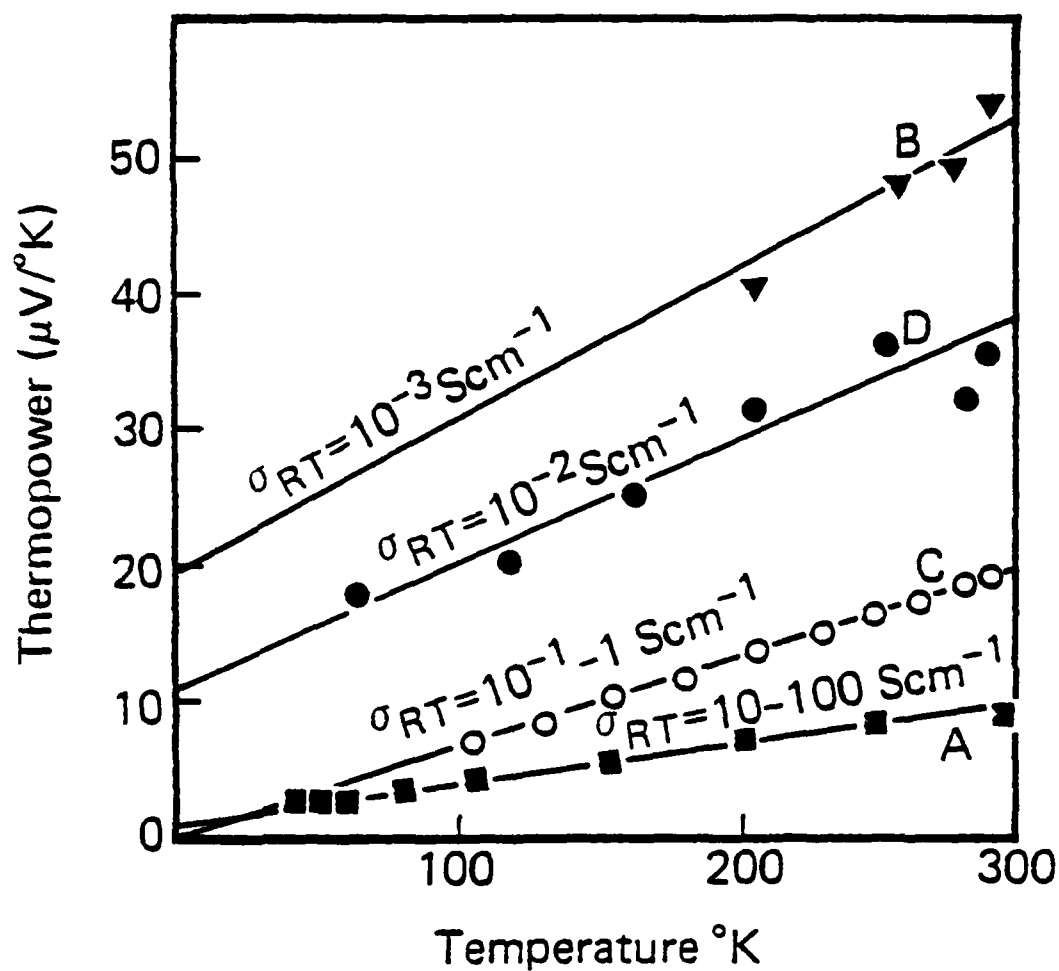


Figure 3. Thermopower data as a function of temperature for (a) pyrrole, (b) N-methyl pyrrole, (c) 1:1 copolymer of pyrrole and N-methyl pyrrole, (d) 1:3 copolymer of pyrrole and N-methyl pyrrole. The room temperature conductivity is shown for each film.

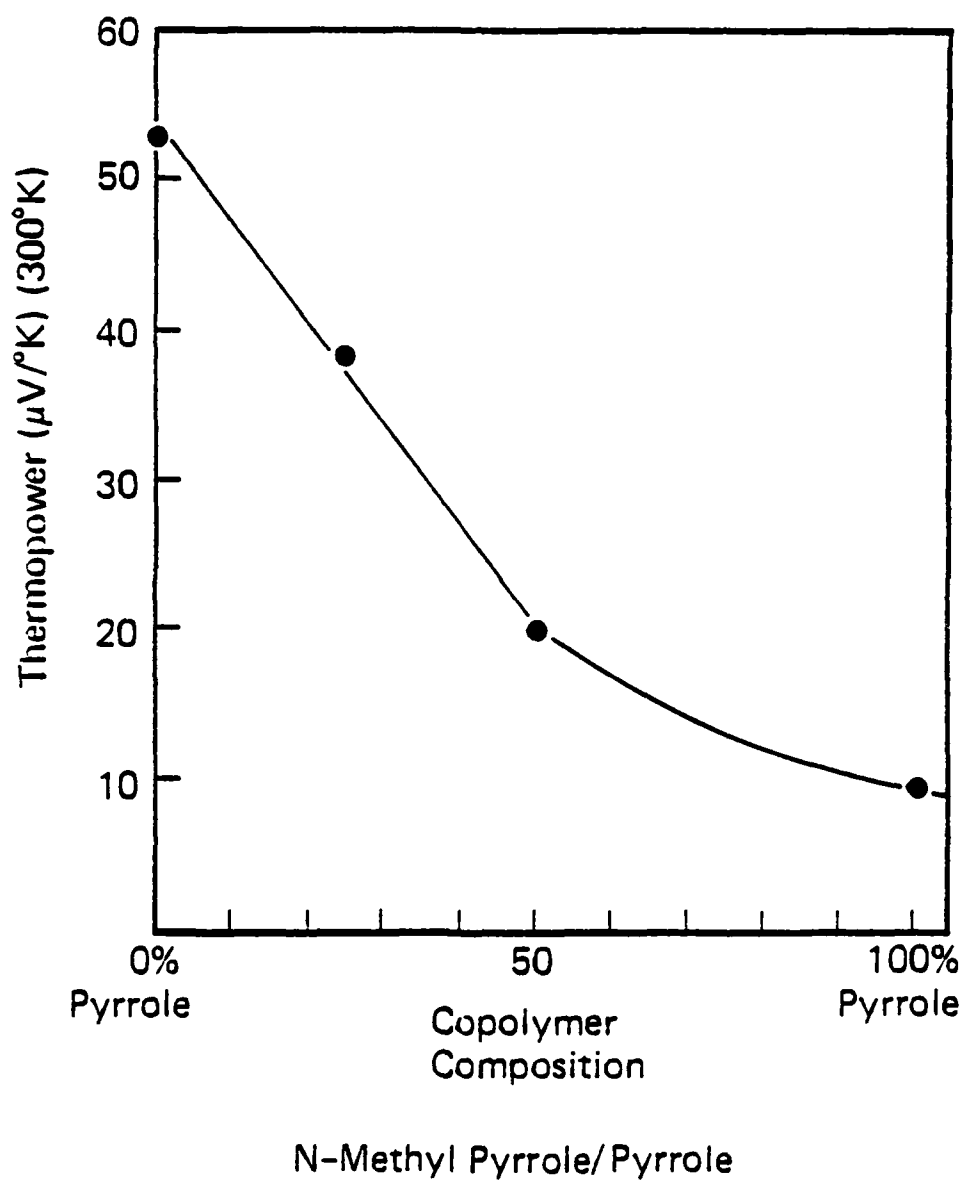


Figure 4. Thermopower at 300°K as a function of composition for a series of pyrrole N-methyl pyrrole copolymers.

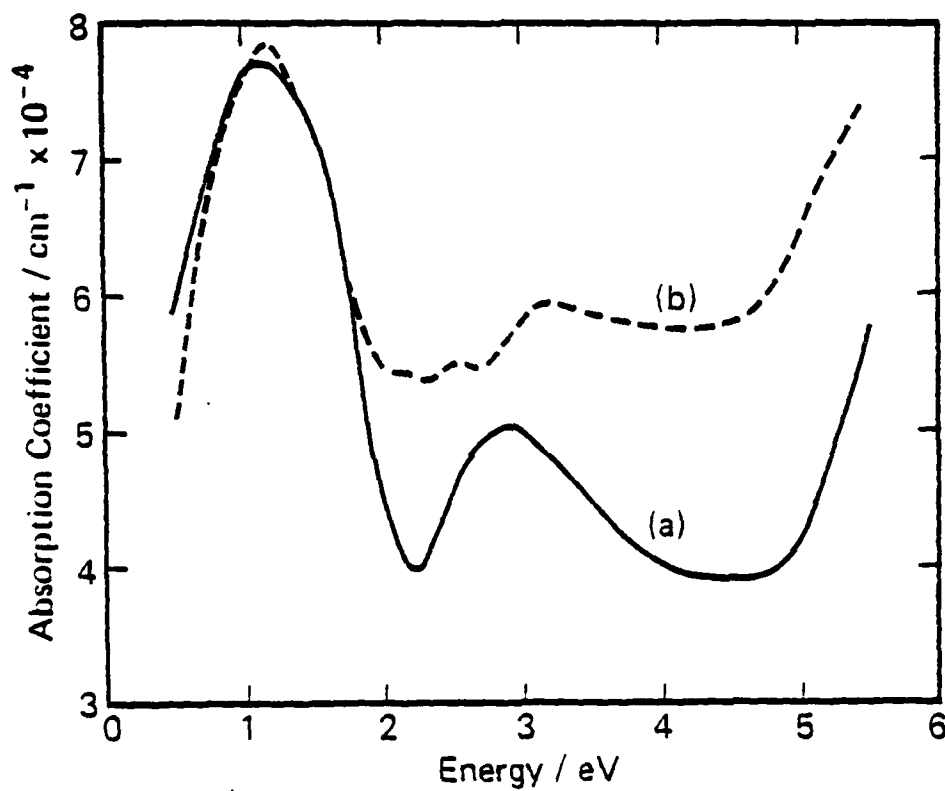


Figure 5. Absorption spectra of (a) polypyrrole tetrafluoroborate, (b) 1:1 copolymer of pyrrole and N-methyl pyrrole; anion is BF_4^- .

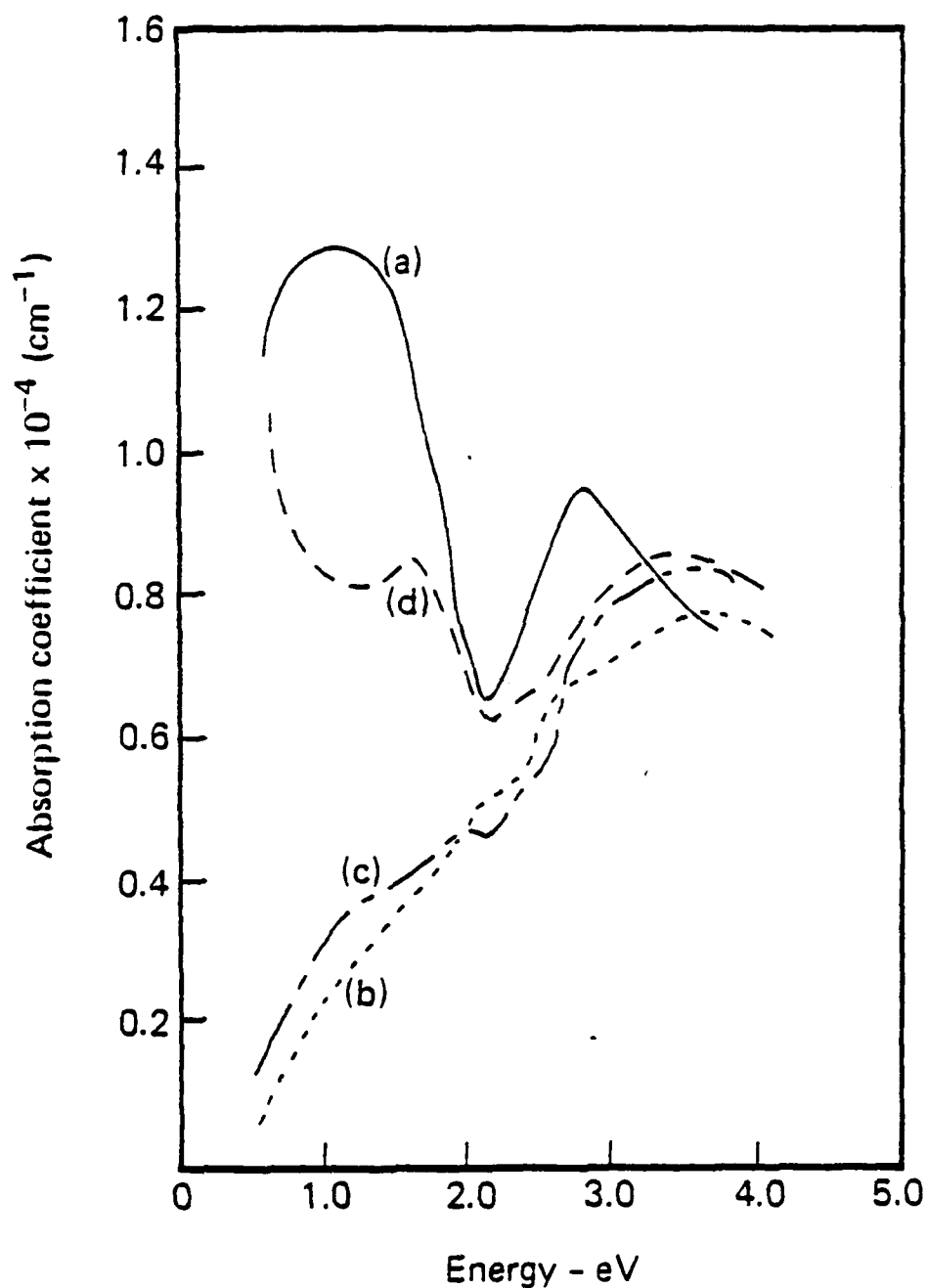


Figure 6. Absorption spectra of poly N-methyl pyrrole. (a) Spectrum of freshly prepared film. (b) spectrum of film several days later. (c) spectrum of neutral polymer obtained by electrochemically reducing the oxidized polymer. (d) spectrum of oxidized polymer obtained by oxidizing the neutral polymer.

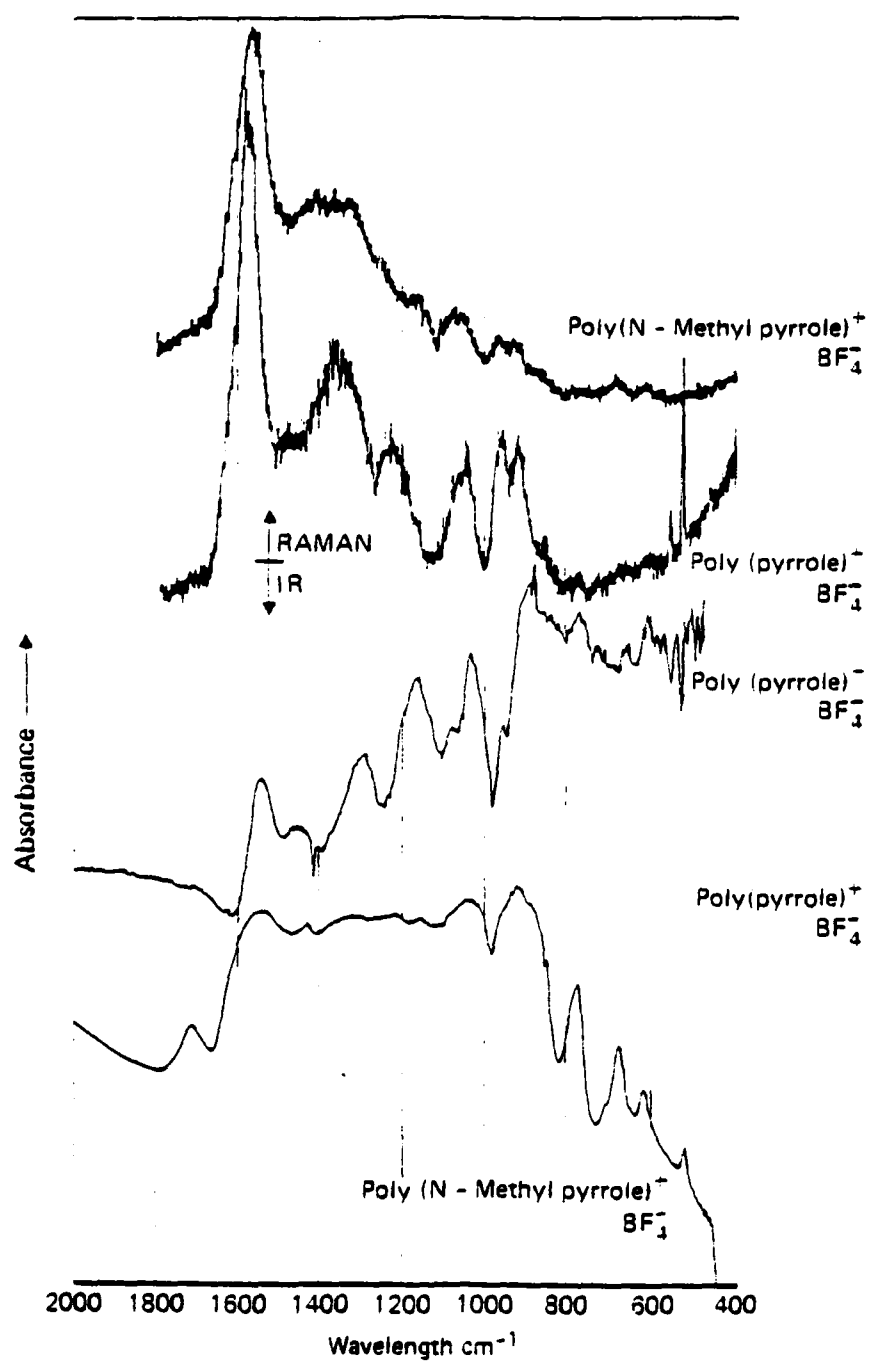


Figure 7. Raman and IR spectra of polypyrrole and poly N-methyl pyrrole tetrafluoroborate.

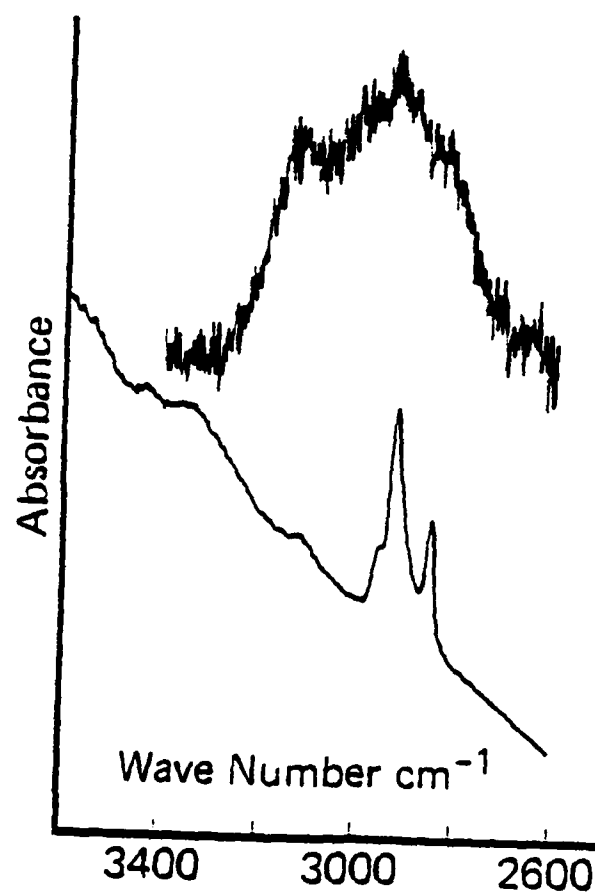


Figure 8. Raman (upper curve) and IR (lower curve) of polypyrrole tetrafluoroborate in the CH and NH stretching regions.

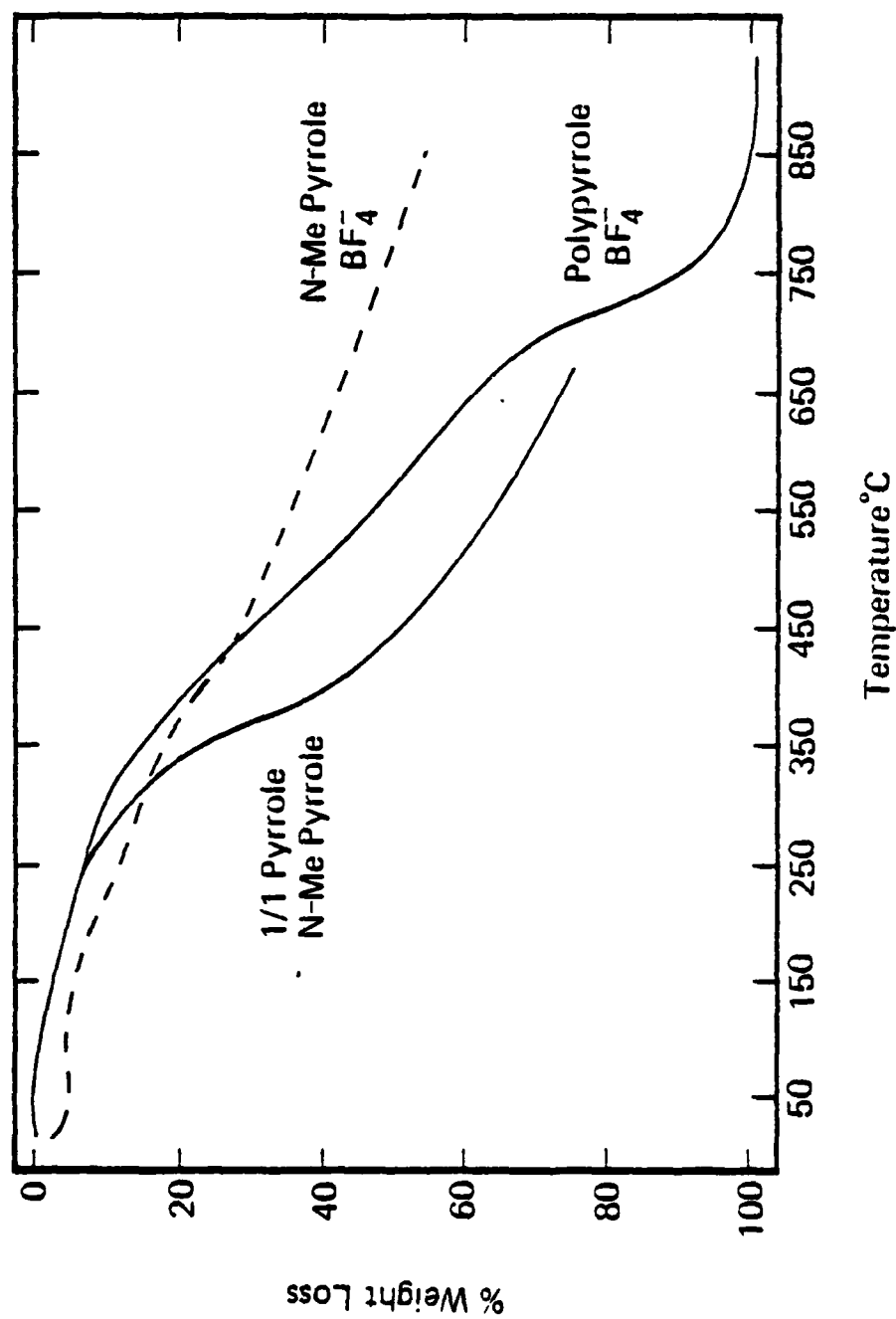


Figure 9. Weight loss as a function of temperature for polypyrrole, poly N-methyl pyrrole and the 1:1 copolymer. Anion is BF_4^- .

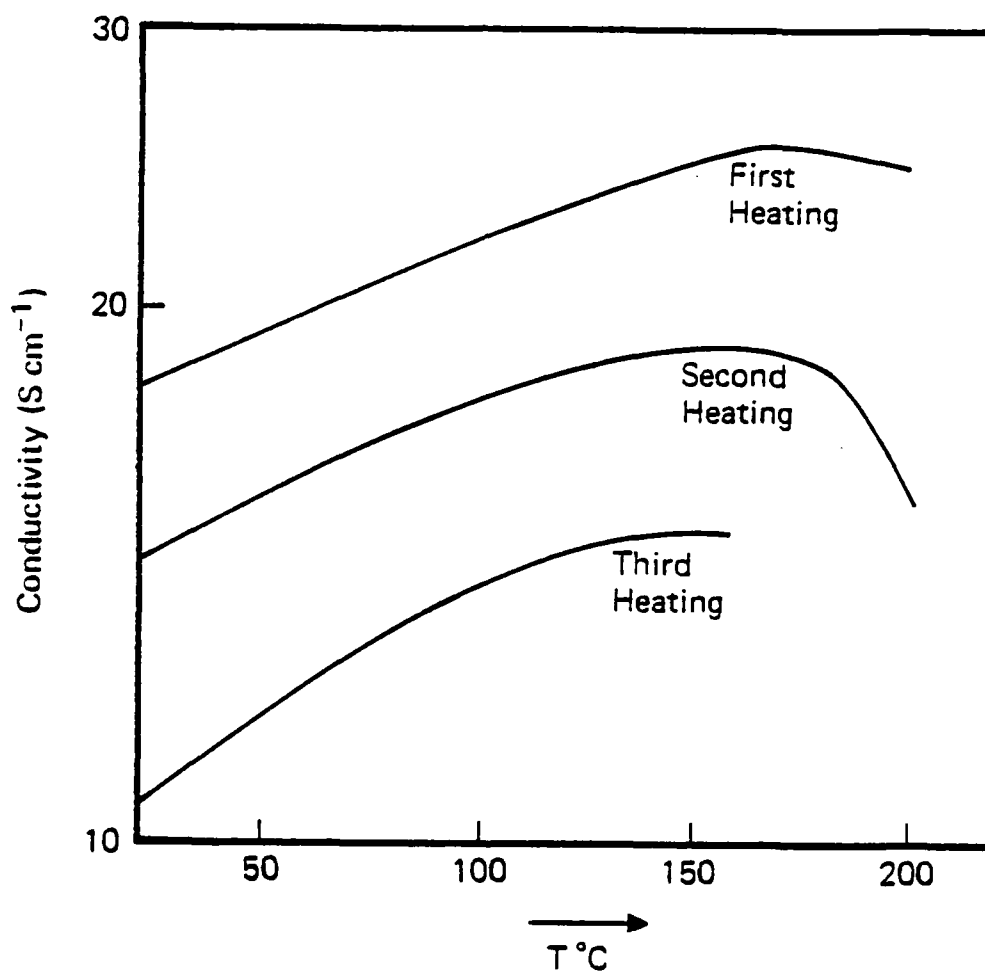


Figure 10. Conductivity versus temperature data for polypyrrole tetrafluoroborate subjected to three heating cycles.

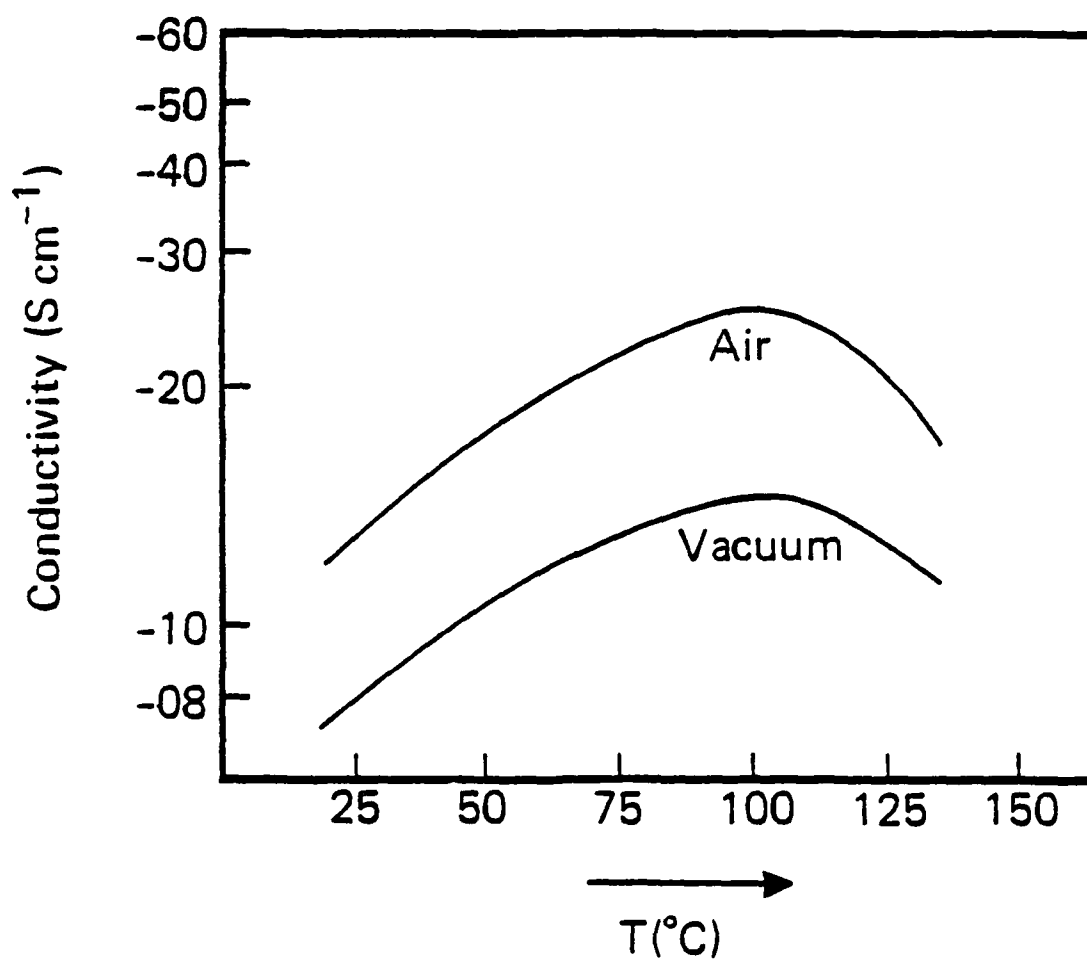


Figure 11. Conductivity versus temperature data for 1:1 pyrrole, N-methyl pyrrole in air and vacuum.

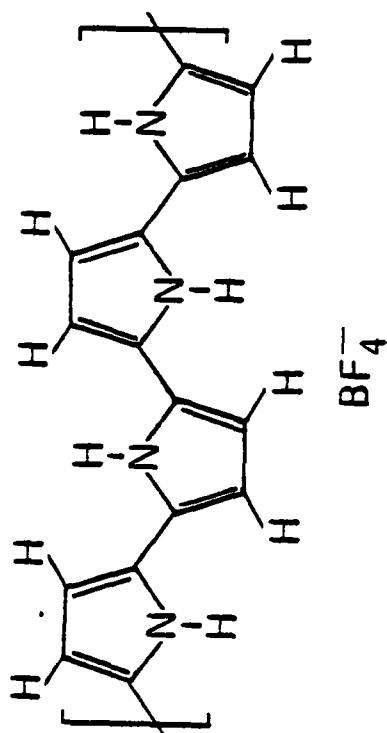


Figure 12. Proposed Structure of Polypyrrole.