

Determination of the thermal conductivity of polypyrrole over the temperature range 280–335 K

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Samples of polypyrrole were synthesised under galvanostatic conditions to produce films possessing a range of electrical conductivity from 10^{-3} to 10 S cm $^{-1}$. The electrical and thermal conductivity of these films has been determined between 280 and 335 K. The electrical conductivity was measured using a four probe technique calibrated against ASTM D4496-87. Thermal conductivity was determined from measurements of thermal diffusivity, specific heat and density. Thermal diffusivity was determined using a modified a.c. calorimetry technique, while differential scanning calorimetry (DSC) was used to determine specific heat. The polymer's density was measured using Archimedes' principle. The results were used to calculate the Lorenz number of polypyrrole. A comparison of the predicted behaviour and experimental results was made. Thermal conductivity is found to be large compared to that predicted from the electrical conductivity measurements on low conductivity films. Molecular vibration effects are found to be non-trivial and experimental means for measuring their contribution are mentioned. While polypyrrole has been regarded as a "synthetic metal" the thermal conductivity results show this classification is wrong.

1. Introduction

The applications of conducting polymers, such as polyacetylene, polypyrrole and polythiophene, have mainly been aimed at exploiting the variable electrical conductivity available from these materials. Some applications suggested include sensors, batteries and photovoltaic devices [1]. In addition, the possibility of achieving suitable electrical conductivity [2] in order to replace metals with these materials, in certain applications, is an area of active research.

The replacement of metals in such applications must be made with a thorough understanding of the basic properties of conducting polymers. Through a better understanding of the conduction mechanism improvements in conductivity may be achieved in the future. This paper presents recent attempts to measure both thermal and electrical conductivity of polypyrrole and treat these results with the Wiedemann-Franz law for metals and semiconductors. This report follows details of preliminary studies on polypyrrole [3].

There has been little attention devoted to the determination of the thermal conductivity of polypyrrole. Kanazawa *et al.* [4] reported a thermal conductivity value of 3.77 W m $^{-1}$ K $^{-1}$ for a copolymer of pyrrole and *N*-methylpyrrole. No information was given regarding the measurement technique or temperature at which the test was made. Using a PIT-1 thermal analyser (Sinku-Riko Inc.), Satoh *et al.* [5] reported a thermal diffusivity value of 0.028 cm 2 s $^{-1}$ for a poly-

pyrrole film doped with sodium *m*-nitrobenzenesulphonate. The film has an electrical conductivity of 70 S cm $^{-1}$. Both authors concluded that the thermal characteristics of the films displayed a significant electronic component, however no systematic study has been reported on thermal conductivity of polypyrrole. In contrast, polyacetylene has received more attention, however conflicting views on the accuracy and analysis of the results still exists [6–8]. Recent work has been carried out on polyaniline that related electrical and thermal conductivity to synthesis conditions [9].

For metals the Wiedemann-Franz law states that the ratio of thermal to electrical conductivity is proportional to temperature. The proportionality constant is the Lorenz number and is constant for a wide range of metals. This behaviour may be explained by applying Fermi-Dirac statistics to the "free" electrons in the material [10, 11]. Hence, it can be shown that the ratio of the electronic component of thermal conductivity K (W m $^{-1}$ K $^{-1}$) to electrical conductivity σ (S m $^{-1}$) is given by

$$K/\sigma = (\pi^2/3)(k/e)^2 T \quad (1)$$

where k is the Boltzmann constant (J K $^{-1}$), e the charge on an electron (C) and T is the absolute temperature (K). Hence the Lorenz number for metals is given by $(\pi^2/3)(k/e)^2$ and is equal to 2.45×10^{-8} W Ω K $^{-2}$.

For semiconductors this behaviour is modified due to scattering and different mobility of holes and electrons. In general, semiconductors have Lorenz numbers between $2(k/e)^2$ and $(2 + (\epsilon_g/2kT + 2)^2)(k/e)^2$, where ϵ_g is the energy gap of the semiconductor [10].

2. Experimental procedure

For this investigation polypyrrole films were electrochemically deposited from an aqueous solution of *p*-toluenesulphonic acid and pyrrole monomer. The dopant anion concentration was varied to yield films of different electrical conductivity, as shown in Table I. Galvanostatic polypyrrole synthesis was carried out using a two electrode electrochemical cell under a blanket of nitrogen. The polypyrrole was deposited on a polished 304 stainless steel sheet anode. The cathode was fabricated from stainless steel wire gauze. Detailed information concerning the preparation of these films is given elsewhere [12].

As thermal diffusivity relates to a material's response to a transient heat pulse (i.e. non-steady state) it is more readily measured in thin samples than steady state thermal conductivity. This technique is appropriate for polypyrrole films which are approximately 100 μm thick. The thermal diffusivity α ($\text{m}^2 \text{s}^{-1}$) of a material is defined by its relationship to thermal conductivity K , where

$$K = \alpha\rho C \quad (2)$$

where ρ represents the density (g m^{-3}) and C is the specific heat ($\text{J g}^{-1} \text{K}^{-1}$) of the film.

A light-irradiated a.c. calorimetry method was used to determine the thermal diffusivity of polypyrrole films. This technique was first refined by Hatta *et al.* [13–15] on thin samples of nickel, stainless steel and alumina. Utilisation of this technique for the determination of α was based on experiments and theoretical work that had examined the applicability of a.c. calorimetry to the determination of a.c. heat capacity [16, 17]. A modified a.c. calorimetry technique has been developed and is described in [18]. The method has been validated by testing thin polyethylene and polystyrene films of known thermal diffusivity. In general the technique involves applying a periodic heat source to one side of a thin plate sample. This was achieved by irradiating the surface of the sample with light chopped at a set frequency. The thermal wave produced in the sample was measured on the rear face as a mask was moved across the sample. The resulting decay in the amplitude of the thermal wave was used to determine the thermal diffusivity of the sample.

Theoretically the system may be considered one-dimensional if there is no thermal gradient between the front and back surfaces of the sample, that is

$$(\pi f/\alpha)^{1/2}d \ll 1 \quad (3)$$

where f is the frequency of periodic heating (Hz) and d is the sample thickness (m) and $(\pi f/\alpha)^{1/2}$ equals k , the reciprocal of the thermal diffusion length. If Equation 3 is satisfied then the solution to the a.c. temperature function gives

$$T(x) = [Q/2wcd]\exp[-kx - i(kx + \pi/2)] \quad (4)$$

where $T(x)$ is the temperature amplitude as a function of distance x (K), x is the distance from the thermocouple to the edge of the mask (m), Q is the energy of the irradiation per unit surface area (W m^{-2}), w is the angular frequency of a.c. irradiation (s^{-1}), c is the heat capacity per unit volume ($\text{J m}^{-3} \text{K}^{-1}$), d is the sample thickness (m) and $k = (\pi f/\alpha)^{1/2}$ (m^{-1}).

Hence, the thermal diffusivity may be determined from the slope m of a graph of $\ln(T(x))/\sqrt{f}$ versus x as

$$\alpha = \pi^2/m \quad (5)$$

This analysis holds for the region where the temperature sensor is first covered by the mask. As the mask covers more of the sample the linearity of the relationship deviates due to the effect of radiation heat losses and noise in the sensing circuit. With the sensor exposed the relationship levels off as the thermal wave travels through the thickness of the sample rather than along its length, and so is independent of mask position x . This maximum gives the relative heat capacity of the sample. The decay rate of thermal wave with change in mask position is described in Equation 4. The shadow, cast by the mask on the sample, need not be perfectly sharp as functions of the same decay rate appear superimposed.

Since the thickness of all the polypyrrole films examined was less than 120 μm the constraint imposed by Equation 3 on sample dimensions was satisfied.

The selection of an appropriate frequency is also governed by Equation 3. Low frequencies are ideal; however, the period should not be so long that the sample can equilibrate during the heating pulse. If the external relaxation time is defined as

$$\Gamma_e = \frac{c.d}{\delta} \quad (6)$$

where c is the a.c. heat capacity, d is thickness of the sample and δ is the thermal conductance of the sample, then frequency should satisfy $2\pi f/\Gamma_e \geq 1$. Γ_e is estimated to be a few tens of seconds in air [13]. A frequency of 0.74 Hz was selected for determination of thermal diffusivity of polypyrrole to satisfy these constraints.

In the experimental rig the temperature sensing element is a thermistor (Bowthorpe U23UD) on which the sample rested balanced between two fine polyester threads (Fig. 1). A small amount of thermal grease

TABLE I Synthesis conditions

Condition	Film code			
	9D	8A	8B	8C
[Pyrrole] (M)	0.2	0.2	0.2	0.2
[<i>p</i> TSA] (M)	0.2	0.01	0.0075	0.0025
Current density (mA cm^{-2})	3	3	3	3
Temperature (K)	278	278	278	278
Expected electrical conductivity at 298 K (S cm^{-1})	10^1	10^{-1}	10^{-2}	10^{-3}

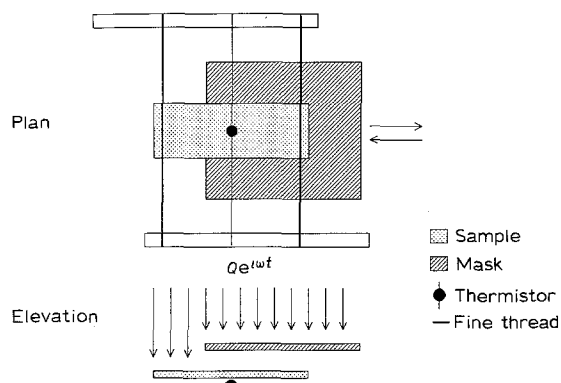


Figure 1 Sample support used in a.c. calorimetry rig.

(Dow Corning 430) was used to ensure good thermal contact between the sample and thermistor. A constant current was applied across the thermistor using a Keithley 224 programmable constant current source. In all experiments on polypyrrole a current of 0.3 mA was found to give optimal signal response. The voltage drop across the thermistor was fed to a Stanford Lock-In Amplifier SR530, as was a reference signal from a chopper. The Lock-In Amplifier was used to extract the thermal wave from background noise and to amplify the signal so it could be readily measured using a Philips PM3365 digital oscilloscope. The temperature of the sample was controlled between 283 and 333 K in a sample chamber. The static temperature of the chamber was determined using the same thermistor as that used in the thermal diffusivity measurement. To determine the temperature of the sample chamber the current source was turned off and the resistance across the thermistor measured using a Fluke 87 digital multimeter. The error in the temperature by taking resistance directly was determined to be in the region of ± 0.5 K.

After the temperature had stabilised a series of amplitude readings were taken for mask positions corresponding to approximately 1.0 mm either side of the expected position of the thermistor in 0.1 mm steps. This was done to find the linear region of the signal response required for the determination of thermal diffusivity. A 0.4 mm region was then chosen lying entirely within the linear region and readings were taken in 0.05 mm steps. This narrow region was scanned three times and the results of the amplitude measurements were averaged and converted to $\ln(T(x))/\sqrt{t}$ values. The linear regression of this data against relative mask position was used to give the slope m and hence the thermal diffusivity. Data was

only accepted if the square of the regression coefficient r^2 was greater than 0.999.

The specific heat of the polypyrrole films was determined between 283 and 333 K using a Mettler TA3000 heat flow differential scanning calorimeter. The density of the polypyrrole films was determined by weighing the films in air and water at 298 K.

Electrical conductivity measurements were carried out using a four probe technique calibrated to ASTM D4496-87. To measure electrical conductivity a sample of known thickness and width was placed between the plates of the four probe as shown in Fig. 2. A constant current was applied to the outer electrodes from a Keithley 224 constant current source and the potential difference measured over the inner electrodes using a Fluke 87 digital multimeter. To minimise heating of the sample the applied current was limited to below 1 mA. Reproducible results are generally found for measured potentials of 5–15 mV.

In the experimental rig a small bead thermistor (Bowthorpe U23UD) was incorporated into the four probe rig to allow simultaneous determination of the temperature of the sample. The rig was placed in a plastic enclosure that allowed immersion in a temperature controlled water bath. The temperature of the sample was varied from 273 to 333 K. Conductivity measurements were made as the water bath was slowly warmed from 273 K.

3. Results and discussion

3.1. Thermal conductivity

The change in the thermal diffusivity with temperature, as shown in Table II, is in all cases less than the average error in the experiment. For subsequent calculations the average thermal diffusivity is taken

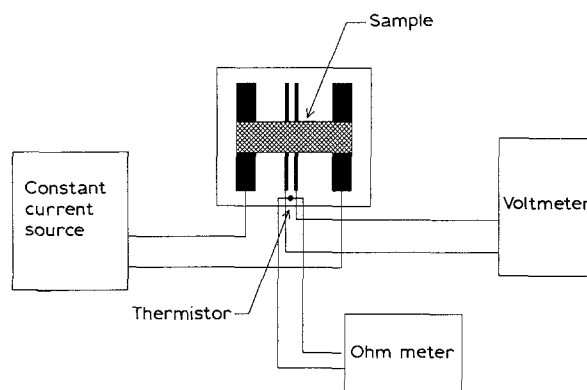


Figure 2 Four probe resistivity measurement.

TABLE II Thermal diffusivity change with temperature for polypyrrole

Temperature (K)	Film 9D α ($\text{cm}^2 \text{s}^{-1}$)	Temperature (K)	Film 8A α ($\text{cm}^2 \text{s}^{-1}$)	Temperature (K)	Film 8B α ($\text{cm}^2 \text{s}^{-1}$)	Temperature (K)	Film 8C α ($\text{cm}^2 \text{s}^{-1}$)
284.8	0.0093 ± 0.0004	283.0	0.0064 ± 0.0003	284.2	0.0053 ± 0.0002	285.3	0.0065 ± 0.0002
300.8	0.0084 ± 0.0004	302.1	0.0061 ± 0.0001	298.2	0.0057 ± 0.0005	301.3	0.0063 ± 0.0005
307.8	0.0086 ± 0.0006	310.0	0.0063 ± 0.0002	311.2	0.0056 ± 0.0003	308.5	0.0063 ± 0.0003
313.6	0.0090 ± 0.0009	319.5	0.0065 ± 0.0004	318.5	0.0058 ± 0.0005	318.3	0.0063 ± 0.0004
323.1	0.0087 ± 0.0005	327.1	0.0063 ± 0.0002	327.7	0.0058 ± 0.0003	328.0	0.0065 ± 0.0006
332.7	0.0091 ± 0.0007	—	—	332.7	0.0055 ± 0.0003	332.7	0.0066 ± 0.0003

over the whole temperature range with the average error.

The magnitude of the measured specific heat for polypyrrole, presented in Fig. 3, $0.8\text{--}1.4\text{ J g}^{-1}\text{ K}^{-1}$, is lower than that of most polymers. Amorphous PET for example has a specific heat of approximately $10\text{ J g}^{-1}\text{ K}^{-1}$ at 273 K, increasing to $12\text{ J g}^{-1}\text{ K}^{-1}$ [19]. Metals generally have specific heats of approximately $1\text{ J g}^{-1}\text{ K}^{-1}$ at room temperature (exceptions are beryllium $1.9\text{ J g}^{-1}\text{ K}^{-1}$, sodium $1.23\text{ J g}^{-1}\text{ K}^{-1}$ and lithium $3.4\text{ J g}^{-1}\text{ K}^{-1}$) [20].

However, the specific heat for polypyrrole appears to be independent of the level of doping. This would suggest that the mechanism for the low specific heat is not linked to the measured increase in electrical conductivity.

The results of the density measurements for the three films are presented in Fig. 4. It appears that the incorporation of dopant has little effect on the density of the polypyrrole films. This suggests that the free space of the polymer film remains relatively constant even when large amounts of dopant are incorporated in the structure. It is assumed that the change in density over the temperature range studied is small compared to the uncertainty in the density determination.

The thermal conductivity was determined from the product of the density, specific heat and thermal diffusivity as given in Equation 2. A total error of approximately 15% in the thermal conductivity measurement was determined (Fig. 5).

The magnitude of the thermal conductivity of polypyrrole is two to five times greater than that for polymers such as polyethylene and polystyrene [21]. This value places polypyrrole between electrically insulating polymers and silica glass. The results show an increase in thermal conductivity with temperature from 273 to 333 K, contrary to the behaviour of most pure metals and polymers. However, some materials

such as silica glass and some alloys do show such behaviour.

This behaviour may be explained in terms of the different contributions from the molecular-phonon interactions and electronic conduction mechanisms in different materials. For the case of metals as the temperature is increased the average electron and phonon velocities increase while their mean free paths decrease. These two phenomena tend to cancel each other out, thus the thermal conductivity is essentially constant for a large temperature range above 100 K. Below this temperature the thermal conductivity approaches a maximum before falling to zero at 0 K. The effect of impurities, grain boundaries and alloying elements limits the phonon mean free path and so decreases the overall thermal conductivity while forcing the thermal conductivity to increase with temperature.

For a better understanding of the mechanisms involved further measurement of the electronic and molecular contributions to thermal conductivity are

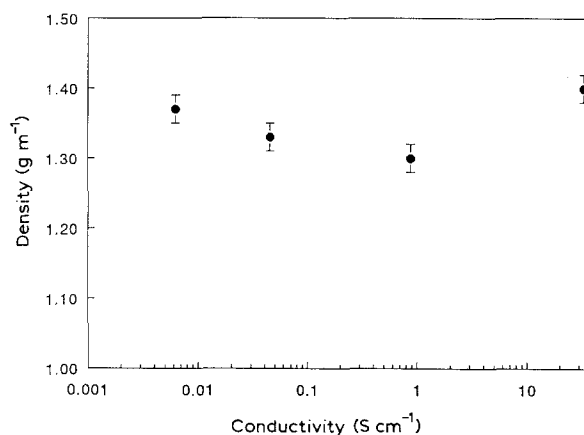


Figure 4 Density of polypyrrole at 298 K.

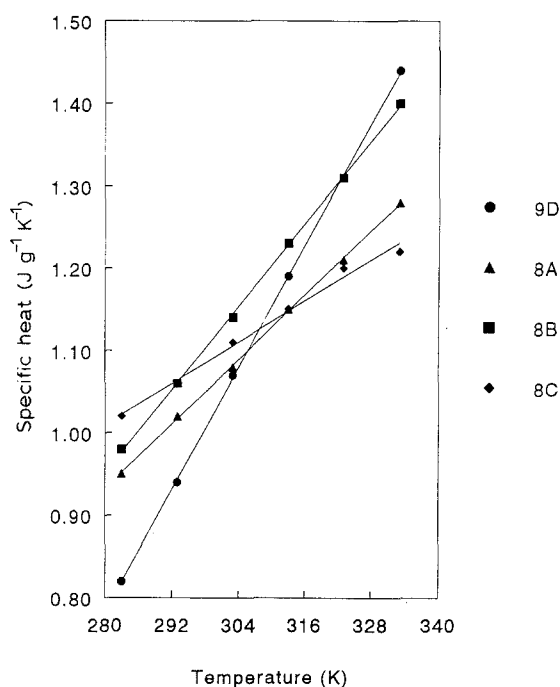


Figure 3 Specific heat of polypyrrole from 283 to 333 K.

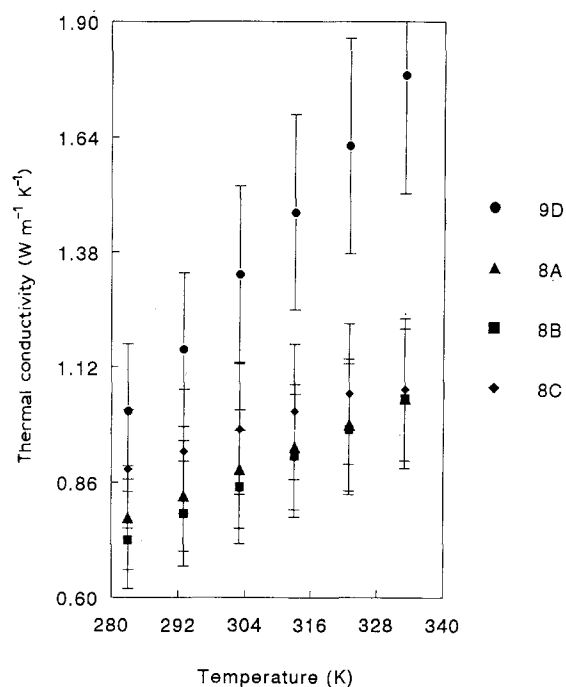


Figure 5 Thermal conductivity of polypyrrole from 283 to 333 K.

required. The contribution of the molecular vibration to the thermal conductivity could be determined by removing the electronic contribution by measuring the thermal conductivity in a strong magnetic field. The molecular contribution may also be determined by plotting electrical conductivity against thermal conductivity and extrapolating back to zero electrical conductivity. Two problems arise with this method. Firstly, if the material approaches the behaviour of an intrinsic semiconductor, as electrical conductivity decreases, a large increase in thermal conductivity may be observed at certain temperatures. This is due to the formation of thermally activated hole–electron pairs. Secondly, the molecular thermal conductivity can be effected by scattering from dopant sites. Hence the molecular thermal conductivity (i.e. that measured at zero electrical conductivity) may not be equivalent to the molecular contribution to thermal conductivity of a highly doped film.

3.2. Electrical conductivity

The temperature dependence of electrical conductivity for polypyrrole follows that predicted by Mott variable-range hopping (VRH) theory [22–24]. The VRH model allows movement of localised states to sites other than nearest neighbours. This can be energetically favourable in a random distribution of sites where the chance for neighbouring sites having small energy separations is low. To optimize the competing factors of hop distance against energy separation the predicted electrical conductivity is given by

$$\sigma = \sigma_0 \exp(-A/T^{1/4}) \quad (7)$$

where σ_0 and A are constants. In order to check the validity of the variable-range hopping theory over the temperatures examined, the data was used to produce a $\ln(\sigma)$ against $T^{-1/4}$ graph shown in Fig. 6. As can be seen, the relationship does hold for all films up to

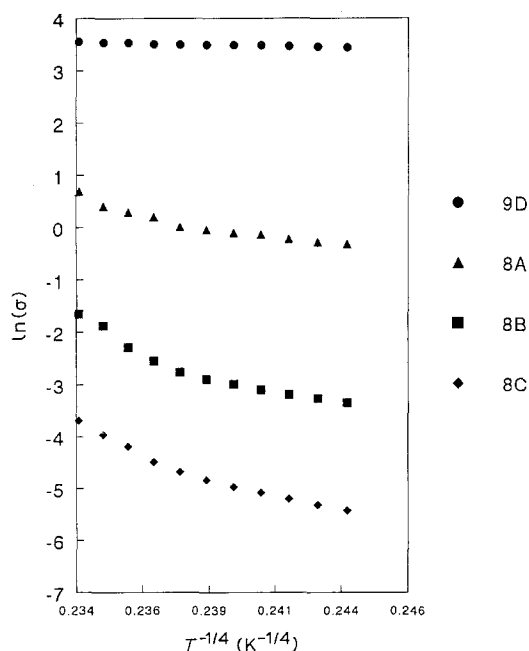


Figure 6 $\ln(\sigma)$ versus $T^{-1/4}$ for films of different conductivity.

approximately 318 K, after which the behaviour deviates markedly from that predicted by the theory. The deviation is most marked for films of conductivity below $10^{-1} \text{ S cm}^{-1}$.

An explanation of this behaviour may be the introduction of the “two channel” model proposed to explain the electrical conductivity change with temperature of an “ideal” amorphous semiconductor [22]. This model applies where the electron states are localised and the conduction is due to thermally activated hopping between sites after phonon interactions. $\ln(\sigma)$ in this regime is proportional to $1/T$ and the constant can be related to the energy of the valence band, Fermi energy and energy splitting in the band gap, all of which are influenced by the temperature of the sample. As temperature increases the behaviour may pass through up to three regions of different slope corresponding to different interactions.

It is difficult to differentiate between the two expected relationships without more data. The development of a different gradient toward higher temperatures may indicate discontinuous changes in the nature of the charge carriers. Further study of this region should prove productive as data of this sort may be used to study the migration of the mobility edge through the band gap region.

3.3. Lorenz number calculation

The ratio of thermal to electrical conductivity K/σ , at selected temperatures for polypyrrole are presented in Fig. 7. For a metal this plot shows a positive linear relationship with the proportionality equal to the Lorenz number. Contrary to the behaviour of metals, the low conductivity films actually show a non-linear decrease in their conductivity ratio with temperature. This is due to the rapid increase in the electrical conductivity of these films that is not accompanied

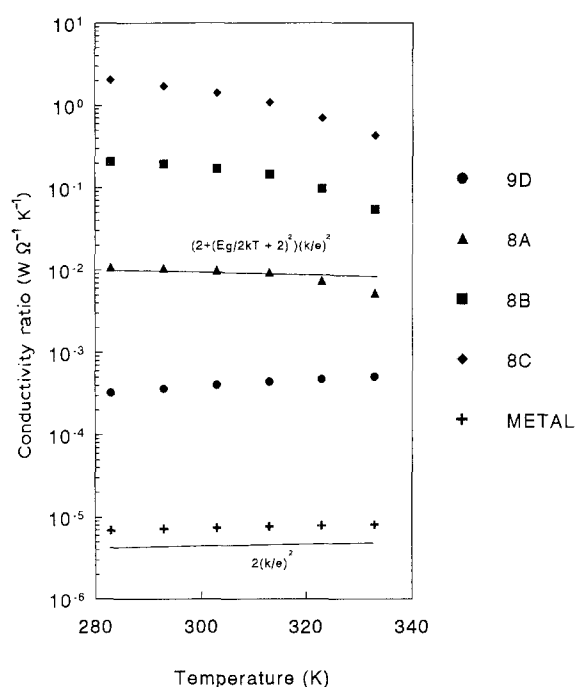


Figure 7 Conductivity ratio (K/σ) of polypyrrole from 283 to 333 K.

by a similar increase in thermal conductivity (Figs 5 and 6).

It was noted when determining the thermal conductivity that the dopant level had little effect on the specific heat. The increase in thermal conductivity is solely due to the change in specific heat with temperature, as thermal diffusivity and density were considered constant with temperature. The amorphous nature of polypyrrole appears to be the determining factor in the thermal conductivity. The scattering of phonons removes the temperature dependence of the mean free path length and hence thermal conductivity becomes linearly proportional to specific heat.

The electrical conductivity, on the other hand, at temperatures below about 323 K appears to increase in accordance with the VRH model [22] and above this temperature rises more rapidly. The lower conductivity films display a steeper electrical conductivity to temperature relationship above 323 K. This gives rise to the drop off in the conductivity ratios of these films as the thermal conductivity does not increase rapidly in this temperature range.

The highest conductivity film does exhibit a near linear relationship with temperature. At this conductivity it appears the change in electrical conductivity with temperature is not as dramatic and the thermal conductivity increases rapidly enough to maintain the conductivity ratio relatively stable with temperature. The electrical conductivity of this film is still an order of magnitude below the minimum metallic conductivity [22] and so it is no surprise that metallic behaviour is not observed.

Also shown in Fig. 7 are the theoretical limits on the conductivity ratio of semiconductors as discussed above. From optical studies it is thought the band gap for polypyrrole lies between 3.2 eV and 3.6 eV, depending on doping [25]. This gives an upper limit for the Lorenz number of a semiconducting film of approximately $3.8 \times 10^{-5} \text{ W } \Omega \text{ K}^{-2}$.

The result of the Lorenz number calculation is given in Table III. From this table it can be seen that the behaviour of polypyrrole does approach that of metals as the conductivity increases. The Lorenz number approaches the value for metals and becomes less dependent on temperature as the conductivity of the polypyrrole film is increased.

While Mott VRH is observed, the nature of the charge carriers is not certain. The presence of charge carriers, other than "free" electrons in polypyrrole, would mean the Lorenz number for a highly conduct-

ive film may not be equivalent to that for metals. Determining this value for "metallic" polypyrrole, i.e. for samples with electrical conductivities greater than 300 S cm^{-1} , may allow a greater insight into the transport mechanisms for this material.

4. Conclusion

The thermal diffusivity, from an a.c. calorimetry technique, specific heat and density have been determined to yield thermal conductivity for the temperature range 283–333 K. The relationship between thermal and electrical conductivity for polypyrrole does not follow a simple Wiedemann–Franz proportionality over this temperature range. Lattice effects enhance thermal conductivity of low electrical conductivity films and rapid increases in electrical conductivity above 313 K are not reflected in increased thermal conductivity. The Lorenz numbers determined do not conform to the theoretical limits of normal semiconductors. The amorphous nature of polypyrrole and the lattice contribution to thermal conductivity seem to be important factors in this analysis.

It is evident that further investigation is required to separate electrical and molecular thermal conductivity so a meaningful value of the Lorenz number for these materials may be determined. Further research is underway to determine the thermal diffusivity and specific heat of conducting polymers over a wider temperature range.

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TABLE III Lorenz numbers for polypyrrole

Temperature (K)	Lorenz number $L \pm 20\%$ ($\text{W } \Omega \text{ K}^{-2}$)			
	Film 9D	Film 8A	Film 8B	Film 8C
	($\times 10^{-6}$)	($\times 10^{-5}$)	($\times 10^{-4}$)	($\times 10^{-3}$)
283.0	1.15	3.83	7.39	7.02
293.0	1.24	3.47	6.59	5.78
303.0	1.33	3.25	5.62	4.67
313.0	1.42	2.99	4.66	3.47
323.0	1.47	2.29	3.00	2.16
333.0	1.53	1.59	1.64	1.29

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