Ageing of electrically conducting organic materials

H. Münstedt
Kunststofflaboratorium, BASF Aktiengesellschaft, D-6700 Ludwigshafen, FRG
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Ageing with respect to conductivity has been investigated for a wide variety of organic materials ranging from polyacetylene and polypyrrole salts to carbon black and carbon fibres, which are conducting materials in their electrically neutral state. For two polyacetylenes of different composition and a polypyrrole phenylsulphonate the influence of temperature on conductivity and its change with time could be described quantitatively. Data on the stability of polypyrrole salts under humidity and under extreme inert conditions are given. The influence of the degree of oxidation on the stability under ambient conditions is reported for a polypyrrole perchlorate. A comparison of the stability of the conductivity of organic salts like tetrathiofulvalene/tetracyanoquinoline (TTF/TCNQ) and those based on polyacetylene, polypyrrole, polythiophene and polyaniline with carbon black and carbon fibres, which are conductive in their neutral state, gives rise to the assumption that carbenium ion-structures are not stable with respect to the attack of oxygen and water. Covalent bonds cause the decrease in conductivity.

(Keywords: conducting organic materials; ESCA analysis; time–temperature dependence of ageing)

INTRODUCTION

One reason for the lack of significant technical use of intrinsically conducting organic materials is that of ageing problems. The scope of future applications of this fascinating new class of materials will depend on the success of making them more stable with respect to environmental conditions, and this requires basic knowledge about the physical and chemical processes underlying the observed deterioration of properties. This paper deals with some aspects of the ageing of polymers by investigating the electrical conductivity as their most interesting physical property.

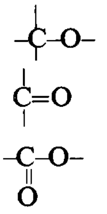
POLYACETYLENE

Unmodified samples

Until now, most of the fundamental research has been carried out on polyacetylene, which can be regarded as the prototype of electrically conducting polymers. Compared with the many investigations dealing with the mechanism of conductivity only little is known about the ageing processes responsible for the decrease of conductivity.

It has been shown in the literature that polyacetylene, which is an insulating material as polymerized, becomes conductive only in its oxidized or reduced state[1,2]. The lower curve in *Figure 1a* demonstrates this behaviour. Upon exposure to air, the conductivity of polyacetylene first increases. In parallel to the conductivity increase an oxygen uptake can be observed (*Figure 1b*). After some time of exposure to air the conductivity reaches a maximum and then falls again. This decrease of conductivity is accompanied by a further oxygen uptake. The oxygen uptake and loss of conductivity are irreversible, as has been shown by vacuum treatment of the sample after the exposure to air.

From the ESCA (electron spectroscopy for chemical analysis) investigations presented in *Figure 2* the findings of *Figure 1* become obvious. The change of the energy distribution of the C_{1s}-photoelectrons of the polyacetylene after exposure to air for 22 days can be explained by the formation of covalent bonds between oxygen and carbon atoms. Simple decomposition of the C_{1s}-peaks gives four peaks which can be ascribed to $(CH)_x$,


$-\overset{|}{\underset{|}{C}}-O-$ (e.g. alcohol, ether, hydroperoxide)

$\overset{|}{\underset{|}{C}}=O$ (e.g. aldehyde, ketone), and

$-\underset{\underset{O}{\|}}{C}-O-$ (carboxylic acid or ester)[4].

The formation of covalent bonds between carbon and oxygen shortens the sequences of conjugated double

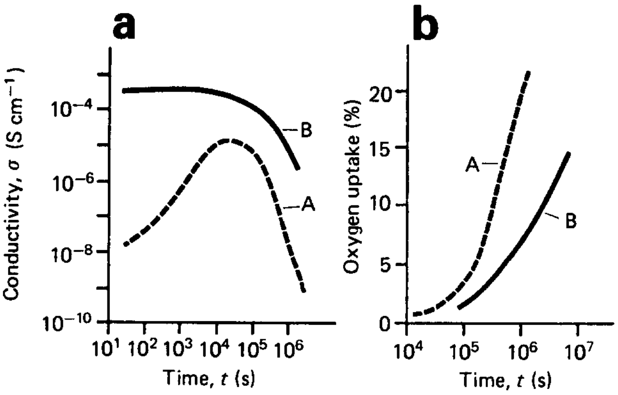


Figure 1 (a) Conductivity change and (b) oxygen uptake of two polyacetylene films as a function of the time of exposure to ambient conditions. A, Polyacetylene of 'Shirakawa' type[3]; B, polyacetylene modified with $ClSO_2NCO$. Film thicknesses are around 50 μm

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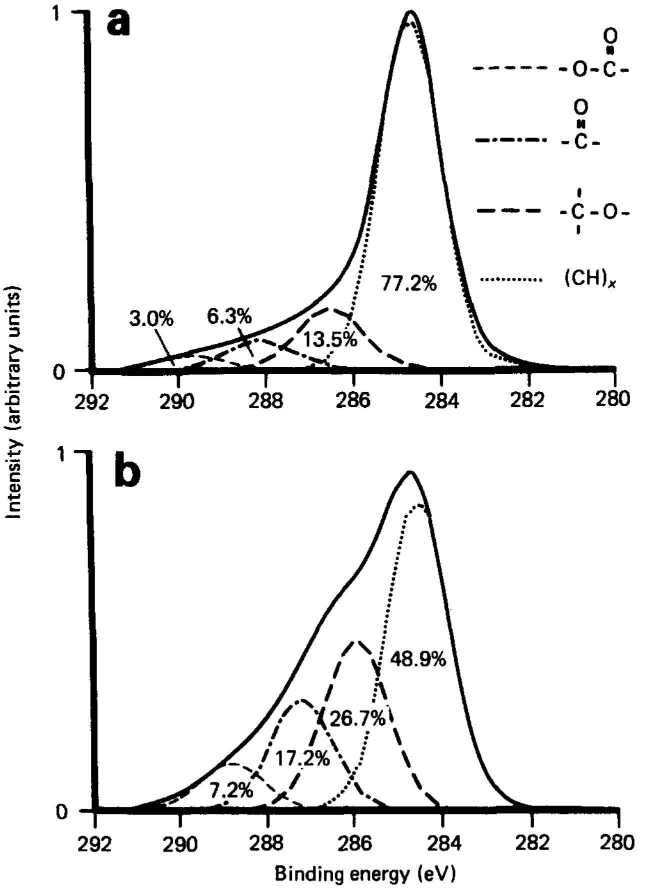

Figure 2 ESCA spectra in the carbon region of a polyacetylene film: (a) as polymerized and (b) after exposure to air for 22 days

bonds in the original polymer necessary for obtaining conductivity. This process leads to a fall in conductivity.

More quantitative data from ESCA measurements are given in *Table 1*. After different ageing times the surfaces of the samples were analysed by ESCA. The concentrations of O and C in *Table 1* (atomic per cent normalized to 100%) were calculated from the areas of the O_{1s} and C_{1s} photoelectron peaks with relative sensitivity factors*. As expected from the analytical results in *Figure 1*, the oxygen content increases with exposure time. The distinctly higher values compared with *Figure 1* can be understood by allowing for the fact that ESCA analyses only a small surface layer of about 50 Å in thickness whereas elemental analysis gives an averaged value for the bulk material. It is clear that reactions with oxygen start at the surface and proceed from there to the interior of the polymer film†. The results of the lineshape analysis of the C_{1s} lines (*Table 1*) demonstrate further that the content of carbonyl and ester groups increases faster than that of the ether group. The reaction mechanisms are not completely understood. In addition to oxygen light can play a role during degradation as the samples were not kept in the dark.

Modification by chlorosulphonyl isocyanate

The reaction of chlorosulphonyl isocyanate with $(CH)_x$ leads to a product having quite high conductivity which does not change significantly during the first day of exposure to air. Because of the low degree of modification of the $(CH)_x$, which lies around 1 mol% related to carbon, it is difficult to determine the exact composition of the reaction product. From the relatively high conductivity it can be concluded, however, that during the modification some kind of oxidation occurs. One could imagine that as a result of the decomposition of the chlorosulphonyl isocyanate chlorine is formed which acts as an oxidizing agent for the polyacetylene. The conductivity increases by about four decades compared with undoped polyacetylene. As can be concluded from *Figure 1*, the conductivity decreases only slightly during exposure to air for one day. After that time a decay of conductivity similar to the unmodified sample is observed. The higher stability of the modified polyacetylene film is reflected in a distinctly lower oxygen uptake (*Figure 1*).

Temperature dependence of ageing

The conductivity of polyacetylene changes faster the higher the ageing temperature applied, as shown in *Figure 3*. The shape of the curves does not seem to be influenced by temperature, as is clearly demonstrated in *Figure 4*. In the double logarithmic plot of conductivity versus time a so-called master curve is obtained by shifting the curves measured at different temperatures along the time and conductivity axis. *Figure 4* shows that master-curves can be drawn for both the unmodified and the modified polyacetylene with high accuracy. Two shift factors can

Table 1 Oxygen content and carbon in various functional groups in a polyacetylene film exposed to air for different periods of time. Measurements by ESCA

	Concentration (atom %)		Quantification of carbon in functional groups			
Ageing time (d)	O	C	$-\overset{\overset{O}{\|}}{C}-O-$	$-\overset{\overset{O}{\|}}{C}-$	$-\underset{\vert}{\overset{\vert}{C}}-O-$	$(CH)_x$
0	8.7	91.3	2.7	5.7	12.0	71.0
1	15.8	84.2	2.5	6.3	16.2	59.3
4	22.1	77.9	3.4	8.9	18.1	47.6
8	25.0	75.0	4.0	10.7	18.7	41.7
15	27.6	72.4	5.6	14.1	16.9	35.7
22	28.8	71.2	5.6	14.8	18.4	32.4

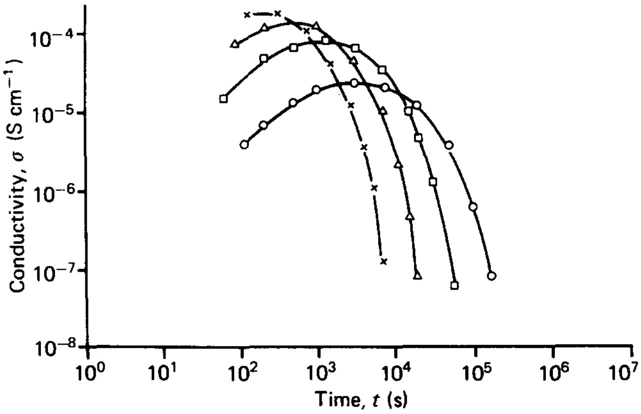

Figure 3 Conductivity of a polyacetylene film of 'Shirakawa' type[3] as a function of the time of exposure to air at different temperatures: ○, 40°C; □, 60°C; △, 80°C; ×, 100°C. Thickness: 50 μm

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* The slight deviations of the values from those in *Figure 2* are due to the fact that two different samples were investigated

† The fact that the freshly synthesized sample already contains some oxygen-carbon components points to some kind of contact with air during the synthesis and handling processes

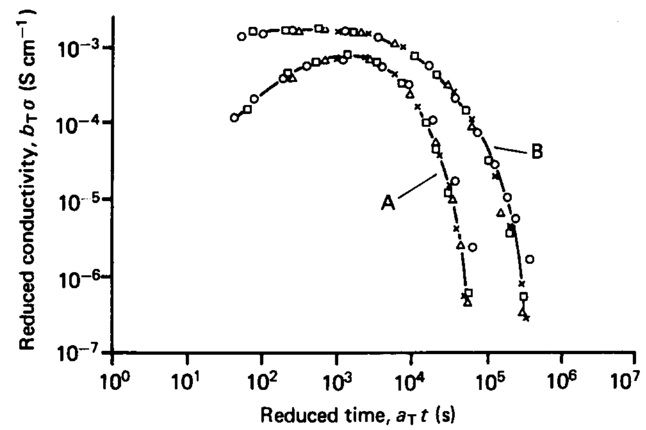

Figure 4 Master curves representing the time dependence of the conductivity change of two polyacetylene films. Symbols as in *Figure 3*. A, Polyacetylene of 'Shirakawa' type[3]; B, polyacetylene modified with $ClSO_2NCO$. $a_T(T)$ and $b_T(T)$ are the shift factors. The reference temperature is 60°C, i.e. a_T (60°C) = 1 and b_T (60°C) = 1

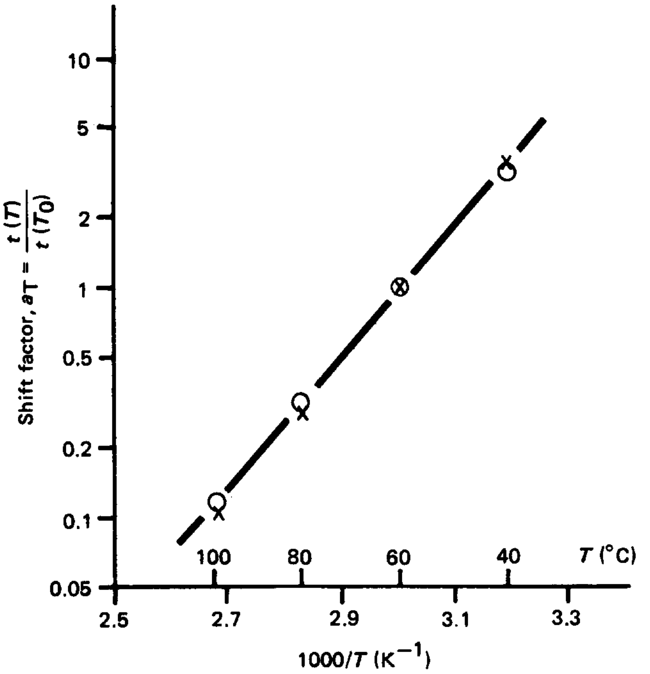

Figure 5 Time–temperature shift factor a_T as a function of the reciprocal temperature $1/T$ for the polyacetylene of 'Shirakawa' type (○) and the polyacetylene modified with $ClSO_2NCO$ (×) (see *Figure 4*)

be defined from the shift procedure. The factor a_T is obtained by shifting the curves along the t-axis, the factor b_T relates to a shift along the σ-axis. The physical meaning behind the existence of a master curve is that the influence of temperature on the conductivity–time behaviour can be expressed by a simple expression:

$$\sigma(T,t) = b_T(T)\sigma[T_0, a_T(T)t(T_0)] \quad (1)$$

where

$$a_T(T) = t(T)/t(T_0) \quad (2)$$

In particular, $a_T(T)$ describes the temperature dependence of ageing and $b_T(T)$ the temperature dependence of the conductivity.

A more quantitative evaluation of these correlations is given in *Figure 5* and *Figure 6*, in which a_T and b_T are plotted semilogarithmically as functions of the reciprocal absolute temperature, $1/T$, for the two polyacetylene samples. From *Figure 5* it can be concluded that at least in the temperature range between 40 and 100°C the temperature dependence of ageing can be described by an Arrhenius equation of the form:

$$a_T = \exp\frac{U}{R}(1/T - 1/T_0) \quad (3)$$

T_0 is the reference temperature and T is the actual temperature, R is the universal gas constant and the activation energy U follows as $U = 55\,\mathrm{kJ\,mol^{-1}}$.

The experimentally determined shift factors for the two polyacetylenes lie on the same straight line, within the accuracy of the measurements. This result means that the time dependence of ageing is the same. Modification of polyacetylene with chlorosulphonyl isocyanate has no effect on the temperature dependence of ageing between 40 and 100°C.

It can be concluded from *Figure 6* that only the temperature dependence of the conductivity of the modified polyacetylene can be described by an Arrhenius equation in the measured temperature range, between 40 and 100°C. In the case of unmodified polyacetylene the value measured at 40°C does not lie on the straight line. The reason for this deviation is not known, but it should be taken into account that only one measurement at this temperature was performed. Other authors have found that the temperature dependence of conductivity follows the so-called $T^{-1/4}$ law. Our findings do not contradict these results because they relate to a small temperature range where Arrhenius behaviour can be regarded as a good approximation.

Following the notation used in semiconductor physics, the corresponding Arrhenius equation can be written as:

$$b_T = \exp E_g/2k(1/T_0 - 1/T) \quad (4)$$

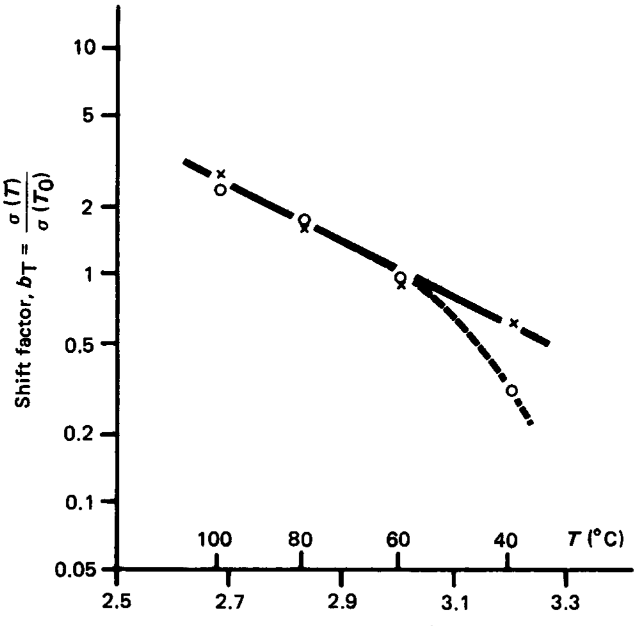

Figure 6 Time–conductivity shift factor b_T as a function of the reciprocal temperature $1/T$ for the polyacetylene of 'Shirakawa' type (○) and the polyacetylene modified with $ClSO_2NCO$ (×) (see *Figure 4*)

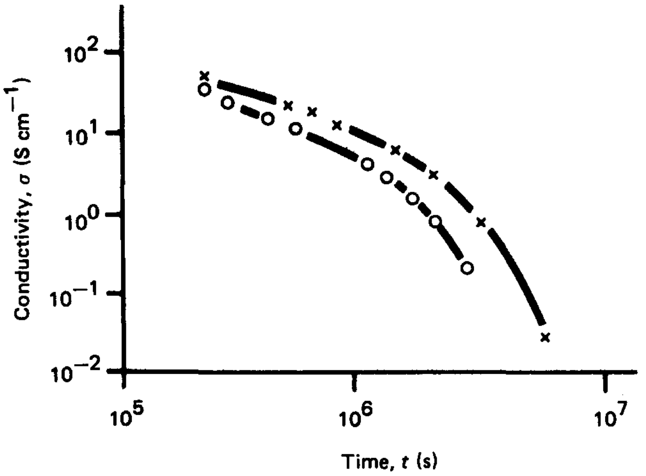

Figure 7 Conductivity change of the polyacetylene of 'Shirakawa' type (○) and the polyacetylene modified with $ClSO_2NCO$ (×) in air. Both samples were oxidized by an exposure to iodine vapour at room temperature for 24 h

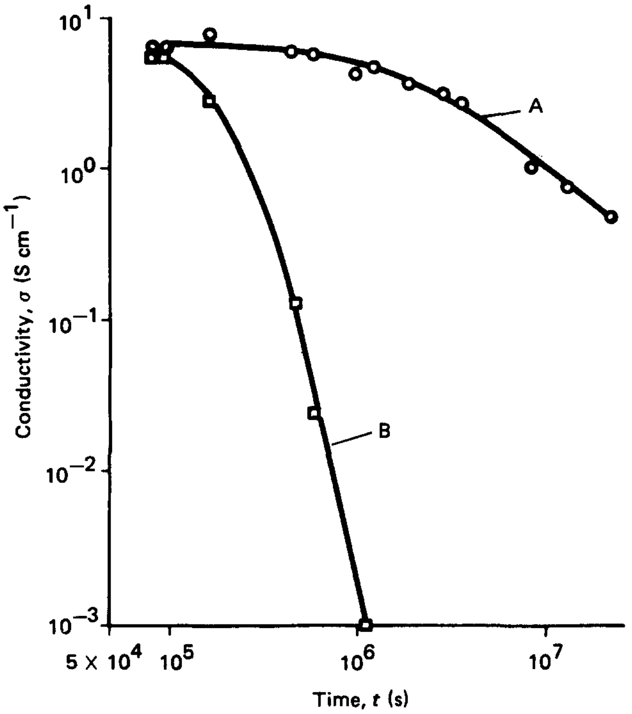

Figure 8 Conductivity change of $[(CH^{+0.06}(BF_4^-)_{0.06}]_x$. Electrochemical oxidation of 'Shirakawa' type polyacetylene in propylenecarbonate/$LiBF_4$ as electrolyte. A, Exposure to argon; B, exposure to air. Ambient temperature

T_0 is the reference temperature, T the actual temperature and k is the Boltzmann constant. The band energy E_g for the modified polyacetylene follows from *Figure 6* as $E_g = 0.5$ eV. This value is smaller than the band width of 1.5 eV found from optical investigations for unmodified polyacetylene. The explanation of these differences lies in the fact that we are dealing with a material already oxidized to some extent by the previous chemical treatment which leads to a significant increase in conductivity. The creation of intermediate states connected with the conductivity increase lowers the activation energy (see above).

Ageing in the highly oxidized state

It is well known that the conductivity of polyacetylene can be increased by oxidation far beyond the values given in *Figure 1*. This oxidation step can be carried out chemically or electrochemically. *Figure 7* gives the conductivities of unmodified and modified polyacetylenes after exposure to an iodine atmosphere for 24 h. The conductivities achieved by this chemical treatment are very similar for both samples, but the conductivities decrease rapidly if the two polyacetylenes are exposed to air. As can be seen from *Figure 7* the modification has no effect on stability.

Figure 8 presents results of conductivity measurements on an electrochemically oxidized polyacetylene of composition $[(CH)^{+0.06}(BF_4^-)_{0.06}]_x$. In air the conductivity drops in a very similar way to the sample chemically oxidized by iodine (cf. *Figure 7*). Curve A of *Figure 8* shows that even in an argon atmosphere a significant decrease of conductivity occurs. This result indicates that as well as reactions between polyacetylene and species like oxygen and water present in air an additional shortening of the conjugation length occurs by reactions with degradation products of BF_4^-, for example HF.

POLYPYRROLE

Temperature dependence of ageing

Electrically conducting polypyrrole has attracted much interest recently because of its superior stability to that of polyacetylene[5], as is clear from a comparison of *Figures 3* and *9*. Whereas the conductivity of polyacetylene drops by a factor of two in less than one hour at 80°C, the same conductivity decrease takes about one week in the case of the polypyrrole film, the performance of which is shown in *Figure 9*. Qualitatively the same feature is observed at 100°C.

Similarly to polyacetylene, polypyrrole undergoes a

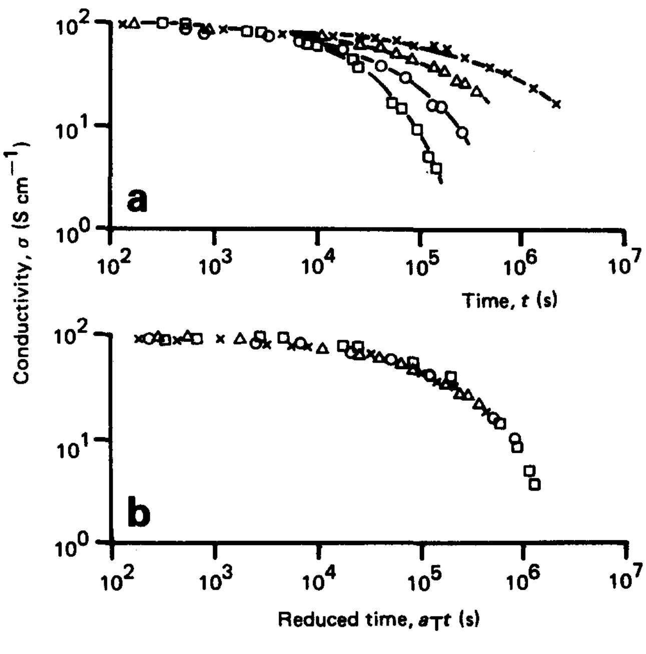

Figure 9 (a) Conductivity change of a polypyrrole phenylsulphonate under air at different temperatures: ×, 80°C; △, 100°C; ○, 120°C; □, 140°C. (b) Master curve related to a reference temperature of 100°C. Film thickness: 60 μm

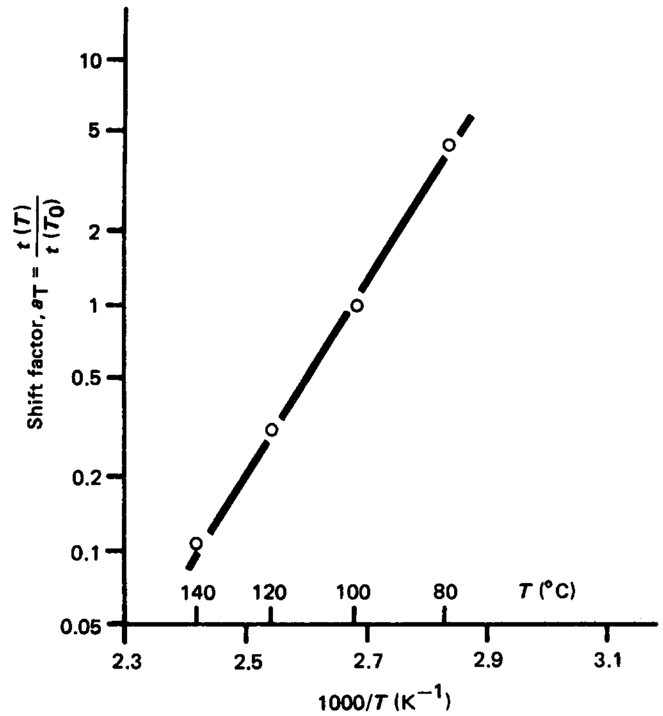

Figure 10 Time–temperature shift factor a_T as a function of the reciprocal temperature $1/T$ for the conductivity change of the polypyrrole phenylsulphonate film represented in *Figure 9*

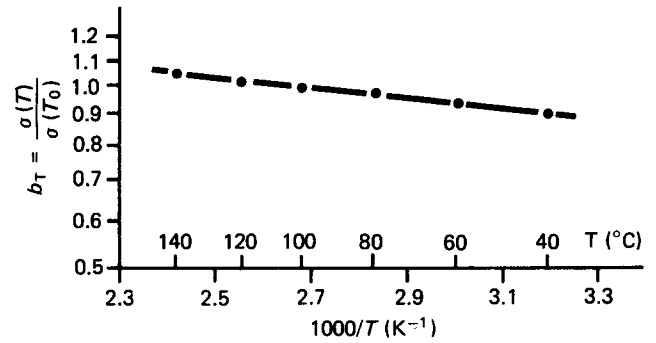

Figure 11 Temperature dependence of the conductivity of the polypyrrole phenylsulphonate film of *Figure 9*. $b_T = 1$ for $T_0 = 100$°C

thermally activated ageing process, resulting in a decrease of the conductivity. The temperature dependence of ageing can quantitatively be described because of the experimental finding demonstrated in *Figure 9b* that a master curve can be obtained by shifting the measured curves along the time-axis.

The shift factor $a_T(T)$ as defined by equation (2) is plotted in *Figure 10* semilogarithmically as a function of the reciprocal absolute temperature. The four points lie on a straight line, which means that the temperature dependence of the shift factor follows an Arrhenius equation analogous to equation (3). *Figure 10* gives a calculated activation energy of 70 kJ mol^{-1}, which is in good agreement with ageing experiments reported by other authors[6].

Temperature dependence of conductivity

The temperature dependence of the conductivity of polypyrrole is so weak that it is not reflected by the logarithmic plot of *Figure 9*. The measured values are plotted semilogarithmically in *Figure 11* as a function of the absolute reciprocal temperature. The conductivity increases with temperature, as is typical of semiconducting materials. The measured points can be approximated by a straight line, indicating that the temperature dependence of the conductivity can be described by equation (4), at least in the temperature range investigated.

The band energy is calculated as $E_g = 0.04$ eV, which is markedly lower than that measured for polyacetylene (see above). The difference can easily be understood taking into account the model of energy bands frequently used in solid state physics. According to this picture, intermediate states are created within the band gap by the oxidation of carbon atoms. The activation energy needed for the carriers to jump from the intermediate states into the conduction band is significantly lower than the band gap. Therefore, a smaller activation energy can be expected for the highly oxidized polypyrrole compared to the tested polyacetylene with a much lower degree of oxidation.

Influence of humidity on ageing

Besides heat, humidity has a considerable influence on the stability of the conductivity of polypyrrole salts, as can be seen from *Figure 12*, which plots the conductivity, σ, related to the initial conductivity, σ_0, as a function of ageing time. At 80% humidity and 80°C both samples show a faster decrease in conductivity than at 5% humidity. The degree of sensitivity to humidity is dependent on the anion of the polypyrrole salt. The difference in stability between low and high humidity is more pronounced for the polypyrrole perchlorate than for the polypyrrole phenylsulphonate salt. It should be mentioned, however, that the thickness of the films are different. The polypyrrole perchlorate film is thinner, so

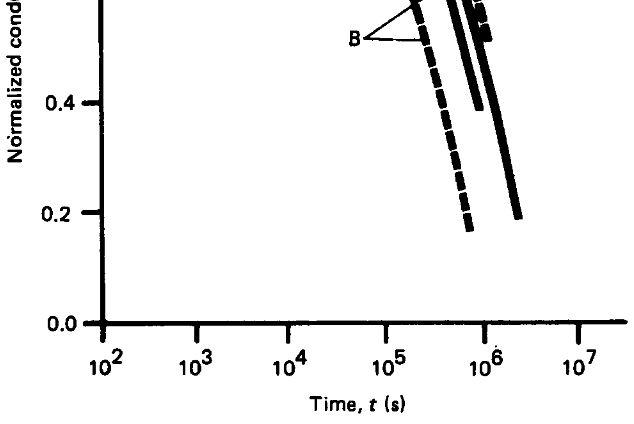

Figure 12 Conductivity changes of polypyrrole phenylsulphonate (——) and polypyrrole perchlorate (– – –) films at 80°C and different degrees of humidity. Thickness: 90 μm for the polypyrrole phenylsulphonate and 50 μm for the polypyrrole perchlorate film. A, 5% r.h.; B, 80% r.h.

Table 2 Comparison of the ageing of two polypyrrole salt films under air and argon

Sample	Ageing at 80°C in	σ_0 ($S cm^{-1}$)	σ/σ_0 4d	10d	100d	200d
Polypyrrole	Air	140	0.7	0.5	0.05	–
phenylsulphonate	Argon	105	1.0	1.0	1.0	1.0
Polypyrrole	Air	34	0.8	0.6	–	–
perchlorate	Argon	43	1.0	1.0	1.0	1.0

that a shorter time is expected for water as the diffusing species to penetrate the entire sample. Despite this fact the polypyrrole perchlorate film is rather more stable at low humidity than the polypyrrole phenylsulphonate film, suggesting that a specific reaction between the perchlorate ion and water may be an essential reason for the decay in conductivity.

Due to the structural and chemical 'impurity' of the polypyrrole salts investigated, direct confirmation of reactions occurring within the samples by exposing them to air could not be obtained. Neither elemental analysis nor physical methods, like infra-red spectroscopy and electron spectroscopy for chemical analysis (ESCA), gave an insight into the origin of ageing in the case of the polypyrroles investigated. This finding on polypyrroles is in contrast to polyacetylene, for which it could be demonstrated by elemental analysis and ESCA that covalent bonds between oxygen and carbon atoms occur during exposure to air (see above).

Stability under inert conditions

Some insight into the rôle of oxygen and humidity with respect to ageing of polypyrrole is given by the findings presented in *Table 2*. Two different polypyrrole salts were aged at 80°C under an argon atmosphere with oxygen and water contents <1 ppm. No change in conductivity was observed in the samples during up to 200 days, although the conductivity of the films exposed to air had decreased significantly over the same period.

These results demonstrate that at 80°C, and at all temperatures below this value, the conductivity of polypyrrole salts remains stable if oxygen and water are not allowed to reach the samples. Furthermore, these findings indicate that internal reactions within the polypyrrole salts which change the conductivity do not exist or are extremely slow. In this aspect the polypyrrole salts investigated differ favourably from polyacetylene salts, whose conductivities decrease even under inert conditions (cf. *Figure 8*).

Influence of oxidation level on stability

The stability of the conductivity of polypyrrole is influenced markedly by the oxidation level, as shown by the results in *Figure 13*. Fully oxidized polypyrrole perchlorate films have electrochemically been reduced down to various oxidation levels. As one consequence of this procedure the conductivity becomes smaller. Due to a reduction by 5.3 mol% related to the carbon and nitrogen content of polypyrrole the conductivity drops by nearly nine decades. At this reduction level a small amount of perchlorate is still to be expected within the sample, whose maximum degree of oxidation reaches 6 mol%, according to the results of elemental analysis.

The conductivity as well as its stability is distinctly influenced by the oxidation level. The more perchlorate ions are removed from the sample the worse becomes the stability of conductivity in air. The polypyrrole film with the lowest remaining degree of oxidation shows a similar conductivity–time behaviour to that of freshly polymerized polyacetylene. Upon exposure to air the conductivity increases up to a maximum and then falls without reaching a plateau value within the time of observation.

In analogy to polyacetylene, the conductivity increase of polypyrrole can be related to an oxidation by oxygen from the air. During the course of the oxidation process, reactions take place between polypyrrole and oxygen which result in a decrease of conductivity. These findings indicate that the counterion has a stabilizing effect on the conductivity of polypyrrole which is much more pronounced than in the case of oxidized polyacetylenes (cf. *Figures 7* and *8*).

OTHER ORGANIC MATERIALS

In the foregoing sections it has been demonstrated by a great number of experiments that neither polyacetylene nor polypyrrole salts possess a stable electrical conductivity if they are exposed to oxygen and moisture.

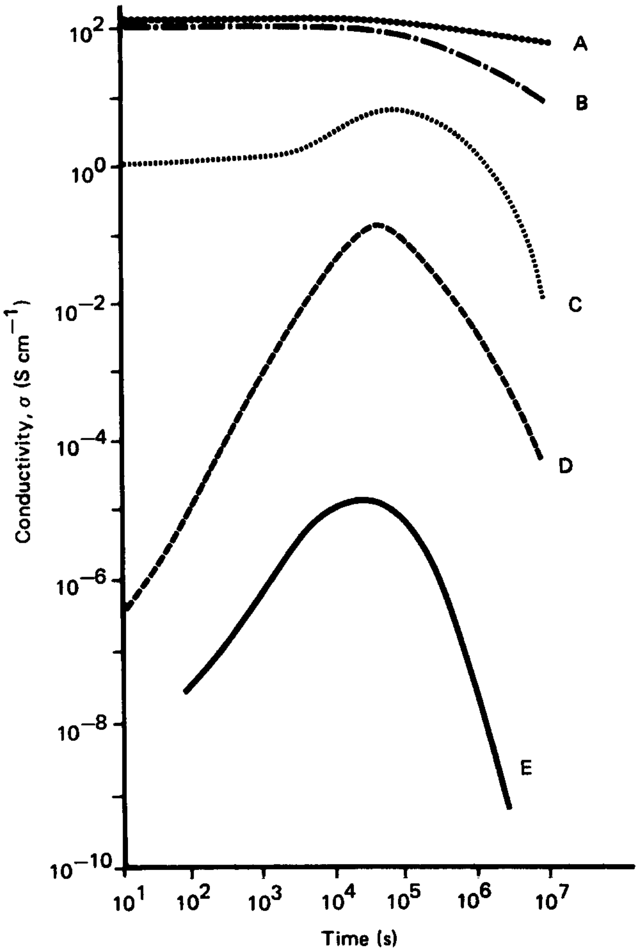

Figure 13 Conductivity change of polypyrrole perchlorate films of different oxidation levels under ambient conditions. Curve of $(CH)_x$ is plotted for comparison. A, as polymerized; B, 2 mol% reduction related to C and N; C, 4 mol% reduction; D, 5.3 mol% reduction; E, $(CH)_x$ as polymerized

Table 3 Conductivity and its stability of various organic materials under air. $t_{1/2}$ describes the time after which the conductivity has fallen to half of its initial value σ_0. The conductivities of the powders were measured at a pressure of 2500 bar

Material	σ_0 (S cm^{-1})	d (μm)	$t_{1/2}$ (h)	Conditions of ageing
PPy^{+y} $(\phi SO_3^-)_y$ (film)	90	90	300	$T = 80$°C; 50% r.h.
PPy^{+y} $(\phi SO_3^-)_y$ (powder)	1.8	~1	24	$T = 80$°C
PTh^{+y} $(BF_4^-)_y$ (film)	11	85	9	$T = 80$°C
$PANI^{+y}$ $(BF_4^-)_y$ (powder)	1.6×10^{-3}	~1	480	$T = 23$°C
TTF^{+y} $(TCNQ^-)_y$ (film) in polypropylene	1.9×10^{-2}	30	240	$T = 80$°C; 50% r.h.
Carbon black	40	–	>2400	$T = 80$°C; 100% r.h.
Carbon fibre	600	7	>2400	$T = 80$°C; 80% r.h.

A question of fundamental interest is whether there exist organic materials with a relatively high conductivity in the oxidized state whose stability is comparable to that of metallic conductors.

Table 3 gives the results of stability measurements on various materials. As well as the initial conductivity, σ_0, and the thickness, d, of the films, or the particle diameter in the case of powders, the table gives $t_{1/2}$, the time taken for the conductivity to fall to one-half of its initial value, as a measure of stability. Because of the differences in ageing experiments the conditions are listed in the last column of the table. In the cases where a value for humidity is not given the ageing was performed under laboratory air. For these conditions it can only qualitatively be said that the humidity at 80°C was much lower than at room temperature.

Several conclusions can be drawn from the results of *Table 3*. The conductivity of a polypyrrole phenylsulphonate film is more stable than that of powder. This may be due to the smaller dimensions and, following from that, to the larger surface area of the particles in relation to the film thickness, which facilitates diffusion processes of oxygen and water. The BF_4^- salts of polythiophene ($PTh^{+y}(BF_4^-)_y$) and polyaniline ($PANI^{+y}(BF_4^-)_y$) do not exhibit an overwhelmingly good stability. The stability of the conductivity of the $PTh^{+y}(BF_4^-)_y$ film is significantly lower than that of the polypyrrole phenylsulphonate film. A direct comparison of the $PANI^{+y}(BF_4^-)_y$ and the polypyrrole phenylsulphonate powders is not possible because of the different ageing temperatures. It is not encouraging that the conductivity decreases by a factor of two during 20 days at room temperature with respect to application of the polyaniline salt. $TTF^{+y}(TCNQ^-)_y$ dispersed in polypropylene does not show a stable conductivity either*. Carbon black and carbon fibres, which are highly conducting materials in their neutral state, did not show any indication of a loss in conductivity at 80°C and high humidity over the investigated period of 100 days.

DISCUSSION

The results reported here lead us to the assumption that carbenium ion-structures necessary for making organic carbon–hydrogen compounds into conducting materials are principally reactive with respect to oxygen and water. Covalent bonds are probably formed that shorten the conjugation length, resulting in a decrease of conductivity.

If this assumption turns out to be correct there will be no chemical means to obtain conducting polymers on the basis of organic salts which are stable in air. Taking this into account one needs to look for organic compounds which become conductive without oxidation simply by narrowing the gap between the valence band and the conduction band to such an extent that the thermal energy will be sufficient to create a carrier density high enough to obtain significant conductivity.

The conducting polymers known up to now have not been able to match the electrical behaviour of carbon black and carbon fibres, particularly from the point of view of stability. However, the latter lack properties typical of many polymers such as flexibility and variable shaping. In film making, for example, carbon black and carbon fibres have to be blended with another material. This necessity often results in a compromise with respect to the properties of the matrix material and the carbon based fillers.

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* The sample provided by Professor Kryszewski was produced according to ref. 7