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Influence of $FeCl_3$ dopant on the electrical conductivity of pyrolysed aromatic polymers

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$FeCl_3$ is used as a dopant of organic semiconductors which have polyconjugated structures (e.g. polyacetylene, polyphenylene), as well as for the intercalation of graphite. Semiconducting polymers can be also synthesized by the pyrolytic conversion of organic polymers. The influence of $FeCl_3$ as a dopant for pyrolysed aromatic polymers at different pyrolysis temperatures up to 1000 °C on their electrical conductivity, σ, has been investigated. In the materials poly-*p*-phenylene, *o, m, p*-polyphenylenes, novolac resin cured with hexamethylenetetramine, biomass of olive stones, lignin Kraft isolated from this biomass, three regions can be distinguished. The electrical conductivity is low up to 500 °C, between 500 and 700 °C it increases greatly, and above 700 °C it increases at a lower rate. For *o, m, p*-polyphenylenes, these regions (especially the first and the second) cannot be distinguished. Similar curves are generally obtained after doping of the pyrolysed materials. The ratio of the electrical conductivity of doped, σ to undoped, σ_0, pyrolysed materials increases mainly between 500 and 700 °C with the exception of *o, m, p*-polyphenylenes, where the electrical conductivity decreases at all of the pyrolysis temperatures. The electrical conductivity of the materials is more strongly influenced by heating than by doping. The results are interpreted based on the structure of the materials using X-ray diffractograms, weight losses during the pyrolysis, and taking into consideration the reactions occurring during pyrolysis. $FeCl_3$ is an effective dopant for organic semiconductors affected by charge transfer, but a less effective dopant for pyrolysed polymers and which do not lead to intercalation because of the low order and extension of the carbon layer formed in comparison to graphite.

1. Introduction

Electroconducting polymers are prepared mainly from polymers which have polyconjugated structures (e.g. polyacetylene, polyphenylene) for which electrons must be withdrawn or additional electrons must be given, i.e. by oxidation or reduction. This effect is called "doping", "intercalation" or "complex formation". As dopant acceptors, ions such as AsF_6^-, I_3^-, $FeCl_4^-$, etc., and donors such as alkali metals, are used [1].

Another approach to prepare electroconducting polymers is by pyrolytic conversion. During the pyrolysis of different precursor polymers such as poly(vinylidene chloride), polyacrylonitrile, polyphenylenes, etc., a progressive increase in conjugation and thus π-orbital delocalization, takes place. Consequently, the development of planar, polycondensed rings, and the electrical conductivity within the carbonaceous mass, are increased [2–5].

The general meaning of intercalation compounds is compounds in which "foreign" atoms or molecules have slipped between the layers of a pre-existing compound without completely disrupting the structure of the original compound. Such intercalated compounds can be used in several applications such as superconductors, catalysts, high-energy-density storage materials for batteries, synthetic metals, membranes and lubricants. The most important class of intercalated materials are the graphite compounds [6–8]. The intercalation in carbons is performed mainly to the natural graphite and secondly to synthetic graphites. Graphite has a typical layer structure with weak van der Waals forces between layers, so that other atoms or molecules can be intercalated between them. The soft or graphitizable carbons obtained by liquid-phase pyrolysis (pitch, petroleum, etc.), as well as pyrocarbons obtained by pyrolysis of a gaseous phase, show good organization and they can intercalate with numerous reagents [6]. The structural faults and the textural disorientation hinder intercalation by a mechanical effect. This effect is notable in the hard or non-graphitizable carbons, obtained by pyrolysis in

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the solid phase of organic compounds (glassy carbons, polyvinylidene cokes, etc.) where only a small number of reagents can intercalate in them. Among the hard carbons, fibres can intercalate better because of their oriented texture [2, 6]. $FeCl_3$, used alone or in molten salts, etc., is a common reagent for graphite intercalation compounds (GICs). The electrical conductivity of the intercalated graphite is increased depending on the concentration of the intercalated $FeCl_3$, the form of graphite used, etc. [6, 9–13].

$FeCl_3$ is often used as a dopant for various polymers and copolymers [14–16]. The electrical conductivity of semiconducting organic polymers, such as polyphenylenes, doped with $FeCl_3$, is increased by five or more orders compared to the undoped state [1, 5, 17, 18]. In pyrolysed polyphenylenes, is the electrical conductivity greatly increased, by more than six orders, at pyrolysis temperatures between ~600 and 800 °C [19]. The electrical conductivity of pyrolysed polyphenylenes which were doped with $FeCl_3$ is increased compared to the undoped pyrolysed polyphenylenes up to 700 °C. However, for polyphenylenes pyrolysed at 800 °C and doped polyphenylenes, is it decreased compared to the corresponding undoped material [5]. The aim of the present work was to investigate the influence of $FeCl_3$ dopant in pyrolysed aromatic polymers at different pyrolysis temperatures on their electrical conductivities. The doping technique at high temperatures (e.g. at 300 °C), which is commonly used for the intercalation of carbonaceous materials, has been chosen instead of doping from solution which is often used for the doping of typical organic polymers.

2. Experimental procedure

Different polymeric materials were used. Poly-*p*-phenylene (PPP) and *o*, *m*, *p*-polyphenylenes were prepared according to the Kovacic method by oxidation–cationic polymerization of benzene or biphenyl, respectively [20–22]. The molar proportions of biphenyl:$CuCl_2$:$AlCl_3$ = 1:3:1.5 for the synthesis of polymer 8A was used. In this case, the insoluble fraction of the polymer in chlorobenzene was used. Novolac resin was prepared by polymerization of phenol formaldehyde by acidic catalysis, which was then cured with hexamethylenetetramine (HTA) [23]. Olive stone biomass, a residue of industrial processes after the removal of oil by pressing and extraction, was also used. Lignin was isolated from this biomass according to the Kraft method [24, 25], which is based on the alkaline hydrolysis of weak ether bonds with NaOH and Na_2S in an autoclave at about 180 °C, 9 atm for 1.5 h and the precipitation with a solution of H_2SO_4. Commercial graphite from Fluka AG was used for correlation purposes.

The polymers prepared were pyrolysed at different temperatures and the weight losses were determined by weighing the samples before and after pyrolysis. All of the pyrolysed and non-pyrolysed materials were also doped with $FeCl_3$ (mixture of material: $FeCl_3$ = 1:3 wt/wt) under a pressure of about 6 Pa and heated at 300 °C for 3 h. The product was washed off the unreacted ferric chloride and then dried at 130 °C [26].

The electrical conductivity, σ, of materials formed into tablets was measured at room temperature using a d.c. current by the four-point method. X-ray diffraction measurements of powdered materials were carried out using CuK_α radiation.

3. Results

Table I shows the materials used and the electrical conductivity of doped materials in relation to the corresponding undoped ones. The results of the electrical conductivity tests will be discussed below.

Fig. 1 shows the weight losses of the materials during their pyrolysis up to 1000 °C. PPP show the lowest weight losses in the whole pyrolysis region. The weight losses of Novo. are low at 500 °C and then are progressively increased. The 8A (*o*, *m*, *p*-polyphenylenes) show higher weight losses at 500 °C while above 700 °C the weight losses are very slightly increased. The other materials (Biom. and Lign.) show high weight losses especially at 500 °C, as well as above 700 °C for Lign.

Fig. 2 shows the electrical conductivity of the pyrolysed materials. For most of the materials (PPP, Novo., Biom., Lign.), three regions can be distinguished.

TABLE I Description of materials used and the ratio of the electrical conductivity of doped, σ, to undoped, σ_0, material at different temperatures

No.	Abbreviation[a]	Description of material	σ/σ_0			
			300 °C	500 °C	700 °C	1000 °C
1	Graphite	Graphite (Fluka AG)	1.84			
2	Novo.	Novolac cured	1.08	15.7	1.09	1.81
3	PPP	Poly-*p*-phenylene	1.10	1.0	1.39	0.36
4	8A	*o*, *m*, *p*-polyphenylenes	1.00	0.75	0.05	0.63
5	Biom.	Olive stones biomass (pressed and extracted)	1.00	1.33	2.40	1.74
6	Lign.	Lignine Kraft (isolated from no. 6)	1.12	1.15	1.19	0.72

[a] In addition, UD and D indicate undoped and doped material, respectively.

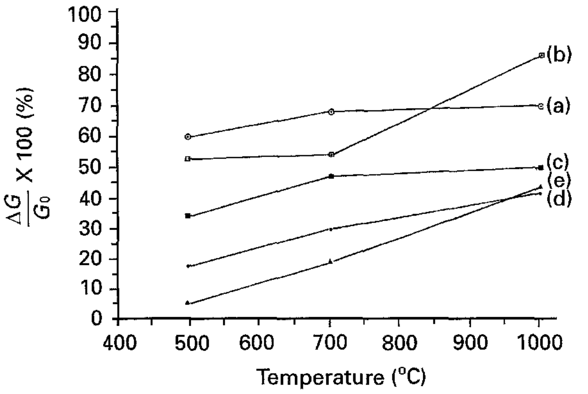

Figure 1 Weight losses of materials during pyrolysis: (a) Biom., (b) Lign., (c) 8A, (d) Novo., (e) PPP (see Table I).

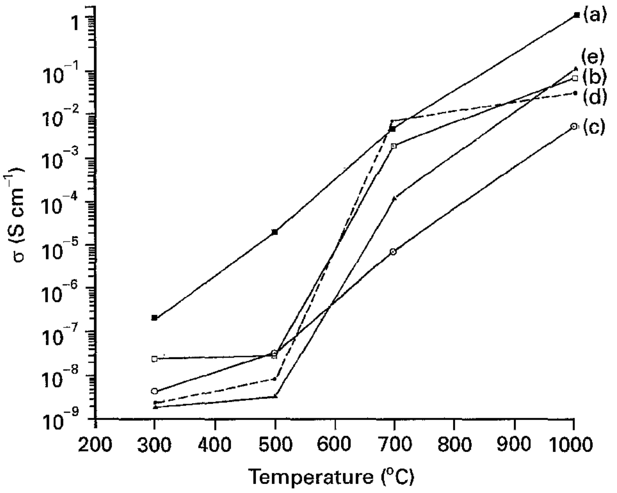

Figure 2 Electrical conductivity, σ, of undoped materials at different pyrolysis temperatures: (a) 8A, (b) Lign., (c) Biom., (d) Novo., (e) PPP (see Table I).

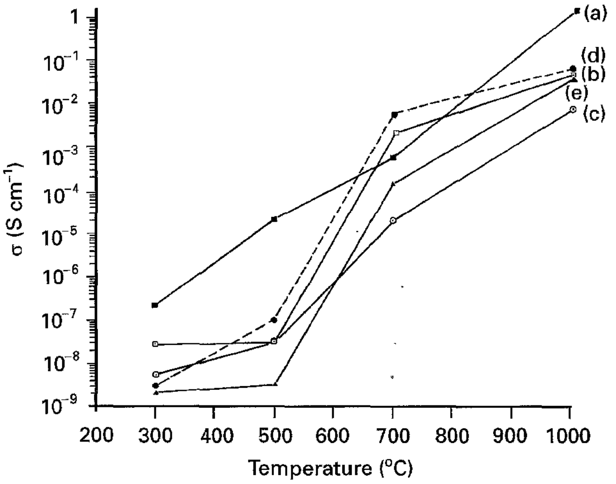

Figure 3 Electrical conductivity, σ, of doped materials at different pyrolysis temperatures: (a) 8A, (b) Lign., (c) Biom., (d) Novo., (e) PPP (see Table I).

Up to 500 °C, the electrical conductivity is low, between 500 and 700 °C it is greatly increased and above 700 °C it increases at a lower rate. For *o*, *m*, *p*-polyphenylenes (8A) these regions (especially the first and second) cannot be distinguished.

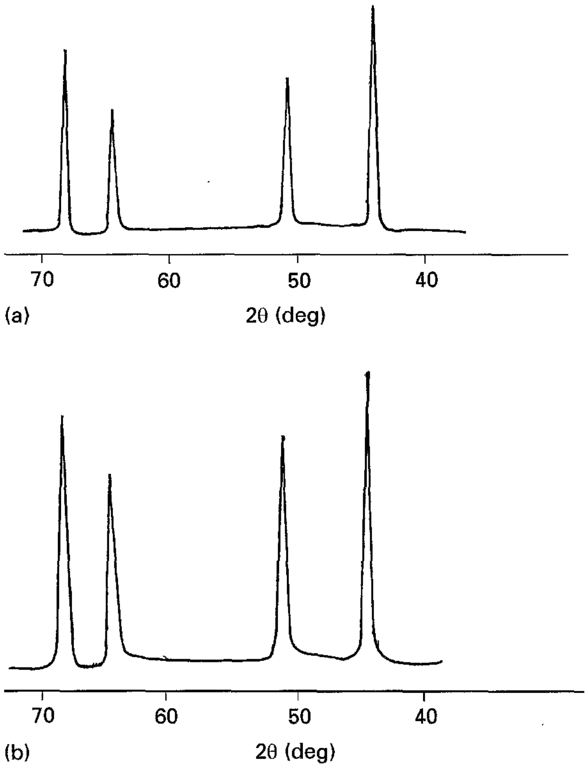

Figure 4 X-ray diffractograms of undoped 8A-UD at (a) 700 °C, and (b) 1000 °C.

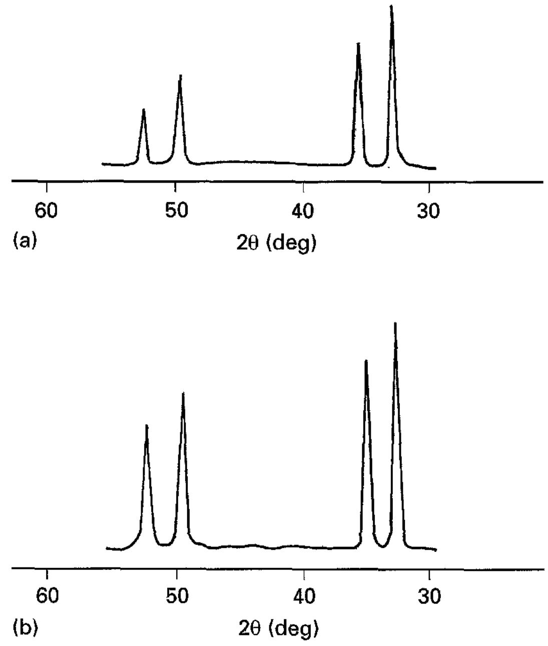

Figure 5 X-ray diffractograms of doped 8A-D at (a) 700 °C, and (b) 1000 °C.

The electrical conductivity of pyrolysed and doped materials are shown in Fig. 3. The curves in this figure and the corresponding curves in Fig. 2 show some similarities. The ratio of the electrical conductivity of doped, σ, to undoped, σ_0, materials which have been pyrolysed at different temperatures is summarized in Table I. The ratio of σ/σ_0 for graphite is increased, which is an indication that intercalation is achieved. The ratio of σ/σ_0 for the other materials at 300 °C is equal to 1.0 or it is very slightly increased. For all

TABLE II Evaluation of crystallographic data for materials pyrolysed at 700 or 1000 °C before or after doping

	Undoped, UD				Doped, D			
	Interferences				Interferences			
	Angle 2θ (deg)	d^a (nm)	I^b	L^c (nm)	Angle 2θ (deg)	d^a (nm)	I^b	L^c (nm)
Graphite	26.3	0.338	vs	9.0	26.6	0.335	vs	28.0
	32.0	0.282	w		43.8	0.206	s	
	45.1	0.201	w		50.7	0.179	w	
	48.6	0.187	vw					
8A (700, 1000 °C)	43.4	0.208	vs	19.0	33.2	0.270	vs	30.7
	50.6	0.180	s		35.7	0.251	vs	
	64.3	0.145	s		49.6	0.184	s	
	67.9	0.138	vs		53.0	0.173	s	
Biom. (1000 °C)	22.0	0.404	w		24.0	0.371	w	
	39.0	0.231	w		34.0	0.264	vs	28.0
	45.0	0.201	vs	4.8	36.0	0.249	s	
					41.0	0.220	w	
					50.0	0.182	w	
					54.0	0.170	w	
					63.0	0.148	vw	
					64.0	0.145	vw	
					72.0	0.131	vw	

[a] Interplanar spacing.
[b] Intensity: vs, very strong; s, strong; w, weak; vw, very weak.
[c] Mean crystallite size (calculated at maximum interference).

materials, except *o*, *m*, *p*-polyphenylenes (8A), the ratio is increased between 500 and 700 °C. The ratio is decreased at 1000 °C not only for the *o*, *m*, *p*-polyphenylenes but also for PPP and Lign. It is also obvious that heating more strongly influences the electrical conductivity of the materials than their doping.

Structural changes during the pyrolysis or doping of the materials were followed by X-ray analysis. Figs 4 and 5 show X-ray diffractograms of 8A pyrolysed residues at 700 or 1000 °C in the undoped and doped state, respectively. The diffractograms of the undoped 8A at 700 °C and that at 1000 °C are similar in the position of the interferences, their number and their relative intensities. The diffractogram of doped 8A at 700 °C is similar to that at 1000 °C. The undoped and doped 8A show different diffractograms due to the influence of $FeCl_3$. The interplanar spacing, *d*, was determined for the corresponding angle 2θ, and the mean crystallite size, *L*, was calculated from the maximum interference according to the Scherrer equation [27], and all are presented in Table II. The materials which are not presented in this table are amorphous.

4. Discussion

It is obvious from Table II that the structure of all pyrolysed materials at 700 and 1000 °C differs greatly from the structure of graphite. This is expected, because the pyrolysis takes place in the solid phase and the residues have not been annealed at higher temperatures (e.g. 2800 °C), as occurs in the case of graphitizable materials. The structure of pyrolysed materials is changed after the doping. The mean crystallite size increases after doping due to the influence of $FeCl_3$. When graphite is partially intercalated, in addition to reflections due to pristine graphite, a new set of reflections is obtained [28] and the structure of the graphite–$FeCl_3$ compounds cannot be described with the help of a single crystalline cell [2]. Glass-like carbon, such as Novo., appears to be the most highly disordered compact form of carbon [29].

The ratio of $\sigma/\sigma_0 = 1.84$ of graphite (Table I) indicates that a relatively low amount of $FeCl_3$ has been intercalated in graphite. This conclusion can be reached, on considering that the electrical conductivity of different compositions of graphite/$FeCl_3$ is increased with increasing $FeCl_3$ content, e.g. $\sigma/\sigma_0 = 1$; 1.7; 14.6 for intercalated $FeCl_3$: 0; 0.8; 13.2 mol% in grafoil [11]. The electrical conductivity of the other materials has been influenced by doping with $FeCl_3$. In those cases no true intercalation takes place because of the disordered structure of those materials compared to graphite. The influence of the pyrolysis treatment and doping on the electrical conductivity of the pyrolysed materials can be explained after taking into consideration the pyrolysis mechanism that leads to their formation and the charge transfer because of the doping, respectively.

Generally, the material pyrolysed at about 500 °C consists of a loose network of linear conjugated systems which are still isolated electronically from each other. At this temperature, the material still contains one hydrogen for every two carbon atoms, which corresponds to the formula of an aromatic ladder polymer. Above 500 °C, hydrogen is gradually eliminated. The electrical conductivity increases rapidly as separate conjugated systems become interconnected to form a conducting network [2]. By raising the pyrolysis temperature, the conjugation of the polymer is progressively increased and thus π-orbital delocalization occurs due to the development of planar, polycondensed rings. The electrical conductivity within the carbonaceous material increases due to the formation of fused rings and the movement of the charge carriers within the individual polycondensed rings and from one ring system to another. A high conductivity is present within the planar fused-ring moieties because of the maximum overlap of π-orbitals. The resistance observed on the macroscopic scale is the result of the many barriers to charge mobility between the individual fused-ring components [5, 29, 30].

The electrical conductivity of pyrolysed and doped materials with increasing pyrolysis temperatures show a similar behaviour as previously described for the pyrolysed materials. The ratio σ/σ_0 differs, however, for the different materials and the different pyrolysis temperatures. The σ/σ_0 of nearly all the polymers pyrolysed at 300 °C is 1, i.e. at this temperature, no doping effect is observed. The σ/σ_0 of Novo. is increased and has its maximum value at 500 °C. This effect could be explained by a chemical condensation of two phenolic groups accompanied by cyclization above 400 °C. The weight losses of Novo. at 700 °C are increased due to various reactions [29]. PPP is extremely stable at high temperatures, showing the lowest weight losses due to its aromatic structure of rigid *para* couplings. Therefore, its typical organic character remains at higher temperatures. Consequently, σ/σ_0 begins to change above 700 °C. The weight losses of the Biom. increase up to 500 °C, from there up to 700 °C they increase at a lower rate, showing its higher value of σ/σ_0, and above that temperature the weight losses are very slightly increased. The weight losses of Lign. at 500 °C are high, then they are low showing its highest value of σ/σ_0, and they are very high above 700 °C because of the removal of sulphur [31]. *o, m, p*-polyphenylenes (8A) show decrease of σ/σ_0 above 500 °C. These materials show higher weight losses than PPP up to 700 °C and also a continuous increase of σ. It seems that the reactions are more progressed, leading to the formation of polycondensed rings at lower temperatures than that of PPP. This formation is facilitated by the macromolecules of *o, m, p*-polyphenylenes which are more flexible compared to the rigid macromolecules of PPP. Therefore, more oriented and extended layers are formed which lead to higher electrical conductivity. The dopant molecules probably destroy the orientation of the layers and the contact between them. Another factor which generally prevents the interaction with the dopant is the rigidity of the layer system because of interlayer bonds [32].

The mechanism of the electrical conductivity of doped polyphenylenes with $FeCl_3$ differs from that of doped graphite. In the first case, the complete reduction of Fe^{3+} to Fe^{2+} and the concomitant oxidation of the π-system of the polymers occur, possibly as a reaction of the type [33]

$$2FeCl_3 + 2e \;=\; FeCl_4^{2-} + FeCl_2 \qquad (1)$$

The reaction of $FeCl_3$ with $(p\text{-}C_6H_4)_x$ differs significantly from the reaction taking place in graphite, because in the latter case, $FeCl_3$ retains its coordination and only a partial charge-transfer occurs to give $C_n^{\delta+}\,(FeCl_3)^{\delta-}$ [33]. When electrons are transferred to the graphite (by using donors), or from it (by using acceptors), the giant π-orbitals are destroyed and the electrical conductivity is increased [32]. From the carbon hexagon sheets, acting as macro-cations, charges are transferred to the intercalated halides which provide sets of anions in each layer. A large increase in the concentration of p-charge carriers in the graphite layers results from this transfer which leads to the large increase in electrical conductivity [34].

All aromatic polymers used in the present work could interact with the $FeCl_3$-dopant. It is generally thought that Friedel–Craft catalysts (e.g. $AlCl_3$, $FeCl_3$) involve the formation of charge-transfer bonds between these halides and individual aromatic molecules [34]. Chemically, graphite layers resemble aromatic ions, i.e. graphite/acceptor compound resembles aromatic radical cations [7].

In conclusion, the doping of the pyrolysed polymers, with the exception of graphite did not lead to real intercalation. However, interactions between the carbonaceous molecules and the dopant molecules take place. These interactions are favoured for pyrolysed Novo., PPP, Biom. and Lign., leading to an increase in the electrical conductivity. However, for pyrolysed *o, m, p*-polyphenylenes (8A), the electrical conductivity is decreased after doping. Because of their higher flexibility compared to the other polymers used, *o, m, p*-Polyphenylenes, seem to form more oriented and extended layers which lead to higher electrical conductivity. The dopant molecules probably destroy the orientation of the layers and the contact between them. In all cases the heating treatment more strongly influences the electrical conductivity of the pyrolysed polymers than does their doping.

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