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Electrically conducting compound synthesized from lignin and sulfur

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Summary

A thermostable polymer, called sulfur lignin, has been obtained when modifying lignin by reactions with elemental sulfur at elevated temperatures. Sulfur linkages are formed between the phenylpropane units of lignin in these reactions. The conductivity of polymers which have a conjugated structure can be increased by doping with electron acceptors or donors. The conductivity of sulfur lignin has been measured after doping with various dopants and from the results it is concluded that the doped sulfur lignin has the properties of a semiconductive polymer.

Introduction

Organic polymers are usually good insulators, having conductivities of about 10^{-12}-10^{-16} Scm^{-1}. Several different polymers, for example poly(phenylene sulfide), can be modified to be conductive upon doping with electron acceptors or donors (1). The sulfur linkage between aromatic rings in PPS permits the conduction along the polymer chain. This enables continuous orbital overlap along the polymer backbone, either in the virgin polymer, or chemically modified polymer by doping. In addition to provide the conjugated backbone necessary for the extended delocalization, the sulfur link affords higher flexibility in the polymer than for instance in poly(phenylene) (2).

Various poly(phenylene sulfides) have been studied in our laboratory. Aromatic thioethers have been prepared from natural products like lignin. The product has been named sulfur lignin (3). According to the structural analysis it is presumable that this polymer has conducting properties.

The reaction of lignin with sulfur involves demethylation, desulfonation and cleavage of ether linkages, and formation of aliphatic and aromatic sulfur-carbon and carbon-carbon bonds between the units (3). The CP MAS-NMR spectrum of sulfur lignin is presented in Figure 1 with the spectrum of the starting material, lignosulfonate. The elemental, thermal and spectroscopic analysis has been recently presented elsewhere. A tentative structure for sulfur lignin is formulated according to these analysis and presented in Figure 2.

In this paper detailed studies of conductivity and spectrometric measurements have been conducted on several kinds of undoped and doped lignins; such as lignosulfonate, modified lignosulfonate and sulfur lignin.

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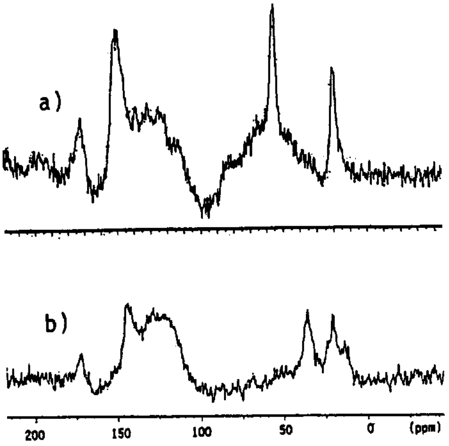

Figure 1. CP MAS-NMR spectra of lignosulfonate (a) and sulfur lignin (b)

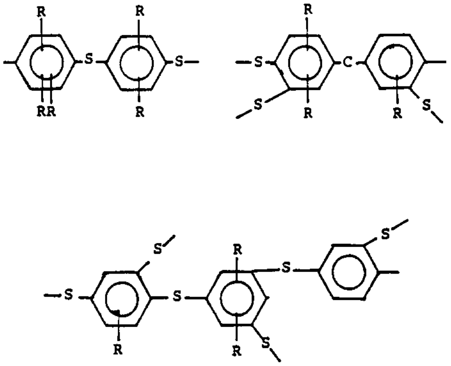

Figure 2. Tentative structures for sulfur lignin.

Experimental

Materials

Lignin derivatives used in the experiments were 1) NaLS U-80 (ultrafiltrated sodium lignosulfonate, 80 % purity, free of carbohydrates, Rauma-Repolà Oy), 2) NaLS U-95 (ultrafiltrated sodium lignosulfonate, 95 % purity, Rauma-Repola Oy), 3) NaLS U-95 treated with alkali at elevated temperatures (523-572 K). Sulfur lignin was prepared by Rauma-Repola Oy. The preparation was carried out at 513 K for two hours in an autoclave using the mixture of ultrafiltrated lignosulfonate and sulfur in N,N-dimethylacetamide (DMAA). The product contains 11 % sulfur (3).

Conductivity measurements

The conducting properties were measured on samples powdered and pressed to the size of IR-pellets (13 mm diameter and 0.5-1.5 mm thickness).

The measurements were made in the standard four-point probe or in a two-point probe. The measurements carried out in these two different devices gave similar results. The both measuring equipments consisted of a power supply (HP 6110 A), elctrometer (Keithley 602), a power supply for heating (Oltronix C 40-080), a pressure measuring device (Baltzer TPG 030) and a digital voltmeter for the temperature readings. The electrical conductivity was measured in a vacuum of 10^{-4} torr.

Doping

Doping with iodine was carried out at ambient temperature by exposing the polymer samples to iodine vapour (6). Exposure times up to 48 hours were used to obtain heavily doped samples. Doping was followed by vacuum pumping for two hours in order to remove any residual iodine absorbed at the surface.

The transition metal halide, $FeCl_3$, was used as purchased without further purification, but evacuated (ca. 10^{-4}torr) for several hours before use. Nitromethane was dried over calcium chloride and distilled. The doping was carried out as follows;20 ml of saturated solution of the metal halide ($FeCl_3$ in nitromethane) was discharged onto the lignins (7). The lignins were partly dissolved in the solution and the precise quantitative measurement of the immersing dopant could not be carried out. Different dopant concentrations were obtained by changing the amount of lignin (1.0-3.0 g) in the solution. After the reaction, the excess salt was removed by washing with the same solvent used in the doping solution, and then dried in the nitrogen atmosphere or under a high vacuum. After drying the samples were pressed into pellets.

Cheimical doping with conc. H_2SO_4 was carried out on the surface of the liqud phase (8). It was not possible to determine the exact amount of dopant because part of the polymer dissolved in the liquid. After the treatment the samples were dried in a vacuum.

All reagents were commercial products and no further purification was used unless separatively mentioned.

Spectroscopic measurements

The IR-spectra of the pellets made from polymers mixed with KBr were recorded on a Perkin-Elmer 457 IR-spectrometer.

The ESR-measurements were performed on a Varian E-4 ESR-spectrometer operating at a frequency of 9.1 GHz using 100 kHz magnetic field modulation. The microwave power was kept below 1 mW in order to avoid saturation. The samples (3-7 mg) were placed in open quartz tubes.

Results

The conductivities of different lignin derivatives (samples 1-4) before and after doping with iodine are presented in Table 1. Although the samples were doped for several hours, there are large differences in the amounts of iodine retained by the lignin derivatives. The conductivities of all samples before doping were at the same degree, although sample 1 showed slightly higher value. It is interesting to notice that the conductivities of samples 1 and 2 did not change by doping. In the case of sample 1 the conductivity as well as the amount of dopant (0.3 %) is lowest, probably due to the large amount of impurities (20 %) ie. carbohydrates, ash etc. The low conductivity of these lignin derivatives (1 and 2) even after doping can be explained by the high content of etherified oxygen. The decreasing effect of these oxygens in the polymer backbone has earlier been observed for synthetic polymers.(9). As well as the ether linkages, the low conductivity is also affected by the presence of sulfonate groups which have reducing effect on the electron mobility. The alkali treatment of lignosulfonate (sample 3) at elevated temperatures causes the desulfonation and the cleavage of ether bonds (5). This treatment resulted in higher doping (7.8 % of dopant uptake) as well as in a remarkable increase in conductivity.

Table 1. The conductivities of lignin samples 1-4 when undoped and doped (48 hrs) with iodine. Samples: 1.NaLS U-80, 2. NaLS U-95, 3. NaLS U-95 treated with alkali at elevated temperature and 4. Sulfur lignin.

Sample	(undoped, Scm^{-1})	(doped, Scm^{-1})	I_2 (wt %)
1	$5.0\ 10^{-9}$	$4.2\ 10^{-10}$	0.3
2	$7.0\ 10^{-10}$	$8.2\ 10^{-10}$	3.2
3	$4.2\ 10^{-10}$	$3.7\ 10^{-7}$	7.8
4.	$1.2\ 10^{-10}$	$2.8\ 10^{-4}$	59.0

The highest conductivity in Table 1 has been obtained with sulfur lignin (sample 4). Sulfur linkages formed in the reaction have obviously a positive effect. The relation between the conductivity and the doping is shown in Figure 3 for sulfur lignin. The conductivity has increased by about 7 orders of magnitude from 10^{-10} to 10^{-4} Scm^{-1}.

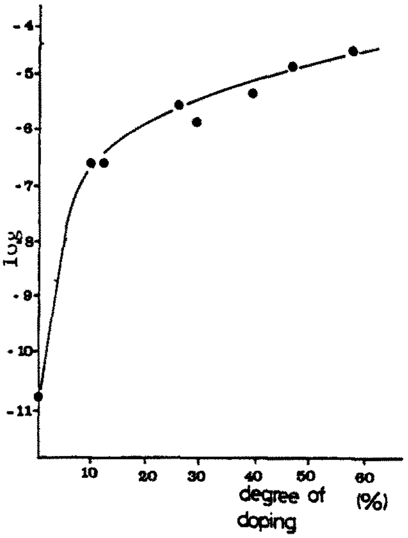

Figure 3. The effect of doping with iodine on the conductivity of sulfur lignin.

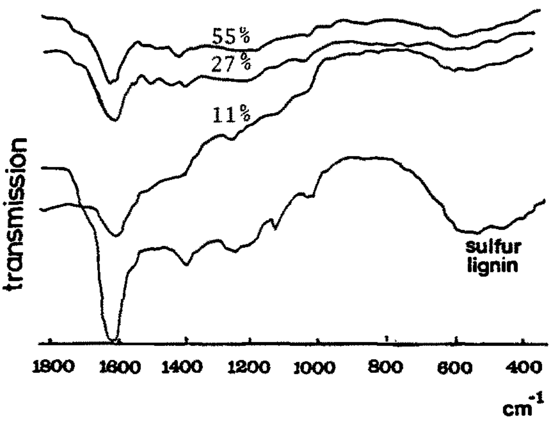

Figure 4. IR-spectra of sulfur lignin undoped and doped with 11, 27 and 55 % uptake of iodine (400-1800 cm^{-1}).

The degree of doping was followed by IR-spectra (Figure 4). It can be seen that the more heavily the samples are doped, the less transmittant the spectra becomes, and it is very difficult to discuss the changes of a particular band during the doping. This kind of featureless spectra is generally consistent with metallic behaviour.

Table 2. The conductivities of sulfur lignin samples undoped and doped with $FeCl_3$.

Sample	Amount of* lignin, g	A B of ESR	Conductivity Scm^{-1}
1	(undoped)	0.91	$1.2\ 10^{-10}$
2	3.0	0.96	$7.7\ 10^{-6}$
3	2.5	0.99	$3.1\ 10^{-6}$
4	2.0	1.12	$1.4\ 10^{-5}$
5	1.0	1.12	$6.0\ 10^{-3}$

* In a 20 ml nitromethane solution saturated with $FeCl_3$.

The conductivities of the sulfur lignins after different doping conditions ($FeCl_3$ as dopant) are presented in Table 2. Changes of the doping degree were estimated based on a comparison of the amount of lignin added in the doping solution, the differences observed in ESR-intesities of spectra (Figure 5) and in the conductivities.

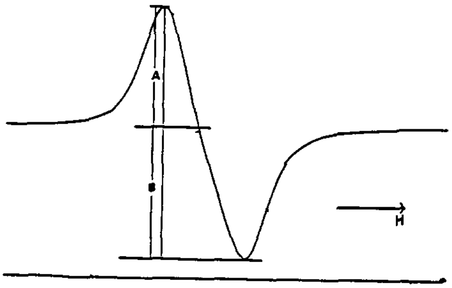

Figure 5. A/B-relation of a doped sample from ESR-spectra.

Thus the results indicate that the smaller the amounts of lignin introduced in the saturated $FeCl_3$-nitromethane solution, the better are the doping results. It was found that at the highest doping levels, the ESR-signal line becomes asymmetric with the increase of the value A/B, which reflects the changes in the conductivity properties by the doping. A strong asymmetry, A B 1, indicates that highly doped samples have the characteristics of the metallic state (9).

The conductivities of sulfur lignin doped by different methods are compared in Table 3. It is obvious that the best conductivity was reached when doped with $FeCl_3$.

Table 3. The conductivities of sulfur lignin sample and doped with three different dopants; I_2, $FeCl_3$ and H_2SO_4.

Sample	Conductivity, Scm^{-1}
Sulfur lignin	$1.2\ 10^{-10}$
doped with I_2	$2.8\ 10^{-4}$
doped with $FeCl_3$	$6.0\ 10^{-3}$
doped with H_2SO_4	$3.2\ 10^{-5}$

Discussion

It is evident from the present results that doping has a distinct effect on the electrical properties of sulfur lignin. As it has been shown in the earlier studies, sulfur lignin differs from lignosulfonate in the extent of cleavage of ether linkages, desulfonation and condensation (4). Furthermore, carbon-sulfur bonds are also formes during the preparations of sulfur lignin. All these changes should be important factors when considering the reasons for the semiconductive properties of sulfur lignin.

It is easier to understand the conduction mechanism of this non-planar natural polymer with the aid of comparisons with the properties of doped synthetic polymers, e.g. poly(p-phenylene sulfide), which are known to have charge-transfer complex structures.

Early studies carried out on conducting polymers, seemed to indicate that conducting polymers must have a planar backbone as the preferred conformation, and that they have continuous system of overlapping π-electrons and p-orbitals along the polymer backbone. However, many other conducting systems have been developed whose preferred conformers are non-planar (2). This has led to the belief that the planarity of the polymer is not the only important criterion for semiconductivity.

The most trivial possibility in the case of PPS is that the doping process somehow allows the phenylene groups to rotate into conformation which better permits π-overlap along the chain (10).

Another possibility is that the electronic overlap is transmitted along the chain through the sulfur d- or p-orbitals in such way that successive phenylene groups need not to be coplanar for effective conjugation (11).

The final possibility is that on doping PPS undergoes an oxidation reaction. In particular, the solution phase electrochemistry of donor-substituted aromatics suggests that oxidative coupling at the phenylene rings should be a facile process. In the case of PPS, this would lead to crosslinking and conjugative overlap perpendicular to the original chain direction (10).

All the above mentioned conducting mechanisms discussed for doped PPS are also possible in the case of modified sulfur lignin. The oxidation reaction has been shown with AsF_5 as a dopant which is a much stronger oxidizing agent than the dopants we used in our experiments. On the other hand the doping effect can be compared with the effect of the initiators in catioinic polymerization. All the dopants in these studies are also used as initiators in cationic polymerization. The initiators are divided in 3 groups; protonic acids (like H_2SO_4), Lewis acids like metal halides ($FeCl_3$) and other cationic generators like iodine (12). Common reaction features of these initiators are that they all form metastable or stable intermediate π-complexes with conjugated bonds before the formation of the carbonium ion for cationic polymerization. If the action of the initiators were compared to the effect of dopants, the importance of π-complexes for increasing the conductivity would become more evident.

The effect of the substituents on the conductivity is also important, especially in the case of modified lignin. This research was done separately with model compounds in the preliminary study (13).

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