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Electrical conductivity in iodine-doped nonconjugated polyanilinefurfural

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Summary

Polyanilinefurfural (PAF) has been prepared. Its chain contains aromatic and furan rings, but the backbone is nonconjugated. However, when treatment with iodine, the color of PAF turns metallic black, and PAF becomes electrically conductive. The electrical conductivity of I_2-doped PAF can reach $10^{-3}S \cdot cm^{-1}$ which is more than 10 orders of magnitude higher than what was observed at the pristine state. The effects of iodine content on the conductivity of PAF and the conductivity stability were investigated. FTIR spectra ,U. v. /vis absorption spectra, E. s. r. measurement and X. p. s. measurement of the undoped and doped PAF were studied. This paper will demonstrate that: if given appropriate substituents and dopants, significant charge transfer may be expected even for nonconjugated polymers and it may display electronic conductivity to a certain level.

Introduction

The recent discovery, made by Thakur, Shang, Suh et al, that the nonconjugated polymer 1,4-polybutadine and some of its derivatives conduct electricity upon doping with iodine has generated great interest in the conduction mechanism. (1-2) It is assumed that cationic species, formed during doping, are responsible for conduction through an intersite hopping process. (3-4) In accordance with this mechanism, nonconjugated conducting polymers should not be limited to 1, 4-polybutadine derivatives, and other types of polymers that can react with electron acceptors such as iodine to form charge-transfer species should also exhibit conductivity upon doping. In our research, we prepared a new kind of polymer, polyanilinefurfural. It can undergo ready doping upon exposure to iodine vapor and become electrically conductive.

Experimental

Materials and methods

The chemicals used were all of analytic–pure grade quality. For conductivity measurements, the polymer samples were cast on to a glass slide and measured by the well-known four-probe method at different dopant concentrations. FTIR spectra were monitored from powdered samples mixed with KBr and pressed into pellets using NICOLET FTIR-60SXR spectrometer. Optical absorption spectra were taken from polymer samples dissolved in ethanol using a Perkin-Elmer Lambda 17 spectrometer. Electron spin resonance(E·s·r·) spectra wre measured on powdered samples using BRUKER ESP300 spectrometer. X·p·s·measurements were performed with Kratos ES300 spectrometer.

The Preparation of PAF

Aniline was placed in a three-necked flask equipped with a stirrer, a refluxcondenser, a thermometer, and a dropping funnel. Furfural was put into the dropping funnel, and then added dropwise with stirring at 30°C. The PH value was adjusted to 6-7. At this time, the reaction system produced heat quickly, and a yellowish sticky resin was formed. When the exothermic reaction was over, the mixture was heated to 70°C, and kept for 3.5h at this temperature. The product was rinsed with deionized water and purified by vaccum distillation in order to remove all impurities. A yield of brownish-red heavy resin was obtained. The I.r spectroscopy of PAF was shown in figure1.

In figure 1, the band at 3025 cm^{-1} , 3050 cm^{-1} can be ascbed to =CH–H stretching vibrations, the band at 1599 cm^{-1}, 1498 cm^{-1}, 1391 cm^{-1} can be ascribed to –C=C– stretching vibrations. and the band at 691 cm^{-1}, 748 cm^{-1}, 883 cm^{-1} may be originate from =C–H bending vibrations. The band at 691 cm^{-1}, 814 cm^{-1} shows that the benzene ring may be monosubstituted . The band at 3366 cm^{-1}, 1635 cm^{-1} belongs to the absorption of NH, and the band at 1249 cm^{-1} may be o riginate from $-\overset{|}{N}-$. The band at 2924 cm^{-1}, 1444 cm^{-1} belongs to the absorption of $-\overset{|}{C}H-$.

The reaction of aniline with furfural is complexed. The former Soviet chemist E·B·O ЮВЧЕНКОet al· had made researches on it. (5) The main product can be inferred to be the mixture of a and b as follows.

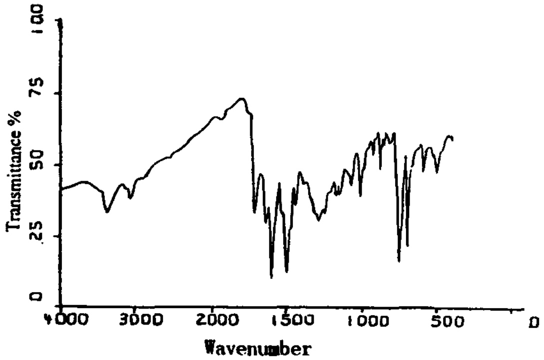
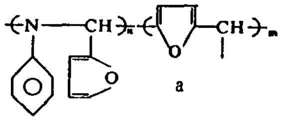
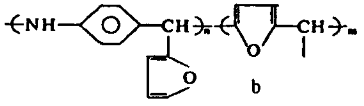


Figure 1. FTIR Spectrum of PAF before doping



a



b

Reaction of iodine with PAF

PAF was dissolved in acetone. Films were formed by letting the solvent evaporate from a thin layer of solution on a glass slide, followed by drying in a vacuum desicator (the thickness of the film is less than 200 μm). Then the samples and I_2 powder were put in a stainless steel container avoiding a direct contact between the polymer and the dopant. The container was evacuated and sealed. Doping of I_2 into the polymer film was attained by keeping the container at room temperature. Periodically, the samples were removed, weighed and returned to the container. The samples approached maximum uptake of iodine in 4 hours.

Results and discussions

Dependence of conductivity on the iodine

In Figure2, the conductivity of a PAF film is plotted versus its iodine content. Undoped films of the polymer have conductivities of about $10^{-13}S\cdot cm^{-1}$. By doping the polymer with increasing time and increasing amounts of I_2, we have found a continuous increase of conductivity. It saturates at a concentration of approximately 180 weight percent. The highest conductivity of the I_2-doped polymer can reach $10^{-2}\sim10^{-3}S\cdot cm^{-1}$, which is more than 10 orders of magnitude higher than the undoped. The polymer turned metallic black after doping.

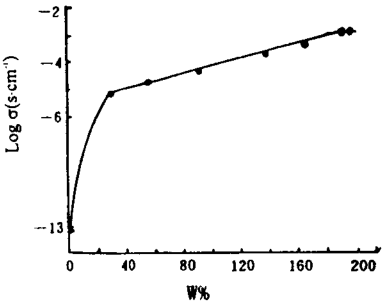


Figure 2 Conductivity(σ) as a function of iodine content (Weight percent w%)

Long-term stability of conductivity

When doped PAF samples were left in air, they lost weight slowly over two months. As shown in Table 1, their conductivity decreased rapidly in the early times. After two months, their iodine content and conductivity tended to be stable.

Table 1 Long-term stability of Conductivity

Settng time (days)	3	20	60	90
Iodine content (weight percent)	195%	167%	115%	112%
Conductivity ($s\cdot cm^{-1}$)	1.18×10^{-3}	4.52×10^{-4}	7.14×10^{-5}	1.05×10^{-5}

Uv/visible absorption spectra

A brownish-red PAF film turned coloured with the progress of doping, and the colour became deeper with the increase of dopant content. These colour change implied the formation of charge transfer complex between PAF and dopants., which was confirmed by the mesurement of optical transmission spectra. As shown in Figure3, the absorption peak of the undoped PAF appeared at about 313nm. After doping, the optical absorption peak shifted to longer wavelength at around 356.8nm. This measurement showed that the new conjugated structure formed after doping.

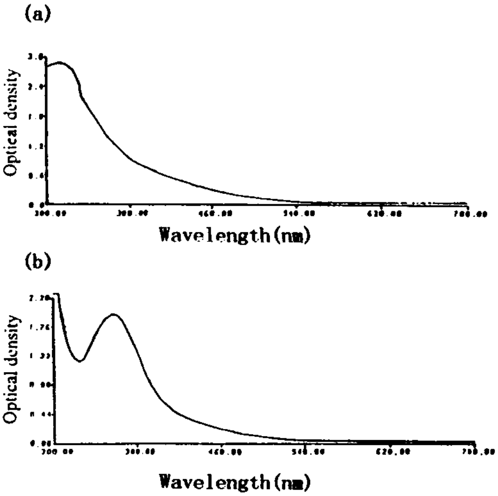


Figure 3 UV/VIS absorbtion spectra
(a) the undoped PAF
(b) iodine-doped PAF

E·s·r· measurement

The E.s.r. measurements showed that the signal intensity increased as the dopant concentraton was increased. As shown in Figure4, the E·s·r· intensity was negligible weak in the undoped state. After doping (W%=167%), the signal intensity of free radical increased . The g value of the E·s·r· signal for the doped samples is 2.0058, and ΔH=14.99G. Doping generates spin 1/2 species. This measurement was coincident with the result of Figure 2, which implied that the conductivity of the doped PAF was consistent with the concentration of free radicals in the doped system, and the free radicals contributed to charge carriers.

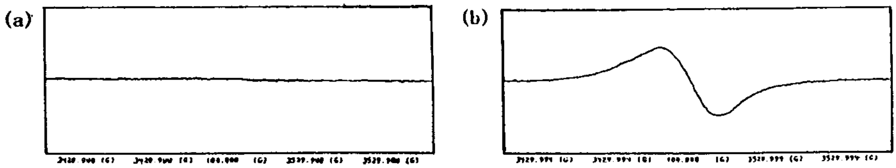


Figure 4 E·s·r signal of
(a) the undoped PAF
(b) iodine-doped PAF (W%=167%)

X·p·s· measurement

The X·p·s· spectrum is shown in Figure 5. The signal at 618.8ev was assigned to I^-, while the binding energe of I_2 is 619.6ev. However, the presence of I^+ is ruled out since no signal appears above 619.6ev. This measurement implies that iodine got electrons to form I^-, while PAF lose electrons.

Molecular iodine dissociated easily in the polymer matrix to form polyiodides species. The doping reaction seemed to lead to $I_2+I^- \rightarrow I_3^-$, $I_2+I_3^- \rightarrow I_5^-$. So there actually coexisted I^-, I_3^-, I_5^-. The equilibrium was more shifted towards one side or the other depending on the nature of the polymer and the doping procedure.

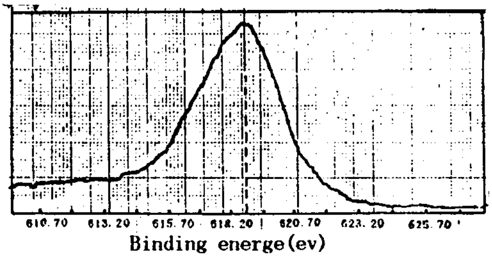


Figure 5 x·p·s spectra of iodine-doped PAF

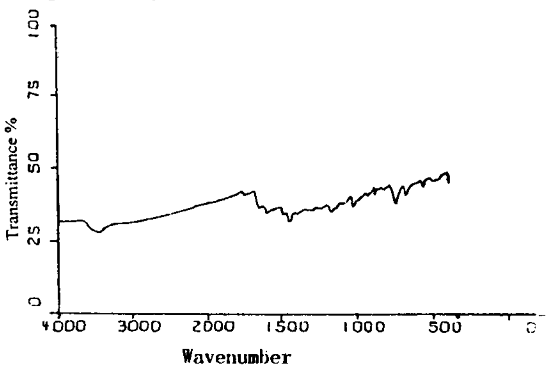


Figure 6 FTIR spectrum of the iodine doped PAF

FTIR spectroscopy

The FTIR spectra of the doped PAF were shown in Figure 6 and 7. The absorption band at 1485 cm^{-1}, 1591cm^{-1} corresponding to $-c=c-$ vibration modes of furan and benzene rings decreased rapidly after doping. The band at 883 cm^{-1}, 748 cm^{-1}, 814 cm^{-1}, 691 cm^{-1} corresponding to $=C-H$ also decreased . An interesting feature is that a new band began to appear at 1549cm^{-1}. This new band maybe due to the radical cation $-\underset{\bullet}{C} \overset{-}{\cdots} \underset{+}{C}-$, (6)which is formed upon charge-transfer. These results agree with the observation made above by E·s·r· and X·p·s· measurement.

Conclusions

Our study shows that PAF can be converted to conducting polymer when exposed to iodine. It may be inferred that the charge-transfer complex($PAF-I_2$) was formed during doping. The radical cation polarons and dopant anions were formed and contributed to the charge carriers. The charge transport may involve an intra and interchain hopping processes. This research shows that under appropriate conditions, significant charge transfer may be expected for the isolated double band structures of the nonconjucated polymer system, and a conjucated backbone is not a prerequisite for a polymer to become electrically conductive.

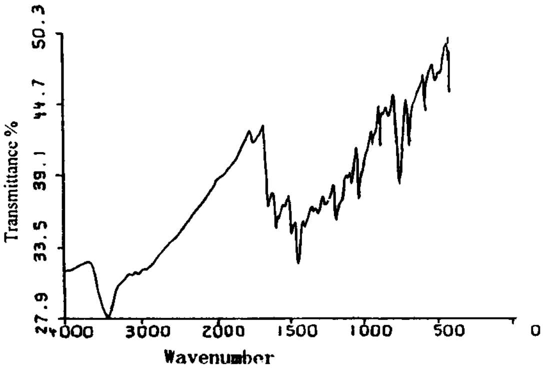


Figure 7 5-Times amplified from figure 6

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