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Synthesis, identification and study of electrical conductivity of the doped copolymer carbazole–phenol formaldehyde



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Carbazole–phenol formaldehyde;
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Abstract The copolymer carbazole–phenol formaldehyde doped with 4 (4-hydroxy-phenyl azo)-benzene sulfonic acid (PABS), 2,5-dimethyl benzene sulfonic acid (PXSA) and 4-hydroxy-*m*-benzene disulfonic acid (PDSA) were prepared. These compounds are identified by FT-IR spectroscopy.

The conductivity of copolymer carbazole–phenol formaldehyde doped with 4 (4-hydroxy-phenyl azo)-benzene sulfonic acid (PABS), 2,5-dimethyl benzene sulfonic acid (PXSA) and 4-hydroxy-*m*-benzene disulfonic acid (PDSA) was studied as a function of weight of the dopant compounds; an increase of conductance of the copolymer by doping with PABS is noted; the conductance became equal to $0.000595 \text{ ohm}^{-1}$ for 0.1 g higher conductance for the copolymer when it is doping with PABS.

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1. Introduction

The discovery of intrinsically conductive polymers (ICPs), such as poly pyrrole, poly acetylene, poly thiophene, and poly aniline (PANI), is unique in that it has provided possible substitutes for metallic conductors and semi conductors. Efforts to

produce tailor – made polymers with respect to the electrical, mechanical, optical, and thermal properties have been pursued by several research groups (Ozdemir et al., 2006; Kumar and Sharma, 1998). ICPs have been intensively studied in the past years because of their potential application in several electronic, electro chromic, and photoelectron chemical devices (Genies et al., 1987; Duek et al., 1992; Bauerle, 1993).

Conducting polymers have been intensively investigated in the last 2 decades due to their fundamental physical properties and potential application in various electronic devices such as chemical sensors, light emitting diodes, organic field effect transistors, electromagnetic interference shielding, antistatic materials, sensing materials, and secondary batteries (Hino et al., 2006; Trivedi, 1997; Huang et al., 2003; Anand et al., 1998).

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Azo dyes are widely used in industry and daily life, for example, as components in permanent hair dyes. Additionally, azo-compounds represent the largest class of dyes applied in the textile, food, and cosmetic industries.

Azo dyes used as components in permanent hair dyes can only be decolorized by drastic methods such as chemical bleaching using hydrogen peroxide. However, this treatment may cause hair damage and health problems. Hence, the use of these methods requires extreme precautions in order to prevent these adverse effects. Therefore, it would be useful to develop a customer friendly and safe treatment method avoiding the use of hazardous chemicals. Enzymes that specifically oxidize or reduce azo-bonds and, thereby, decolorize dyed hair could be an elegant alternative since they can be used under mild conditions and they do not have negative effects both on hair and skin (Pricelius et al., 2007).

Azo dyes are a group of compounds characterized by the presence of one or more azo bonds ($-N=N-$) in association with one or more aromatic systems; this makes them relatively resistant to biological and chemical degradations (Moutaouakkil et al., 2003).

Azo-dyes are currently either dispersed or grafted into polymer matrices, or into organic-inorganic composite materials. Birefringence has been found to be photo induced in an azo-dye doped polymer, so that special attention has been paid to the basic mechanism in view of improving the efficiency of this phenomenon. The photo induced birefringence relied upon the local orientation of the azo groups and is the result of successive *trans-cis-trans* isomerizations initiated by a linearly polarized laser beam. This photo orientation is responsible for the refractive index change (Maertens et al., 2000).

Dispersion of azo benzene in copolymer carbazole-phenol formaldehyde, plasticized and doped with a charge generator, this type of azo-dye doped copolymer carbazole-phenol formaldehyde has also proved to be useful to increase the conductivity of this copolymer. The possible effect of the azo dye grafting, the weight of the azo dye. It is also important to compare the properties of these new materials of the dopants. We report herein the chemical synthesis of copolymer carbazole-phenol formaldehyde resin and several of sulfonic acids such as 4 (4-hydroxy-phenyl azo) benzene sulfonic acid, 4-hydroxy-*m*-benzene disulfonic acid, and 2,5-dimethyl benzene sulfonic acid as dopants and study the effect of these materials on the conductivity of the resin. The sulfonic acid doped resin is highly stable and the properties of the materials can also be controlled by varying the structural parameters of dopants.

2. Experimental

2.1. Sample synthesis

2.1.1. Synthesis of copolymer carbazole-phenol formaldehyde

The little well-flowing resins were prepared from carbazole (I), PhOH or cresol and HCHO by alkaline and acid two-step condensation. Thus a mixture containing I 584 g, PhOH 987 g, 38% CHOH 773 g, and NaOH 9.87 g (in 50 ml of water) was heated for 15 min to boiling; 11.14–90 g and 31.43–250 g oxalic acid–water mixture were added successively within 3 and 40 min, respectively; the mixture reacted for 3.5 h at 100 °C, and H₂O distilled within 3.5 h up to 120 °C and then within 1 h in oven up to 140 °C to give 1615 g clear carbazole-phenol formaldehyde copolymer (II) (Chemical Abstract, 1972).

2.1.2. Synthesis of 4 (4-hydroxy-phenyl azo)-benzene sulfonic acid (PABS)

Sulfanilic acid (51.9 g, 0.3 mol) and sodium carbonate (13.6 g, 0.13 mol) were taken in a 1000 ml conical flask. Water (500 ml) was added and heated to 60–70 °C to dissolve the entire solid. It was further cooled to 10–15 °C and a cooled solution of sodium nitrile (18.5 g, 0.29 mol) in water (55 ml) was added. The mixture was poured into ice (350 g) containing concentrated HCl (53.2 ml) at 5 °C and stirred using mechanical stirrer for 30 min. The diazonium salt was added dropwise into a solution containing sodium hydroxide (30 g, 0.75 mol) and distilled phenol (23.5 g, 0.25 mol) in water (250 ml) at 5 °C. The coupling reaction was continued under stirring for 3 h in the ice cold condition using mechanical stirrer. Concentrated HCl (250 ml) in crushed ice (600 g) was slowly added into the reaction mixture for neutralizing and the neutralization was confirmed by pH paper. The red precipitate was filtered and washed with water (Jayakannan et al., 2006).

2.1.3. Synthesis of 2,5-dimethyl benzene sulfonic acid (PXSA)

Place 5.2 g (6 ml, 0.05 M) of *p*-xylene in a 25 ml round-bottomed flask and add, with gentle swirling agitation, 10 ml of concentrated sulfuric acid.

Heat the mixture on water bath for 10–15 min, remove the flask from the bath and mix the contents with a circular motion every 2 min. The reaction is complete when the xylene layer on the surface of the acid has disappeared.

Cool the mixture to room temperature and add 5 ml of H₂O cautiously with gentle swirling. Pour the warm reaction mixture into a 100 ml beaker and cool in ice. Filter the crystal-

Table 1 The main functional groups and their frequencies in FT-IR of the prepared samples.

Samples	O–H	C–H	C=C	S=O	N=N	C–H	O–H
PABS	3448		1593	1155 (Sym.)	1535 1377	844	626
PXSA		2931	1488 1620	1024 (Asym.) 1190 (Sym.)		823 out of plane	
PDSA	3456		1631 1604	1126 (Sym.)			622 out of plane
Carbazole-phenol formaldehyde	3413	3022	1598 1498			756	692

line solid with suction on a sintered glass funnel (Kahol et al., 2003).

2.1.4. Synthesis of 4-hydroxy-*m*-benzene disulfonic acid (PDSA)

Place a mixture of 31 g (0.33 M) of phenol in a dry 500 ml flat-bottomed flask and add 116 g of concentrated sulfuric acid. Heat in a boiling water bath for 3 h with mechanical stirring. On cooling to room temperature or below by immersing the flask in ice water and then adding slowly a solution of 95 g of NaOH in 235 ml water, the solid salt separates (Kahol et al., 2003).

2.2. Doping of the copolymer

The copolymer carbazole–phenol formaldehyde (1 g), a certain amount of DMF was dissolved in the copolymer, then different weights of material dopant were added to the solution and the mixture was stirred at room temperature and the conductivity was measured.

3. Results and discussion

3.1. Identification of the synthesized compounds

3.1.1. FT-IR analysis

The samples were identified by FT-IR spectrum and recorded with FT-IR 8400S model (2000) from SHIMADZU Japan and the spectrum is recorded as KBr pellet.

New azo benzene sulfonic acid dopants were synthesized from commercially important phenols; diazotized sodium salt of sulfanilic acid was reacted with sodium salt of phenol in water and subsequent neutralization produced 4 (4-hydroxy-phenyl azo)-benzene sulfonic acid (PABS); *p*-xylene was reacted with concentrated sulfuric acid to produce 2,5-

dimethyl benzene sulfonic acid (PXSA); phenol was reacted with concentrated sulfuric acid to produce 4-hydroxy-*m*-benzene disulfonic acid (PDSA). The chemical structures of the synthesized compounds (PABS, PXSA, PDSA) and the copolymer carbazole–phenol formaldehyde were identified using FT-IR analysis. Table 1 and Fig. 1 show the absorption bands of the active groups. The FT-IR spectra of PABS, PXSA, and PDSA and the copolymer carbazole–phenol formaldehyde were determined using KBr pellets; the main functional groups and their FT-IR frequencies for the prepared compounds are presented in Table 1 and Fig. 1.

For the sample (PABS), the peak at 3448 cm^{-1} is assigned to aromatic (OH) stretching, whereas the peak at 1593 cm^{-1} to aromatic ring (C=C), stretching vibrations. The peak at 1155 cm^{-1} is due to (S=O) symmetrical stretching. The peaks at 1535 cm^{-1} and 1377 cm^{-1} are assigned to N=N. The peak at 844 cm^{-1} is due to (C–H) aromatic ring, the peak at 626 cm^{-1} is assigned to aromatic (OH).

Table 2 The values of conductivity for the copolymer doped with sample dopants (PABA, PXSA, PDSA).

Weight (g)	Conductivity (ohm^{-1}) (PABA)	Conductivity (ohm^{-1}) (PXSA)	Conductivity (ohm^{-1}) (PDSA)
0.01	0.000105	0.00007	0.000092
0.02	0.00016	0.000088	0.0000975
0.03	0.000185	0.000138	0.0000975
0.04	0.000285	0.000158	0.000097
0.05	0.000315	0.000163	0.000097
0.06	0.000375	0.000178	0.0000975
0.07	0.000435	0.000233	0.00009
0.08	0.000485	0.000258	0.000078
0.09	0.000515	0.000268	0.000097
0.1	0.000595	0.000273	0.000097

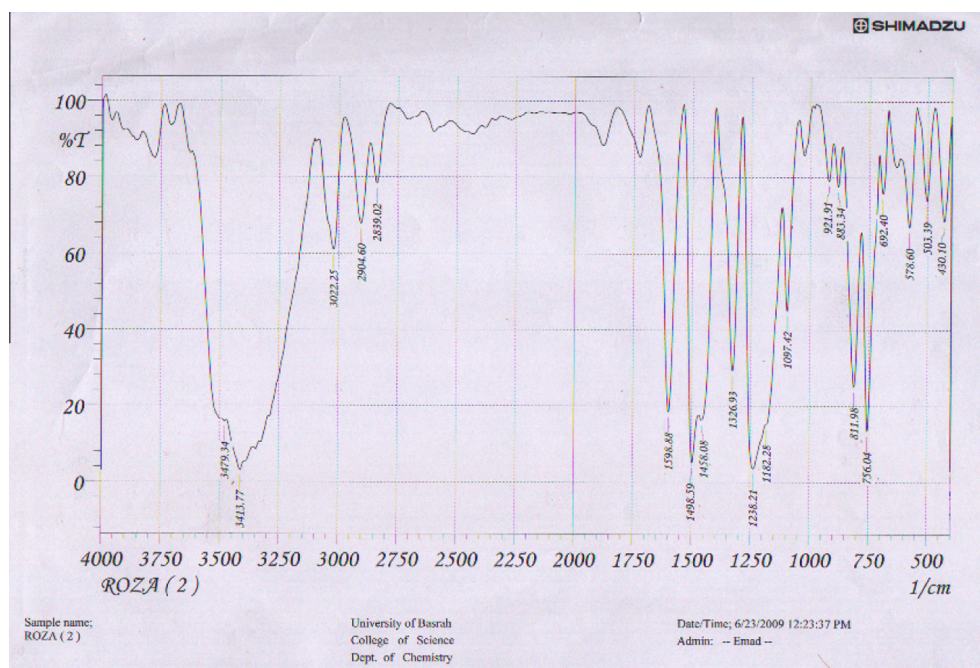


Figure 1 FT-IR of copolymer carbazole–phenol formaldehyde.

For the sample (PXSA), the peak at 2931 cm^{-1} is assigned to aromatic (C–H) stretching, whereas those at 1488 cm^{-1} and 1620 cm^{-1} to aromatic ring (C=C), stretching vibrations. The peak at 1024 cm^{-1} is due to (S=O) asymmetrical stretching.

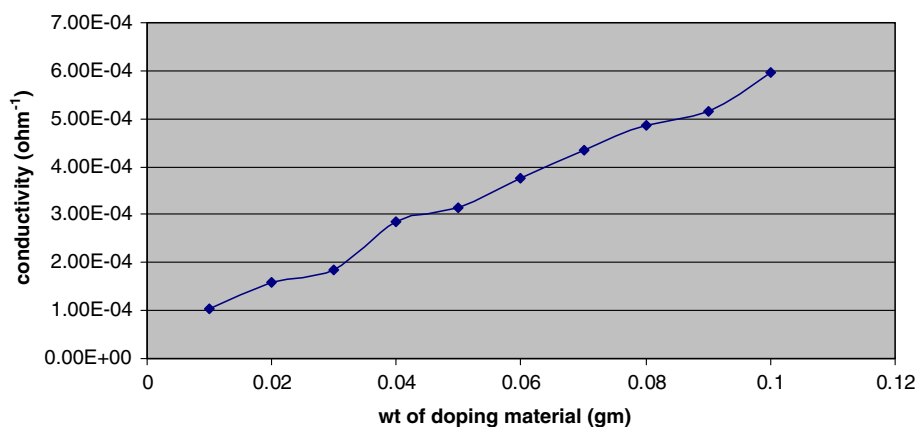


Figure 2 Effect of PABA on conductance of the copolymer.

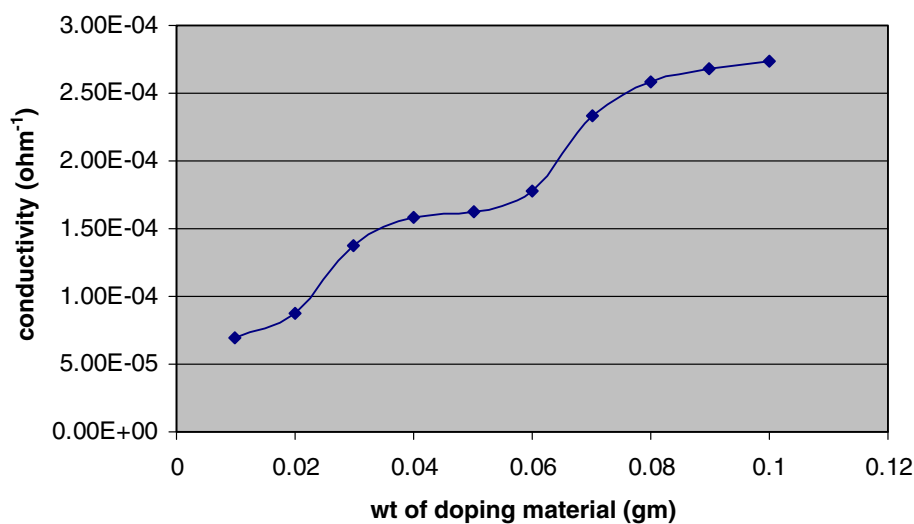


Figure 3 Effect of PXSA on conductance of the copolymer.

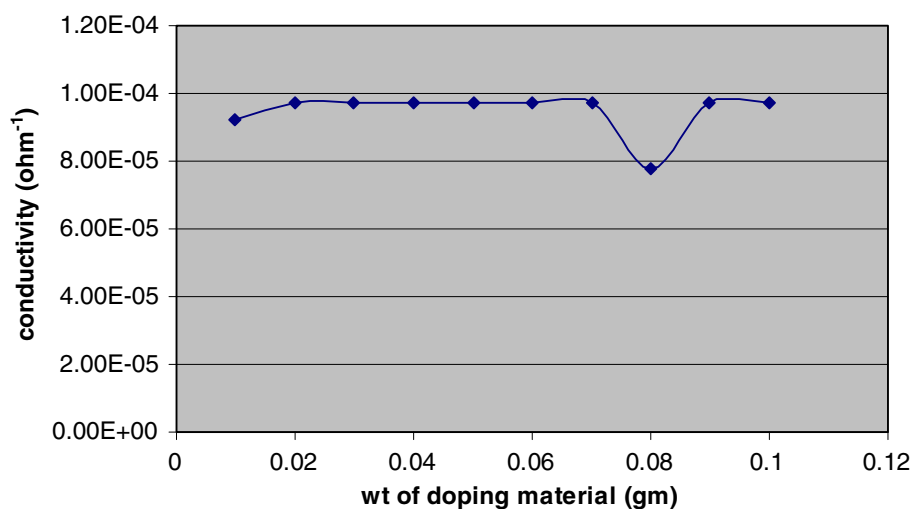


Figure 4 Effect of PDSA on conductance of the copolymer.

The peak at 1190 cm^{-1} is due to (S=O) symmetrical stretching, the peak at 823 cm^{-1} is due to (C-H) aromatic ring.

For the sample (PDSA), the peak at 3456 cm^{-1} is assigned to (O-H) stretch, and the peak at 1126 cm^{-1} due to (S=O) symmetric stretching, the peaks at 1631 and 1604 cm^{-1} due to (C=C) aromatic ring, the peak at 622 cm^{-1} is due to (O-H) out of plane deformation.

For the copolymer carbazole-phenol formaldehyde, the peak at 3413 cm^{-1} is assigned to (O-H) stretch, and the peak at 3022 cm^{-1} due to (CH) stretching, the peaks at 1598 and 1498 cm^{-1} due to (C=C) aromatic ring, the peak at 1182 cm^{-1} is due to (C-N), the peak at 756 cm^{-1} to C-H out of plane deformation, the peak at 692 cm^{-1} to O-H out of plane deformation.

3.2. Measurement of the conductivity

The conductivity of the samples is measured as the solutions in DMF as the solvent; the values of conductivity for the copolymer doped with sample dopants (PABA, PXSA, PDSA) are summarized in Table 2.

In Table 2, the sequence of conductivity is $\text{PABA} > \text{PXSA} > \text{PDSA}$, in the weight of the dopant sample 0.1 g ; from Figs. 2–4 it is observed that the conductivity is found to be increased with the increase in weight, the increase in conductivity could be due to the increase of efficiency of charge transfer between the copolymer chains and the dopant with increase in weight. In order to investigate the effect of the amount of dopant on the conductivity of the copolymer carbazole-phenol formaldehyde, the conductivity values of the copolymer were plotted against the weight of the doped samples shown in Figs. 2–4; it is very clear from the plot that the conductivity values of the copolymer increase with increase in the weight of the dopant, which suggests that minimum $(0.1)\text{ g}$ of dopant is required to obtain high conductivity $(0.000595)\text{ ohm}^{-1}$ of doped sample PABS; while the doped sample PXSA suggests that minimum $(0.1)\text{ g}$ of dopant is required to obtain high conductivity $(273 \times 10^{-6})\text{ ohm}^{-1}$; while the doped sample PDSA suggests that minimum $(0.02, 0.03, 0.06)\text{ g}$ of dopant is required to obtain high conductivity $(97.5 \times 10^{-6})\text{ ohm}^{-1}$; all other three dopants produce a very good doped copolymer.

4. Conclusion

The copolymer carbazole-phenol formaldehyde was synthesized by chemical polymerization method, as a resol resin in alkaline solution (NaOH). 4 (4-Hydroxy-phenyl azo)-benzene sulfonic acid (PABS), 2,5-dimethyl benzene sulfonic acid (PXSA), and 4-hydroxy-*m*-benzene disulfonic acid (PDSA) were used as dopants during the polymerization process. Spectroscopic and conductivity of the dopant sample are found to be affected by the type of the dopant sample used for doping purpose. Room temperature conductivity is found to be higher in 4 (4-hydroxy-phenyl azo)-benzene sulfonic acid (PABS) doped copolymer than that doped with 2,5-dimethyl benzene sulfonic acid (PXSA), 4-hydroxy-*m*-benzene disulfonic acid (PDSA).

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