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Influence of the anion on polyaniline

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Abstract Polyaniline exists in various forms distinguished by the number of protons bonded to nitrogen, which determines the degree of oxidation of the polymer. At a macroscopic scale, doping involves electron transfer as well as protonation of the nitrogen heteroatom, which stabilises localised bound states to impart electronic conductivity to the system. However, it has been observed that the processability of this intractable polymer is greatly influenced by the anion associated with the protonating agent. Here we briefly summarise the influence of the anion on the behaviour of polyaniline.

Key words Anion · Polyaniline · Processability · Intractable · Protonation

Introduction

The elucidation of the unique properties and characteristics of polyaniline provides a challenge of considerable current scientific interest. Conductivity and processability are twin phenomena which require the use of concepts which encompass electrochemistry and organic chemistry on the one hand and the field of condensed matter science on the other. Particularly interesting are systems whose composition can be selectively altered, thereby leading to electronic properties which can vary between transcend semiconductor to metal-like behaviour.

During the course of undertaking detailed studies on the use of a variety of dopants, we observed that the conductivity and processability of polyanilines not only

depend on protonation level but are strongly influenced by the counter anion. Electrical conductivity, thermal stability, processability and electrochemical growth not only depend on the oxidation state of polymer but are also dependent on the nature of the counter anion, which can be defined in terms of its electronegativity, molecular size, orientation and solvation [1–3].

The molecular size of the dopant is an important aspect, because the polymer undergoes substantial volume changes during the doping and dedoping processes. These dimensional changes are extremely large, and influence the mechanical strength of a polymer. They have been utilised to convert electrical energy to mechanical energy [4].

Not all dopants can induce charge transport in a polymer. This depends upon the redox energy of the host and guest molecules, because transfer of an electron is from high to low redox energy. The initial charge transfer on doping is between the dopant molecule and the proximal polymer site, but subsequently some diffusion of polymer charge away from the immediate dopant to the site can be expected to generate pair states in the polymer. In equilibrium, the number of polymer pair states is equal to the number of ionised dopants. These findings find support from ESR [5], electron energy loss spectroscopy [6], NMR [7] and thermopower studies [8].

Electrochemical studies

Electrochemical studies reveal the influence of the counter anion on peak potentials as well as on the polymer deposition rate, indicating that the electron transfer and protonation processes are greatly influenced by the anion, as illustrated in Table 1 [3, 9–11]. The anions associated with various dopants, which not only influence the solution processability but its conductivity and electrochemistry, are illustrated in Fig. 1.

The anion, which promotes the growth of the polymer, is also responsible for the degradation of the

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Table 1 Electrochemical data

Dopant	Cyclic voltammetric peaks vs SCE (mV)		Polymer deposition rate in 0.1 M acid + 0.1 M aniline ($\text{mC cm}^{-2} \text{ cycles}^{-1}$)	Conductivity of pressed pellets (S/cm)	Reference
	Electron transfer	Protonation			
5-sulfosalicylic acid	140	720	3.2	1.0	9
<i>p</i> -toluenesulfonic acid	130	710	3.2	2.0	9
Benzenesulfonic acid	100	700	2.9	5.0	9
Methylsulfonic acid	210	650	–	0.2	*
Sulfamic acid	125	670	3.2	1.2	10
Sulfuric acid	90	625	2.0	0.5	3
Perchloric acid	–	–	4.2	2.0	3
Fluoroboric acid	–	–	3.8	0.8	11
Trifluoroacetic acid	–	–	1.25	0.7	11
Hydrochloric acid	220	840	0.47	1.4	3
Nitric acid	–	–	0.51	1.9	3
Oxalic acid	240	460	–	0.2	This work

* M. Vijayan and D.C. Trivedi unpublished results

polymer film by way of overoxidation; for example, perchlorate and nitrate ions can cause degradation of an electrochemically grown polyaniline film [3]. It has been observed that a polyaniline film grown in a reducing medium such as oxalic acid has very high stability. In this system, the surface electron transfer occurs at 240 mV and protonation around 460 mV vs SCE. This narrow potential range, observed in an oxalic acid medium, is particularly suitable for electrochromic display

because of the reduction in the time required for cycling the film between extreme potentials. The π - π^* transition, observed at 427 nm, is due to the semiquinone structure, and the band due to trapped excitons is found around 648 nm in the polyaniline-oxalic acid system. However, in all other systems, such as sulfuric acid, the band due to the charge carrier is observed between 800 and 900 nm. This suggests that, in polyaniline with oxalate as a counter ion, the majority of excitons are polarons.

The anion effect is possibly related to the hydration shell of the anion, as suggested by Desilvestro and Scheifele [12], who have shown that the hydration enthalpies and Gibbs free energies show a good correlation with polymerization rates. However, the onset potential for the oxidation of aniline is independent of the anion. Once the polymerization process is initiated, it is influenced by the anion for the following reasons:

- (1) adsorption of the anion on the electrode surface,
- (2) the redox potential of the anion,
- (3) the ionic charge,
- (4) the ionic size,
- (5) the hydration shell.

Otherwise, polymerisation is a self-catalysing reaction and obeys the law $i/nFA = K_c$, where K_c is the autocatalytic rate constant and has a value of approximately 0.47 s^{-1} for a film of 140 nm [13].

Aqueous solution

The achievement of solubility in water has its own attractions, from the scientific as well as the application point of view. It has been shown that a polyanion like poly(styrenesulfonic acid) as a dopant can yield water-soluble polyaniline containing 25 repeat units [14]. Water-soluble polyaniline has also been reported using phosphoric acid esters [15] and ring sulfonation of emeraldine base [16].

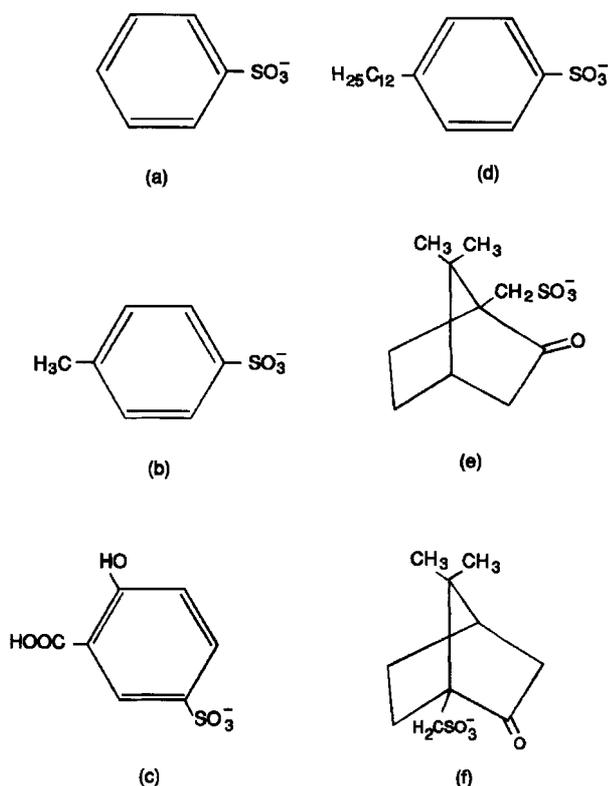


Fig. 1 Structures of various counter ions. a) Benzene sulfonate, b) *p*-toluenesulfonate, c) 5-sulfosalicylate, d) dodecylbenzenesulfonate, e) (-), f) (+) camphor-10-sulfonate

Non-aqueous solution

The use of aromatic functionalised sulfonic acid as a dopant induces certain changes in the properties of the polyaniline due to the formation of a ternary system involving the polymer, the dopant and the solvent.

Solvation of polyaniline is a result of a number of interactions between the polymer dopant and the solvent, such as Born-type, hydrogen bonding, hard-soft acid-base interactions and Lewis acid-base (donor-acceptor) interactions. Change in the structure of a polymer due to restructuring of the solvent in the presence of ions cannot be ruled out. Thus, a functionalised protonic acid yields, in DMSO, chloroform, xylene and various common organic solvents, soluble conducting polyaniline from which a free-standing film can easily be obtained [1, 9, 10]. The free-standing film has been shown to be of importance in controlling electromagnetic radiations [1].

Blends and composites

The morphology and threshold for the onset of electrical conductivity in polyaniline blends is strongly influenced by the anion associated with dopant. The percolation threshold and the continuous increase in conductivity with increase in concentration of polyaniline are important in the fabrication of free-standing films with the desired mechanical and electrical properties of the matrix polymers such as polyolefins, polyesters, and poly(methyl methacrylate). In these systems, the counter ion acts as a surfactant; for example, dodecyl benzenesulfonic acid and camphor sulfonic acid can yield a polyblend with polymethyl methacrylate with 2% polyaniline, with an electrical conductivity of 100 Scm^{-1} [17].

Conclusion

Intercalated polyaniline with protonic acids exhibits a variety of properties, depending upon stoichiometries

and functional groups associated with the dopant, due to electrostatic and van der Waals interactions involving either close contact, overlap, or both. There are still not enough reliable data to understand the electrochemistry and charge transport in polyaniline, because the overall redox process depends not only on hydrogen ion concentration but also on the nature of the counter anion.

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