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Electrosynthesis and properties of conducting polymers derived from aminobenzoic acids and from aminobenzoic acids and aniline

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Abstract

The electrochemical polymerisation of 2-, 3-, and 4-aminobenzoic acids and of mixtures of aniline and aminobenzoic acids in various ratios has been carried out by cyclic potential sweep in sulphuric acid solution. Polymers are formed in all cases and the rate of polymerisation is increased by the addition of aniline. The polymers formed have been characterised voltammetrically and evidence concerning the polymer structure and chemical composition has been obtained from IR spectroscopy and scanning electron microscopy. The results suggest that 2-amino-, 3-amino- and 4-aminobenzoic acid all form short-chain conducting polymers. Films from polymerisation of aniline and aminobenzoic acid mixtures show characteristics of both components and demonstrate the influence of aminobenzoic acids and their oligomers on the electrochemical and morphological properties of polyaniline formed by electropolymerisation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aminobenzoic acids; Polyaniline; Self doped polyaniline; Electrosynthesis; Electropolymerisation

1. Introduction

Polyaniline (PANI) has been extensively studied [1–3], but the number of investigations on polymers formed from substituted anilines has been less. PANI is commonly prepared as a film by electropolymerisation of aniline in acid solution on a variety of electrode substrates under controlled potential conditions.

An important limitation to the application of polyaniline derives from the fact that on increasing the pH during electrosynthesis and during use there is a significant decrease in the conductivity of PANI films in the conducting state and the rate of polymerisation is lower. These effects can be reduced to some extent by choice of appropriate counterions which enter the film (external doping), e.g. [4–8], in order to compensate the charge on the amino groups. As an alternative to the counterion strategy, co-polymerisation with different monomers has been suggested, e.g. with *para*-phenylenediamine [9] or dodecylbenzene sulphonic acid [10], which can lead to higher conductivities and higher film growth rates.

Another way of reducing the pH dependence is through substituted (self doped) polyanilines, achieved by introduction of the substituent into the pre-formed polymer or by polymerisation of substituted anilines. An example of the former is sulphonic ring-substituted polyaniline obtained by treatment of PANI with fuming sulphuric acid, leading to substitution in the *ortho*-position [11,12]. Most work, however, has involved the latter procedure using chemical or electrochemical polymerisation of different types of substituents in the aromatic ring. These substituents can be electron-donating — for example, alkylated (e.g. [13–18]) or alkoxy (e.g. [17,19–21]) — or electron-withdrawing such as chloro or nitro groups, e.g. [17,22,23], but lead to significantly lower conductivities than PANI itself.

The introduction of acidic groups as ring substituents influences the acidity constants of the amine groups and appears to offer advantages at less acidic pH values, since conductivity does not fall off dramatically with increase in pH as happens with PANI. This has been done with carboxylic [24,25], sulphonic, e.g. [24,26,27] and phosphonic [28] acid substituents.

A further synthetic variation, which appears to lead to partial self-doping, results from the polymerisation of mixtures of aniline and the substituted aniline. This procedure has been applied to many different cases [29–42], particularly to co-polymerisation of aniline and sulphonate-substituted

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aniline [35–39] and to aniline and 2-aminobenzoic acid [40–42], using chemical polymerisation initiators and electropolymerisation synthesis. In general, the influence of reaction conditions and the nature of the monomer on the course of the polymerisation has not been clarified.

In order to elucidate further the effect of the substituent on the resulting polymer, anilines with a carboxylic acid group substituent — 2-, 3- and 4-aminobenzoic acid (ABA) — have been polymerised alone and in mixtures with aniline. Their electrochemical properties are revealed mainly through cyclic voltammetry; IR spectroscopy and scanning electron microscopy have also been employed. Comparison is made with PANI films and with results obtained through the electropolymerisation of aniline/substituted aniline mixtures in various ratios. A systematic study of this kind has not, to our knowledge, been carried out on aminobenzoic acids.

2. Experimental

Aniline (Riedel-de Haen), anthranilic acid (2-aminobenzoic acid) (Aldrich), 3-aminobenzoic acid (Aldrich), 4-aminobenzoic acid (Aldrich), sulphuric acid (Riedel-de-Haen) and sodium sulphate were used as received, except for aniline which was distilled under a nitrogen atmosphere at reduced pressure, kept in the dark, and used within 3 days. The electrolyte was usually 0.5 or 1.0 M sulphuric acid, in some cases with the addition of sodium sulphate as will be detailed below. Tridistilled water was used to make all solutions. Experiments were carried out at 25°C.

The electrochemical cell for electropolymerisation and electrochemical characterisation contained a glassy carbon disc working electrode (GCE), diameter 0.5 cm, a platinum foil auxiliary electrode in a separate compartment connected by a glass frit and a Radiometer K401 saturated calomel electrode (SCE) as reference. Prior to use, the working electrode was polished with diamond lapping compound (Kemet International Ltd.) down to 1 μm particle size on a polishing cloth. Following this, it was held at a potential of +1.6 V versus SCE in sulphuric acid electrolyte for 6 min and then cycled in the potential range −0.5 to +1.5 V at a sweep rate of 50 mV s^{-1} for 15 min. After this treatment a reproducible voltammogram of the GCE was obtained showing much reduced background currents.

Electrochemical polymerisation was carried out by cyclic potential sweep in electrolyte solutions containing the monomer between potential limits to be specified below, normally at a scan rate of 50 mV s^{-1} for 30 cycles, using an analogue potentiostat constructed in this laboratory. All electropolymerisations were performed in sulphuric acid (0.5 and 1.0 M solutions). A 0.05 M solution of the aminobenzoic acid was used, whereas the solutions used for copolymerisation experiments had a total concentration of 0.1 M, i.e. 1:1-, 1:2- or 2:1-mixtures of the aminobenzoic acid with aniline in sulphuric acid were prepared.

The coated electrodes were transferred to a solution of pure electrolyte for electrochemical characterisation. Cyclic voltammetry was done using the same potentiostat; three cycles were necessary to establish steady-state conditions after which the voltammogram obtained was the same as that after the 30 cycles of polymerisation.

For electrochromism experiments, films were deposited on a optically transparent electrode (OTE) (indium-doped tin dioxide on a glass substrate of area 4 cm^2 — Phosphor Products Ltd.) using the same arrangement. The OTE was wiped with ethanol and washed with distilled water before use.

Scanning electron microscopy (SEM) was performed on films deposited on OTEs with a JEOL T 330 microscope fitted with a Tracor Northern Microanalysis Accessory. Electrodes were sputter-coated with a thin gold film before SEM was carried out (magnification 7500× at 20 kV).

For infrared (IR) measurements, pellets were pressed using KBr. The spectra were obtained on FT-IR instruments (Mattson Genesis Series). Polymer was obtained by carefully scraping the product from the electrode surface. Before scraping, adherent monomers were removed by cycling the coated electrode three times in 1 M H_2SO_4 electrolyte, the electrode was then washed with ethanol to remove any remaining sulphuric acid. Three polymer deposits were necessary when a scan rate of 50 mV s^{-1} was used during electropolymerisation, one was sufficient at 10 mV s^{-1} scan rate, when a voluminous powdery film was formed. The influence of the two different scan rates for polymer preparation on the IR spectra was tested, but no difference was found.

3. Results and discussion

In the following sections, results obtained will be presented and discussed, each with data both from the polymerised substituted aniline alone and from the polymerised mixture of substituted and unsubstituted anilines.

3.1. Electropolymerisation by potential cycling

The course of an electropolymerisation by potential cycling can, in principle, be influenced by several factors. These include the concentration of the electrolyte, the potential range (particularly the positive limit), the potential scan rate and the electrode material.

Preliminary experiments to estimate the effect of the electrolyte concentration showed that the electrolysis of aminobenzoic acids by themselves and in mixtures with aniline in 1.0 M sulphuric acid without addition of sodium sulphate, as in [43], gave the best results, i.e. the polymers formed faster than in 0.5 M sulphuric acid solution. This behaviour is in contrast to the preparation of PANI, where monomer to polymer conversion is only favoured up to 0.6 M H_2SO_4, because in more concentrated acid a higher number of ion pairs is said to be formed. Our experiments with polyaniline confirm these results by Nunziante and Pistoia [44].

Electrosynthesis of polyaniline was performed by potential cycling between 0.0 and 0.8 V versus SCE. To oxidise the aminobenzoic acids, a slightly higher potential than that used to oxidise aniline is necessary [45]. Different positive potential limits were investigated, it being found that a limit of between 0.9 and 1.0 V gave the best results in terms of film formation with minimum degradation products. Degradation was evidenced by the appearance of new peaks in the cyclic voltammograms and decrease in observed currents on cycling in pure electrolyte.

A polymer film is obtained not only from 2- and 3-, but also from 4-ABA at a glassy carbon electrode. In the latter case polymerisation cannot occur through the *para*-position as occurs with aniline. All films formed shiny strongly adherent deposits. No coloured electrolyte-soluble oligomeric products [17] were observed. However, whereas 2-ABA and 4-ABA formed clearly visible films on an optically transparent electrode (see below for SEM), only dark red streaks were visible during the electrolysis of 3-ABA.

In Fig. 1, cyclic voltammograms of films prepared from solutions of 2-ABA, 3-ABA and 4-ABA are presented. The CVs recorded during the electropolymerisation of the aminobenzoic acids differ in shape from those recorded for polyaniline under the same conditions: the first anodic peak corresponding to the insulating to conducting transition is shifted towards a higher potential. The peaks are also less clearly defined, as has been noted elsewhere [24].

Taking into account the literature data it seems probable that these films contain more oligomeric than polymeric material. This would explain the observed lower conductivity in films from aminobenzoic acids, as the conductivity decreases with a decrease in the chain length of the polymer [46].

For polyaniline, extensive studies have been made to associate the peaks observed during electropolymerisation with the proposed reaction mechanism. A detailed study by Shim et al. [47] suggests that a shoulder at ~0.33 V versus SCE (0.28 V versus Ag/AgCl/sat. KCl) might arise from the oxidation of oligomers whose chain lengths are between that of polyaniline and dimers, whereas a peak at ~0.50 V versus SCE [48] was identified as that of the oxidation of the head-to-tail dimer of aniline, 4-aminodiphenylamine. Concerning the origin of the peaks in the middle region of the CV opinions differ. It was concluded that the polyaniline growth reaction competes with degradation reaction pathways. Shim et al. [47] showed that *p*-aminophenol and *p*-benzoquinone, as the main product with a peak at ~0.5 V, are the oxidative degradation products of polyaniline and its oligomers. However, Geniès et al. [49] observed a peak at 0.45 V (versus Cu/CuF_2) together with a satellite peak while using phenazine or *m*-phenylenediamine as co-monomers, and thus, attributed these peaks to the formation of cross-linked polyaniline chains. A similar result was obtained by Mailhe-Randolph and Desilvestro [50] when they modified aniline films with *p*-phenylenediamine. Thus, the oxidation of several different species can be responsible for the peaks observed in the middle potential region of the CV during the

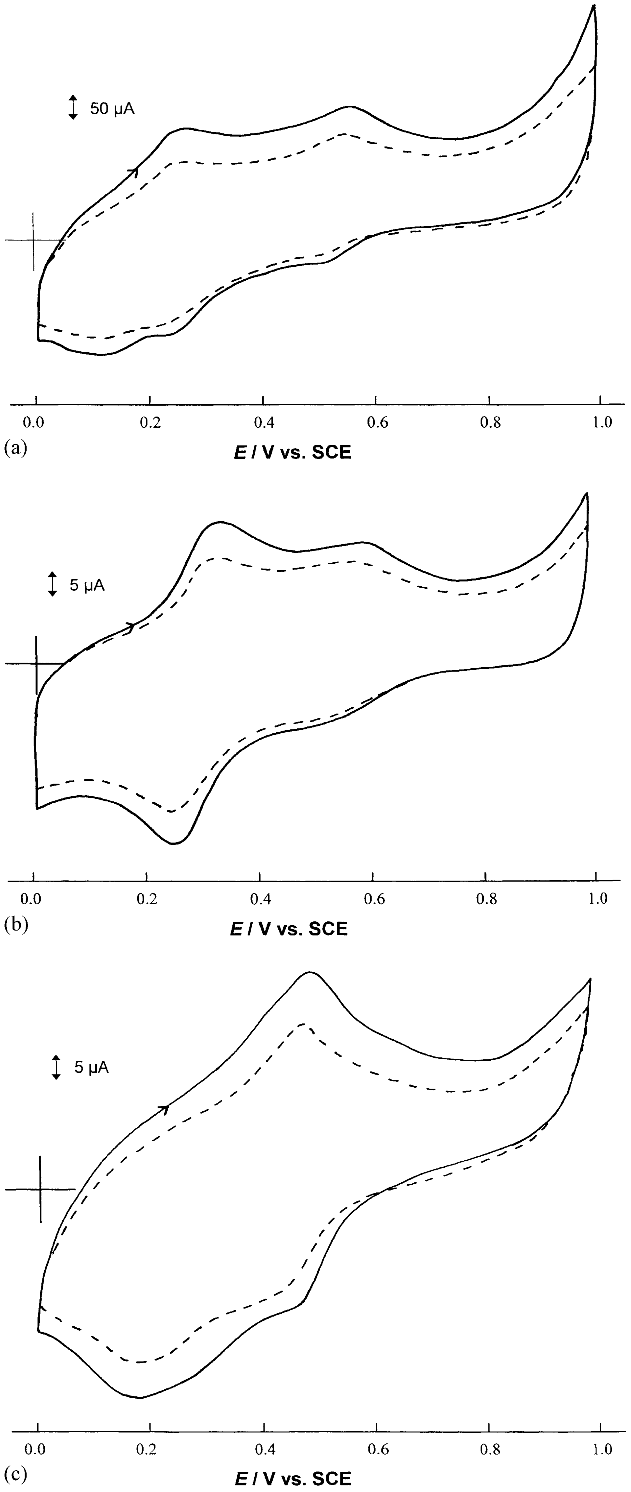


Fig. 1. Cyclic voltammograms of polymer films formed in 1.0 M H_2SO_4 on glassy carbon electrodes from: (a) 2-aminobenzoic acid; (b) 3-aminobenzoic acid; (c) 4-aminobenzoic acid after 30 cycles of polymerisation. The dotted lines show the voltammograms corresponding to the sixth cycle.

preparation of films from polyaniline. The following order of rising peak potentials should be expected: E_p (polymer) < E_p (oligomer) < E_p (benzoquinone) < E_p (dimer) < E_p (monomer). Similar considerations can apply to the substituted monomers.

Examination of the form of the cyclic voltammograms during polymer growth shows that the position of the peaks remains constant. However, the values of current have reached approximately 70–80% of their final 30-cycle values after five cycles of applied potential; this is the case for all three ABA monomers. It shows that the film formed is not highly conducting and is further evidence for the formation of oligomer species rather than long-chain polymer [46].

The influence of the scan rate on the CV profiles was studied by electropolymerising 2-ABA at scan rates ranging from 10 to 500 mV s^{-1}. While peak potentials and peak shapes were essentially unchanged, the relation between the relative heights of the different peaks varied with scan rate. The peaks only broadened at the highest scan rates tested ($v = 500$ mV s^{-1}).

Co-polymerisation of aminobenzoic acids and aniline in ratios 2:1, 1:1 and 1:2 was undertaken at glassy carbon and ITO electrodes. Some representative cyclic voltammograms are shown in Fig. 2 for 1:1 monomer mixtures and a positive potential limit of 0.9 V. It can be seen that the currents are significantly larger in the case of 4-ABA/aniline (Fig. 2c) as compared to the other two mixtures. This can be ascribed to the lack of competition in the polymer chain during electropolymerisation which thus becomes more similar to that of aniline. Differences between the substituted monomers are more evident than at 1.0 V potential limit.

Table 1 shows values of the peak current for the first anodic peak from the CVs of the aminobenzoic acids by themselves and in mixtures with aniline, for positive potential limits of 1.0 V. As discussed above, the rate of film growth is much lower for the polymerisation of substituted anilines than for aniline. Based on an analysis of peak currents, a 2:1 and a 1:1 mixture of the monomers leads to film growth very similar to that of polyaniline, whereas ABA inhibits film growth at a ratio of 1:2 aniline/ABA. However, the morphology is rather different from PANI in all cases — scanning electron microscopy results are shown below.

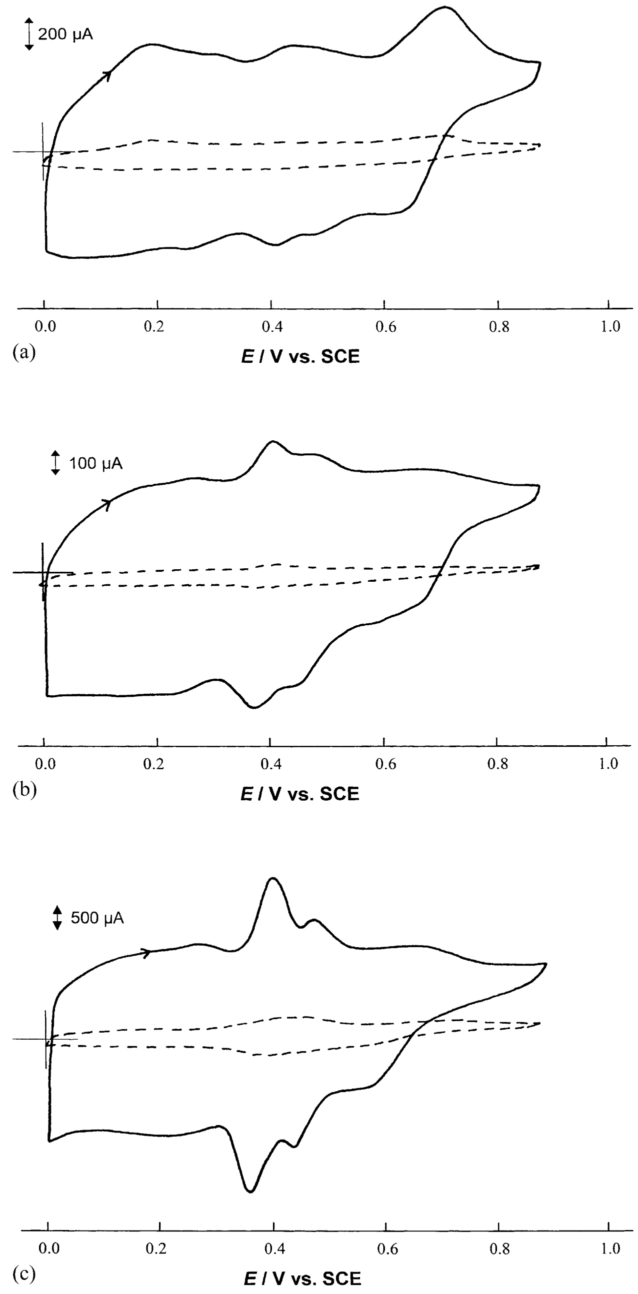


Fig. 2. Cyclic voltammograms of polymer films formed in 1.0 M H_2SO_4 on glassy carbon electrodes from 1:1 mixtures of aniline and (a) 2-aminobenzoic acid; (b) 3-aminobenzoic acid; (c) 4-aminobenzoic acid. The dotted lines show the voltammograms corresponding to the sixth cycle.

Table 1
Cyclic voltammetry of polyaniline and co-polymers from anilines with aminobenzoic acids (ABA), for different monomer ratios formed at glassy carbon electrodes[a]

	One monomer	Two monomers (aniline/ABA ratio)		
		2:1	1:1	1:2
Aniline	2.25	–	–	–
2-ABA	0.05	2.43	2.65	0.19
3-ABA	0.03	2.35	2.70	0.90
4-ABA	0.035	2.40	2.90	1.05

[a] Peak currents (mA) for the first anodic peak after 30 cycles at 50 mV s^{-1}, positive potential limit 1.0 V.

As for polymerisation of the substituted monomers alone, further information can be gained from examination of the rate of variation of currents in the cyclic voltammograms during film growth. Fig. 2 shows the cyclic voltammogram corresponding to the sixth cycle as well as that of the film after 30 cycles. In contrast to Fig. 1, significant polymer film growth continues during the whole 30 cycles. More detailed analysis shows that for 1:2 and 1:1 mixtures, after an initial parabolic growth, there is a linear variation of current with time. For 2:1 mixtures, the initial parabolic growth is up to about three cycles and linear growth ends at ~25 cycles, when the growth rate begins to fall off. These alterations with time (and therefore, film thickness) have often been observed for polyaniline, e.g. [46].

3.2. Chromatic properties

The visual aspect of the as-formed films was noted. Except for the colour at a potential of −0.2 V, all observations were made during formation of the film on the conducting glass surface.

Two kinds of reaction are connected with the electrochromism of polyaniline. One, at 0.15 V versus SCE, is a proton and electron addition/elimination reaction, accompanied by a colour change from yellowish green to dark green [51]. The other is related to insertion/elimination of electrolyte anions into/from the polymer film [52]. Since this latter reaction involves anion exchange, it is not surprising that different colours have been observed for oxidised polyaniline, prepared under different conditions, at higher potentials [6,53].

No coloration was observed in films prepared from the aminobenzoic acid alone. The films made from mixtures showed the same variation in colour observed for polyaniline itself, and the colours intensified with film thickness.

3.3. Morphology

Fig. 3 shows several SEM micrographs from different electropolymerisations. Fig. 3a and b show poly(2-ABA) and poly(4-ABA) formed in 1.0 M sulphuric acid. Contrary to unsubstituted polyaniline formed in sulphuric acid solution, there appears to be no background film, and film growth occurs at specific sites to give a dendrite-like appearance. The small dot-like structures seen in Fig. 3b are attributed to residual sulphuric acid (this was checked by microanalysis) and become insignificant as the film grows in thickness. Similar globular structures have been observed in the initial deposits of polyaniline from hydrochloric acid, although these globular structures were said to derive from polyaniline itself and not from the solvent [50,54]. Electrochemically-prepared polyaniline is generally agreed to consist of less densely packed and more fibrous structures for thick films, while thin films have non-fibrillar textures [55]. This is explained by a change in the mechanism of deposition of polyaniline — when the film becomes sufficiently thick, direct access of unreacted monomers to the electrode surface is inhibited [56]. The difference in morphology between films from aminobenzoic acids and from polyaniline reflects the different monomer reactivity; less reactive intermediates tend to be more selective and form short oligomer chains, which may have a crystalline nature. Additionally, as the growing polymer chain is more easily oxidised than a monomer, the (compared to aniline) less reactive ABA monomer would preferably react at an already-growing polymer chain rather than at the electrode surface leading to formation of linear polymers [7,57,58].

The SEM micrographs from co-polymerisations with aniline all exhibit a covered substrate. Fig. 3c and d show the morphology of films derived from 2-ABA and 3-ABA in a 2:1 mixture with aniline. Both polymers are characterised by a duplex film consisting of a compact background film covered by a second structure, which is more fibrous for the 2-ABA copolymer. The texture of 3-ABA copolymer represents something between that of the 2-ABA copolymer and the 4-ABA copolymer (Fig. 3e). In the copolymer derived from 4-ABA, the nuclei coalesce to give very homogeneous films with some cracking, whereas the others have a heterogeneous nature.

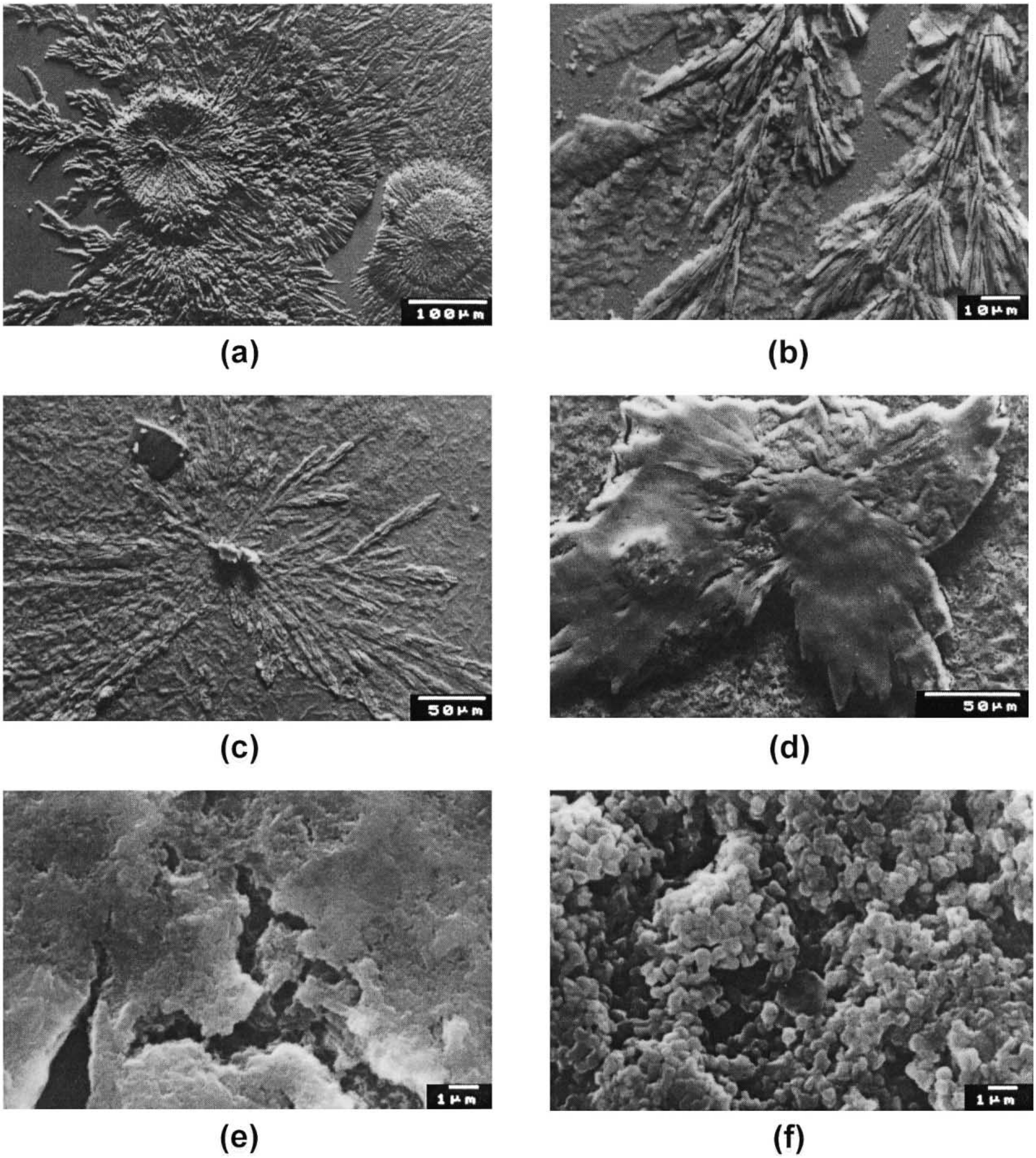
All SEM micrographs of the co-polymerisations with aniline contain characteristics common to both poly(aminobenzoic acid) and polyaniline textures. The polymer structure becomes more dense and contains fewer fibrillar elements with increasing aniline concentration in solution.

There are some evident differences between "1:1 copolymers" formed from aniline and the various ABAs, and there is also some influence of scan rate. Under the normally employed conditions of 50 mV s^{-1} scan rate, whilst 3-ABA and 4-ABA mixtures with aniline give rise to fibrous features on top of a background film, the copolymer from 2-ABA resembles the highly porous morphology typical for pure polyaniline prepared in sulphuric solution (Fig. 3f) [44]. The use of a lower scan rate of 10 mV s^{-1} leads to a more homogenous film for all three aminobenzoic acid copolymers, closely resembling that for polyaniline under the same conditions.

3.4. IR spectroscopy

IR spectra of polymer films formed on glassy carbon from 1:1 mixtures of aminobenzoic acid and aniline are shown in Fig. 4. Absorption peaks at ca. 3400, 2929, 2609, around 1600, 1320, 1287, 1176, 1069, 1006, 884, 850 and two bands below 700 cm^{-1} are common for all spectra, although with different intensities. Relatively strong absorption peaks between 900 and 680 cm^{-1} arise from out-of-plane bending of a C–H bond [59]. Peaks in this region can be used to determine the substitution pattern of an aromatic ring. Polyaniline itself shows only one band, as is expected for 1,4-disubstituted aromatic compounds, that is at 814 cm^{-1} [4,53] (at 815 cm^{-1} for 4,4-diaminodiphenylamine sulphate [60]), while in all copolymers absorption bands at 884 and 850 cm^{-1} were found. Therefore, the films contain probably not only linear elements derived from coupling in 1- and 4-position, but also branched structures derived from a coupling in 1-, 3- and 5- or in 1-, 2- and 4-positions of the aromatic ring [49].

The peaks between 3500 and 3300 cm^{-1} (3425 and 3314 cm^{-1} for the 2-ABA copolymer, 3388 cm^{-1} for the 3-ABA copolymer and 3417 cm^{-1} for the 4-ABA copolymer)



(a) (b) (c) (d) (e) (f)

Fig. 3. Scanning electron micrographs of polymeric films formed on ITOs in sulphuric acid solution from (a) 2-aminobenzoic acid; (b) 4-aminobenzoic acid; (c) 2-aminobenzoic acid/aniline 2:1; (d) 3-aminobenzoic acid/aniline 2:1; (e) 4-aminobenzoic acid/aniline 2:1; (f) aniline.

correspond to N–H bond stretching. Broad absorption peaks between 2700 and 2250 cm^{-1} can be ascribed to ammonium salts. They are clearly visible in the IR spectra of films derived from mixtures of aniline with 2-ABA (2627, 2484 and 2365 cm^{-1}), while in the spectrum from the 3-ABA mixture (2609 cm^{-1}) they are less pronounced.

Peaks in the region between 1690 and 1490 cm^{-1} correspond to the deformation of different types of N–H bonds. Absorption above 1600 cm^{-1} suggests the existence of carbon-nitrogen double bonds, while weak absorption between 1580 and 1490 cm^{-1} is typical for secondary amines. All IR spectra of the mixtures show some absorption in the latter region, which is feasible since all films were collected at 0.0 V in the reduced state of the polymer.

The peaks at 1174 and 613 cm^{-1} derive from the presence of sulphate ions in the film [61], as sulphuric acid was used as electrolyte during preparation and characterisation of the polymer films.

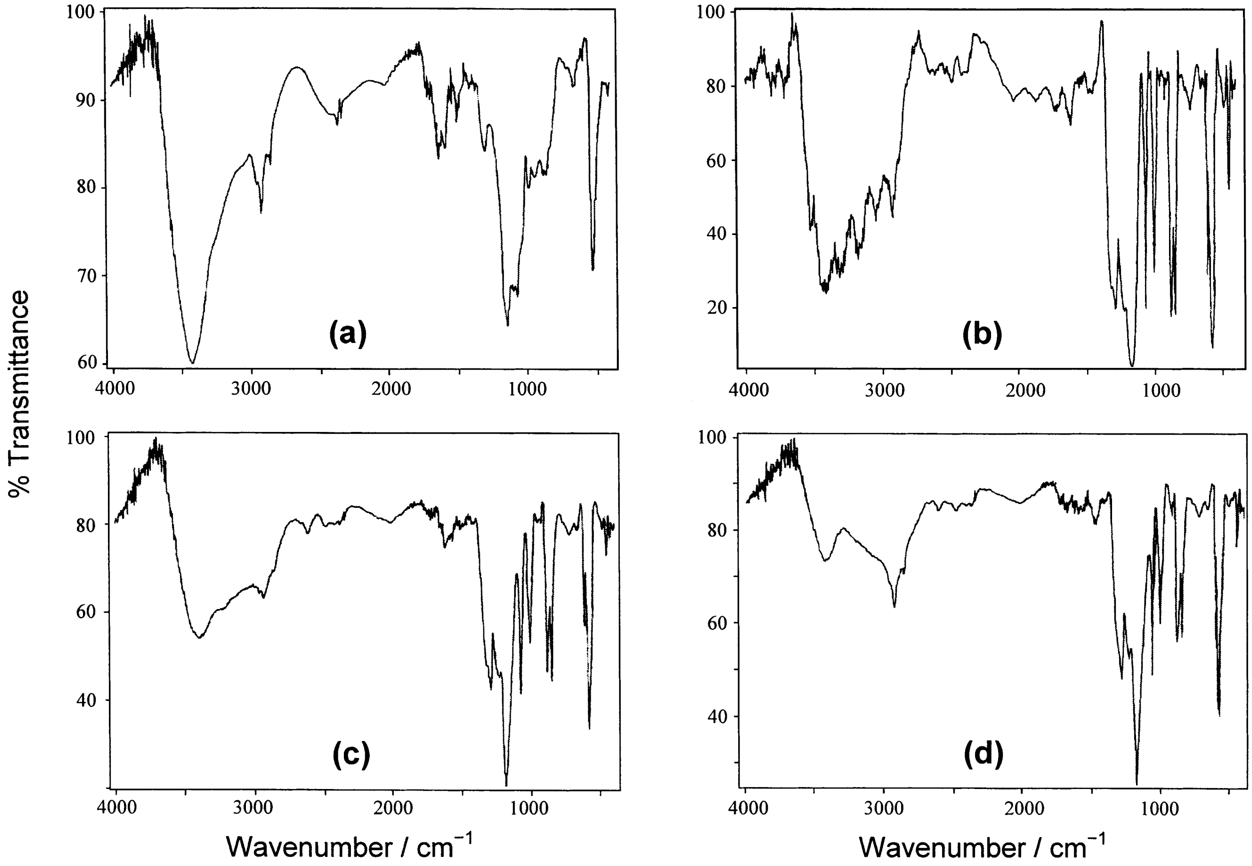


Fig. 4. Infrared spectra of polymer films formed in 1.0 M H_2SO_4 at glassy carbon electrodes from (a) aniline, and from 1:1 mixtures of aniline and (b) 2-aminobenzoic acid; (c) 3-aminobenzoic acid; (d) 4-aminobenzoic acid.

Carboxylic acid groups give rise to strong absorption bands at ca. 1700 cm^{-1}. These bands are absent in the spectra which suggests that the incorporation of substituted monomer is small. Nevertheless, the spectra do show differences with respect to polyaniline so that the presence of the substituted monomer in solution clearly alters the growth pattern of the polymer film.

The scan rate had no influence on the shape of the IR spectra of the films.

3.5. Polymerisation mechanism

There is some disagreement concerning the nature of suitable monomers for polymerisation [17,24] and the effect that substituents in the aromatic ring of aniline have on the backbone of the resulting polymer [62]. Although, in principle, there is agreement as to the nature of the attacking species, there seems to be no model that takes both electronic and steric factors into consideration to explain the reactivity of substituted anilines.

The reactivity of the incipient cation is probably most important for the formation of a polymer [63]. Due to the electron-withdrawing effect of the carboxyl group, the aromatic system of an aminobenzoic acid is deactivated with respect to an electrophilic substitution reaction. Therefore, the growth rate of the polymer from an aminobenzoic acid should be slower than that from aniline, as observed here. This electronic effect is also responsible for the higher potential needed to oxidise the aminobenzoic acid monomers, compared to aniline [45].

It is known that groups with negative inductive and mesomeric effects direct any new substituent to the *meta*-position. For 2-ABA this implies preferred coupling in the 4-position of the aromatic system, i.e. in the *para*-position relative to the amino group. Therefore, a polymer with 1,4-coupling as occurs for polyaniline is possible, though with different properties. Besides this electronic effect, steric effects also have to be taken into consideration. In the case of the polymerisation of 3-ABA, the predicted 1,5-coupling is sterically hindered — in fact, at ITO, only coloured oligomeric product, but no polymer, was formed.

Following these rules, 4-ABA will preferably couple in the *meta*-position to the acidic group, i.e. in the *ortho*-position relative to the amino-group, yielding a polymer in which the monomers are connected via their 2- and 6-positions. Indeed, *ortho*-coupling was postulated by Geniès for the polymerisation of *p*-fluoraniline [55], and Rodrigue et al. [64] found cross-linking in heat-treated polyaniline. On the other hand, substituted anilines with *para*-substituents such as methoxy, chloro, or carboxy groups, are said to react under acidic conditions via head-to-tail coupling to give the corresponding 4′-substituted *p*-aminodiphenylamines and unspecified polymer films [65,66]. Under such conditions, the *para*-substituent is predicted to be eliminated: in the case of 4-ABA the leaving group should be CO_2. Although in our experiments, no gas generation could be observed on the surface of the electrode, although the quantity would probably not be detectable.

Such results can be contrasted with cases involving other types of substituent. For example, the electropolymerisation of toluidines (methylanilines) was investigated by several authors, e.g. [17,43]. The methyl group, through its electron-donating effect, activates the aromatic system and directs a new substituent into the *ortho*- and *para*-position. Since the *para*-position is blocked in *p*-toluidine, polymerisation is hindered in this sterically preferable position. Thus, only *o*- and *m*-toluidine gave uniform and insoluble polymer films, while for *p*-toluidine gave a trimer derived from the *ortho*-coupling of three toluidine rings [67].

Taking all this into consideration it is possible to explain the fact that 2-ABA, 3-ABA and also 4-ABA are able to form conducting polymers, and experimental evidence has been presented in the previous sections. The rate of polymerisation is slow and many short chain oligomers may well be formed. Regarding polymerisation of aniline/ABA mixtures, although we have no direct evidence of incorporation of each monomer in the same polymer chain, the morphological studies demonstrate that the presence of the aminobenzoic monomer does influence the degree of branching, and therefore, the properties of the polymer. Cyclic voltammograms are different from those from pure polyaniline. This may be due to incorporation of ABA polymers rather than co-polymerisation, as demonstrated by the IR data.

4. Conclusion

The rate of polymer film growth resulting from electropolymerisation of aminobenzoic acids is much lower for the polymerisation of substituted anilines than for aniline; substitution radically alters the nature of the resulting polymer. Properties such as conductivity and voltammetric behaviour are different from polyaniline. Polymerisation of *para*-substituted anilines occurs to a similar extent as for *ortho*- and *meta*-substituted anilines.

Films from co-polymerisation of aminobenzoic acids and aniline show electrochemical and other properties that are characteristic both for poly(aminobenzoic acids) and polyaniline. Therefore, it can be deduced that aminobenzoic acid and poly(aminobenzoic acid)s are incorporated in these polyaniline films, probably not to a great extent although sufficient to alter the physical and chemical properties. Experiments are planned to determine the exact structure of the polymer films obtained in this way.

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