Comparison of different synthetic routes for sulphonation of polyaniline

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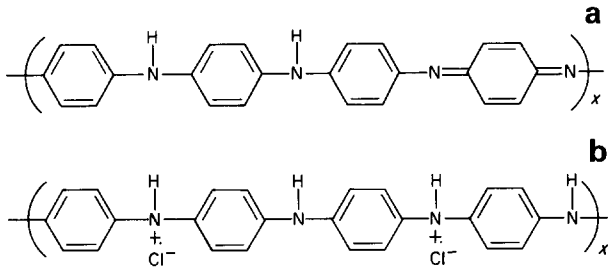
Polyanilines containing sulphonic groups covalently bonded to the backbone were synthesized from parent polyaniline via sulphonation of the polymer utilizing differing sulphonation agents and differing means. The sulphonation conditions were studied as a function of several parameters including sulphonation time, starting forms of the precursor polymer, presence of oxidizer $[(NH_4)_2S_2O_8]$ and temperature. The sulphonated polyanilines were characterized by *FT*i.r., elemental analyses, d.c. conductivity and electrochemical methods. It was found that using fuming sulphuric acid as the sulphonation agent gave both higher conductivity and higher sulphonation level for sulphonated polyaniline than implementation of other sulphonation agents and means.

(Keywords: polyaniline; sulphonation; synthesis)

INTRODUCTION

The polyaniline family of polymers has been under intense study because of its facile chemistry and ability to be both a protonic acid and oxidatively or reductively doped to a highly conducting state[1,2]. The ideal emeraldine base (EB) oxidation state of polyaniline contains equal numbers of alternating amine and imine repeat units (*Scheme 1a*)[2,3]. When EB is doped by a protonic acid, the protonation occurs preferentially at the imine nitrogen sites[2], as for example shown for the emeraldine hydrochloride salt (ES) in *Scheme 1b* (polysemiquinone or polaron lattice form).



Scheme 1

Recently sulphonated polyaniline (SPAN), the first self protonic acid doped polyaniline, was reported[4]. In order to establish the relationships between a variety of synthesis variables and characteristics of this interesting polymer, results are presented on the effects of the type of sulphonation agents, sulphonation time and precursor polymers on the resulting SPANs.

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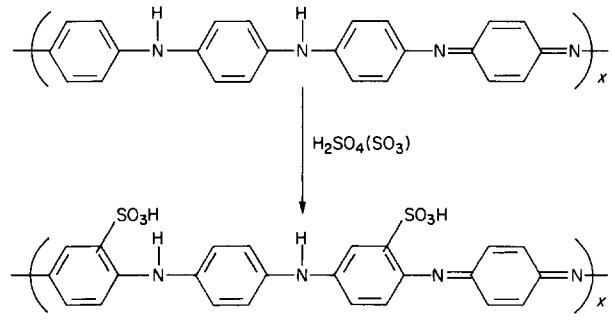
EXPERIMENTAL

Several sulphonation methods can be applied to synthesize SPAN. The synthetic routes listed below have been carried out in this laboratory.

Route 1. Sulphonation of solutions of EB in fuming sulphuric acid

EB was synthesized by using a previously described method[5]. The self protonic acid doped polyaniline was synthesized by sulphonation of EB in fuming sulphuric acid[4]. In a typical procedure, EB (0.5 g) was sulphonated by dissolving EB powder in 40 ml of ~30% fuming sulphuric acid which was previously cooled to ~5°C with constant stirring in ice-water (*Scheme 2*).



Scheme 2

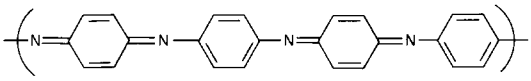
After addition of the polymer, the solution was stirred for 10 min in the ice bath. Subsequently, the solution was removed from the ice bath and allowed to reach room temperature while stirring was continued (~5–10 min). The colour of the solution changed from dark purple to

dark blue during ~0.5 h at room temperature. The solution was then slowly added during ~20 min to methanol (200 ml) to precipitate most of the product, the temperature during this step being held between 10°C and 20°C by an ice bath. The green powder was then collected on a Buchner funnel and the precipitate cake was washed at least 10 times with ~50 ml portions of methanol until the filtrate had a pH of 7 when tested by wet pH paper. It was then permitted to remain under suction for ~10 min; the filter cake was then transferred on the filter paper to a vacuum desiccator and dried under dynamic vacuum for 24 h at temperatures between room temperature and ~30°C.

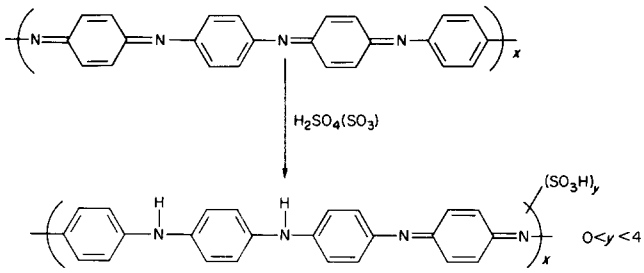
The above procedure was repeated at room temperature but differing periods of sulphonation time were used to determine optimum sulphonation conditions.

Route 2. Sulphonation of solutions of pernigraniline base and salt in fuming sulphuric acid

Polyaniline in its pernigraniline oxidation state was used as a precursor polymer in order to determine if the sulphonation level of polyaniline could be increased. The procedure described in route 1 was repeated. Pernigraniline base

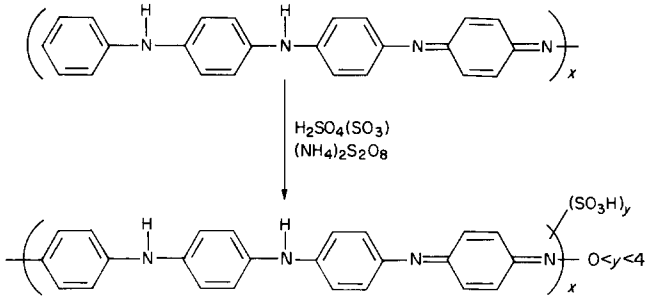


was either used directly (as was EB in route 1), see *Scheme 3*, or alternatively, pernigraniline salt was used



Scheme 3

as the starting material for sulphonation, being obtained by converting emeraldine salt in ~30% fuming sulphuric acid in the presence of a strong oxidizer such as ammonium persulphate, $(NH_4)_2S_2O_8$ (*Scheme 4*).

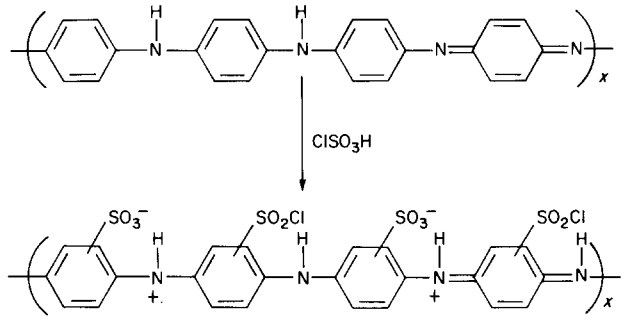


Scheme 4

The procedure for converting emeraldine salt to pernigraniline salt is as follows: $(NH_4)_2S_2O_8$ (1.25 g, 5.5×10^{-3} mol) dissolved in 10 ml of ~30% fuming sulphuric acid was added into a flask containing EB (0.5 g, 5.5×10^{-3} mol, treat $C_6H_{4.5}N$ as a repeat unit) in 40 ml of ~30% fuming sulphuric acid, which was previously cooled to ~5°C with constant stirring in an ice-water bath. The colour of the solution changed from dark purple to dark green–blue within 0.5 h. This procedure was repeated three times with the mixture stirred at room temperature for 0.5, 1 and 2 h, respectively. In each case, the sulphonated polymer was precipitated, washed and dried by repeating the procedure given in route 1.

Route 3. Sulphonation of solutions of EB using chlorosulphonic acid

Besides using fuming sulphuric acid as a sulphonation agent, EB can also be sulphonated by dissolving it in chlorosulphonic acid, $ClSO_3H$. Fine ground EB powder (0.2 g) was dissolved in 2 ml of $ClSO_3H$ (*Scheme 5*).

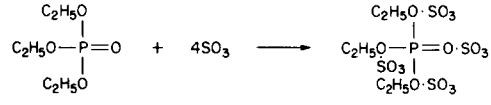


Scheme 5

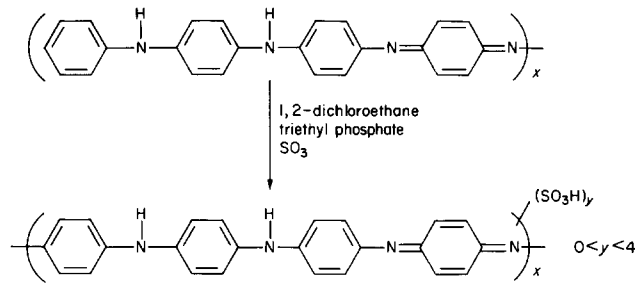
The solution was either stirred at room temperature for 72 h or at 100°C for 1 h. The sulphonated polymer was then precipitated in methanol and washed completely with it. The polymer cake was then transferred into a vacuum oven and dried at 50°C for 24 h.

Route 4. Sulphonation of dispersion of EB

Another known sulphonation method[6] is to disperse powders of the precursor polymer in a suitable solvent which contains a sulphonation agent. For example, a typical sulphonation procedure for synthesizing SPAN utilizing this method is to use a sulphur trioxide/triethyl phosphate complex:



as a sulphonation agent[6], in 1,2-dichloroethane solvent (*Scheme 6*).



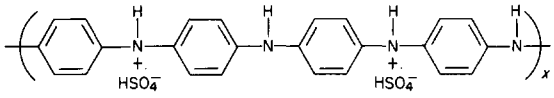
Scheme 6

A 4/1 sulphur trioxide/triethyl phosphate complex in 1,2-dichloroethane solution was prepared by adding 2 ml (3.8 g, 0.048 mol) of sulphur trioxide to a solution of 2 ml (2.2 g, 0.012 mol) of triethyl phosphate in 20 ml

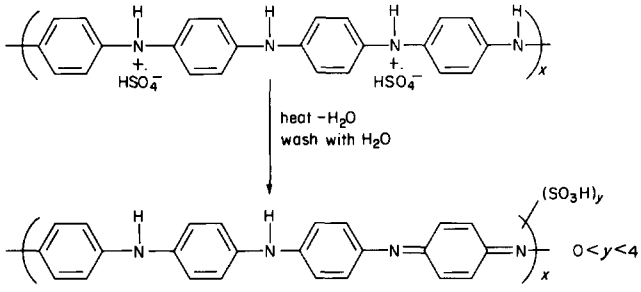
of 1,2-dichloroethane. The temperature of the solution was kept below 25°C by adding the sulphur trioxide slowly and by cooling the solution with an ice bath. Meanwhile, EB powder (1.0 g) was dispersed in 40 ml of 1,2-dichloroethane. The sulphonation solution was then added dropwise into the precursor dispersion solution during 20 min with ice-water cooling. The resulting dispersion was further stirred for different times with ice bath cooling and subsequently filtered to separate the polymer, which was then washed with 1,2-dichloroethane and dried at 50°C under vacuum for 24 h.

Route 5. Sulphonation via heating of emeraldine sulphate salt

Since EB can be doped by a protonic acid to form emeraldine salt, sulphonation of EB can be achieved by heating the salt of emeraldine hydrogen sulphate



which is EB doped by sulphuric acid, under N_2 (*Scheme 7*).



Scheme 7

Emeraldine hydrogen sulphate (1 g) was placed into an oven which was preheated to 120 or 130°C. The flow rate of N_2 was set to 1.4 l min^{-1}. After a set period of time the heating was stopped and the oven was cooled to room temperature while the flow of N_2 was continued until the sample was removed from the oven.

RESULTS AND DISCUSSION

Route 1

It is very important to wash sulphuric acid completely out of the SPAN powder, otherwise evaporation of the solution from the SPAN powder could result in the formation of a thin layer of concentrated sulphuric acid on the surface of each powder particle. This is expected to affect many of its properties.

A conducting polymer can be derived from the emeraldine oxidation state of SPAN which has the composition[7]:

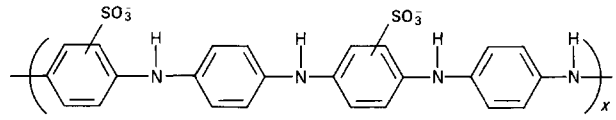
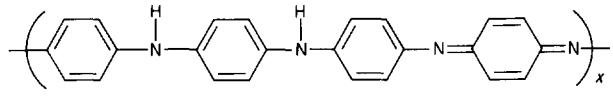


Table 1 gives elemental analyses data for SPAN prepared via route 1 using differing sulphonation times. The formulae given are those which best fit the analytical data.

For all samples the atomic ratio of oxygen to sulphur is higher than the expected value of 3. The most likely explanation is the presence of water molecules associated with the polymer chain. This is consistent with our X.p.s. studies[8] where we observed excess oxygen per two ring repeat unit in SPAN, presumably present as water.

Elemental analyses for hydrogen are not sufficiently accurate to determine the degree of protonation (doping level) of the polymer. However, it can be safely assumed that each SO_3^- group found in the polymer will be accompanied by one proton. Hence the overall extent of protonation can be assessed accurately from experimental sulphur and nitrogen elemental analyses. It is assumed that only imine nitrogen atoms are protonated[5]. In the as-synthesized SPAN analyses show that the atomic ratio of nitrogen and sulphur is ~2, in other words, ~50% of the total number of nitrogen atoms present in the polymer are protonated.

Generally, the sulphonation level tends to increase with increasing sulphonation time. We found that long sulphonation times do not, in fact, favour the further sulphonation of EB. *Table 1* shows typical results for the sulphonation of EB for various sulphonation times at standard conditions (described in the previous section). It shows that the sulphonation level, i.e. the atomic ratio of sulphur and nitrogen, was virtually independent of the sulphonation time over periods from 0.5 to 24 h. The mean value for the ratio is 0.50; the average deviation from the mean is ± 0.02. Hence the per cent protonation (doping level), i.e. the per cent of the total number of nitrogen atoms in each repeat unit



which are protonated is $50 \pm 2\%$. However, *Figure 1* shows that the maximum conductivity was observed at a sulphonation time of 1–2 h; decreased conductivities were found beyond this time. These results indicate that the sulphonation occurred relatively rapidly and was essentially finished within 2 h. Prolonged sulphonation

Table 1 Elemental analyses for EB sulphonated in fuming sulphuric acid

Time (h)	C	H	N	S	O[a]	S:N	Formula
—[b]	51.61	3.94	10.04	11.47	22.94	0.50	$C_{12}H_9N_2SO_3(H_2O)$
0.5	51.72	4.55	9.93	11.44	22.36	0.49	$C_{12}H_{12.6}N_{1.98}S_{0.98}O_{3.8}$
1	52.12	3.98	10.13	11.19	22.58	0.48	$C_{12}H_{11}N_2S_{0.96}O_{3.8}$
2	51.35	4.02	9.85	11.15	23.63	0.50	$C_{12}H_{11.2}N_{1.96}S_{0.98}O_{4.2}$
3	49.98	4.01	9.33	11.16	25.52	0.52	$C_{12}H_{11.6}N_{1.92}SO_{4.6}$
10	50.81	4.21	9.61	11.60	23.77	0.52	$C_{12}H_{12}N_{1.96}S_{1.04}O_{4.2}$
24	48.17	4.3	9.27	10.43	27.83	0.49	$C_{12}H_{13}N_{1.98}S_{0.98}O_{5.2}$

[a] By difference
[b] Calculated for $C_{12}H_9N_2SO_3(H_2O)$

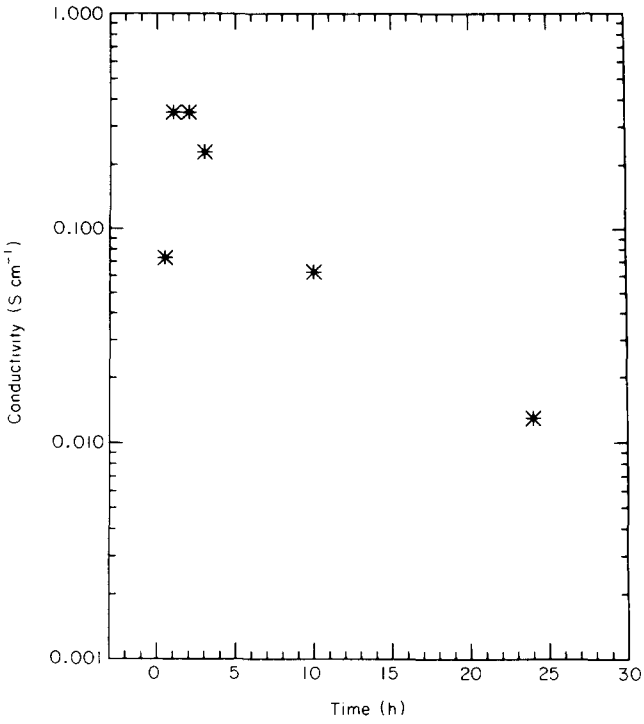


Figure 1 Conductivity as a function of sulphonation time for polymers synthesized by route 1

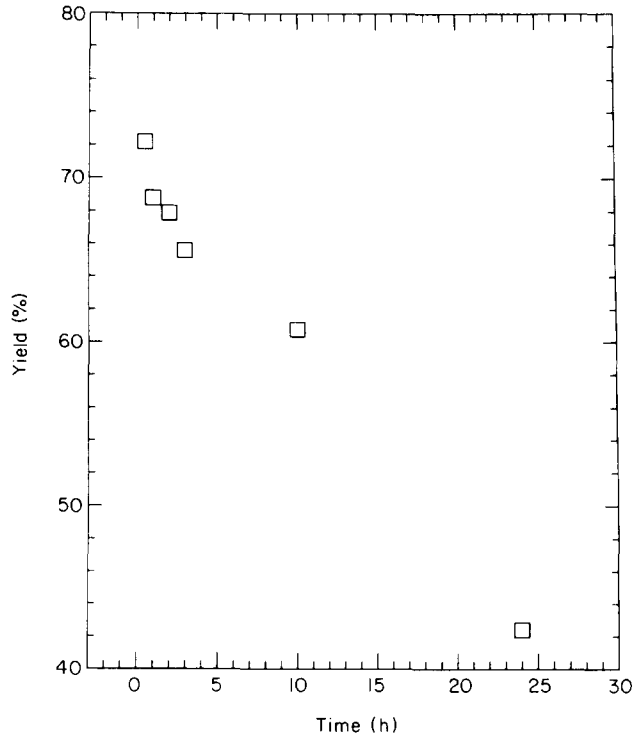


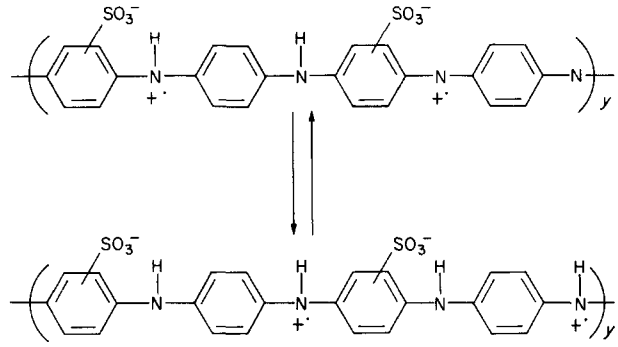
Figure 2 Yield as a function of sulphonation time for polymers synthesized by route 1

periods seemed to cause a slow hydrolysis of EB in fuming sulphuric acid resulting in a decrease of conductivity.

It is implicit from the structure of SPAN that under the experimental conditions employed, only half the rings are sulphonated. This is consistent with the fact that only half the rings need to be sulphonated in order to produce the stable polysemiquinone form of the polymer. Indeed, additional sulphonation and consequent protonation of amine nitrogen atoms would convert some of the $-(NH)-$ to $-(NH_2^+)-$ groups and hence destabilize the polymer by reducing the extent of its π conjugation.

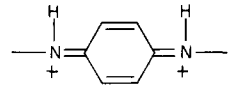
Figure 2 reveals that the yield of SPAN, calculated according to *Scheme 2*, was sensitive to the sulphonation time. The yield decreased almost linearly with increasing sulphonation time probably because the fuming sulphuric acid, which is a strong oxidant, promoted decomposition/depolymerization of SPAN and resulted in a large amount of methanol-soluble material.

It has been known for more than 80 years[9] that polyaniline in the emeraldine oxidation state in aqueous acids is the most stable form in the polyaniline family. This should be also true for SPAN as suggested schematically by the resonant structure of the doped form shown in *Scheme 8*.

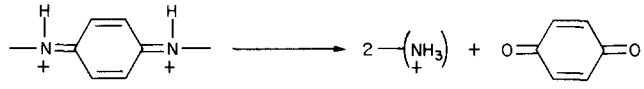


Scheme 8

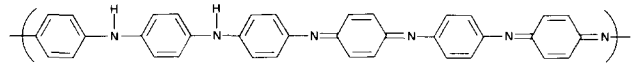
The resonance between the oxidized and reduced repeat units permitted in the protonated emeraldine oxidation state (i.e. the polysemiquinone radical cation), derived from equal numbers of oxidized and reduced repeat units, eliminates the presence of the



groups which are known to hydrolyse readily in aqueous acid[10,11], namely



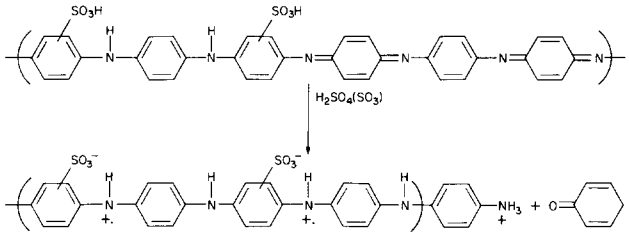
However, in addition to being a sulphonation agent, fuming sulphuric acid is also a strong oxidant. Prolonged sulphonation may raise the oxidation state of emeraldine to higher levels causing the polymer to hydrolyse more readily. By way of an example, two oxidized repeat units are placed adjacent to each other in the reactant polymer in *Scheme 9* to represent an excess of the oxidized



Scheme 9

repeat units above that required by the emeraldine oxidation state (which contains equal numbers of oxidized and reduced repeat units). The adjacent oxidized repeat units would reduce the possibility of the resonance in the vicinity of these groups and hence, in this case, hydrolysis would occur until excess oxidized repeat units

have been removed and the emeraldine oxidation state has been regained. This process will reduce the length of a given polymer chain, with the introduction of the chain terminating groups shown in *Scheme 10*. This accounts for the yield of the sulphonation product decreasing as the sulphonation time is increased.



Scheme 10

Thus, for maximum reaction yield, sulphonation level and conductivity, it can be concluded that the sulphonation of EB in ~30% fuming sulphuric acid during 1–2 h is best and that long sulphonation times are not necessary, and, in fact, are harmful. On the other hand, a sulphonation time of 0.5 h, even though it gave highest yield, was not sufficient to achieve maximum conductivity possibly due to the random substitution of sulphonic groups on the phenyl rings during the initial sulphonation, which causes increased disorder in the polymer. The sulphonation should be executed at no higher than room temperature and for no longer than ~1.5 h. All polymers synthesized in this route dissolve in basic aqueous solutions.

Route 2

Since only half the rings of EB need to be sulphonated in order to produce the stable polysemiquinone form,

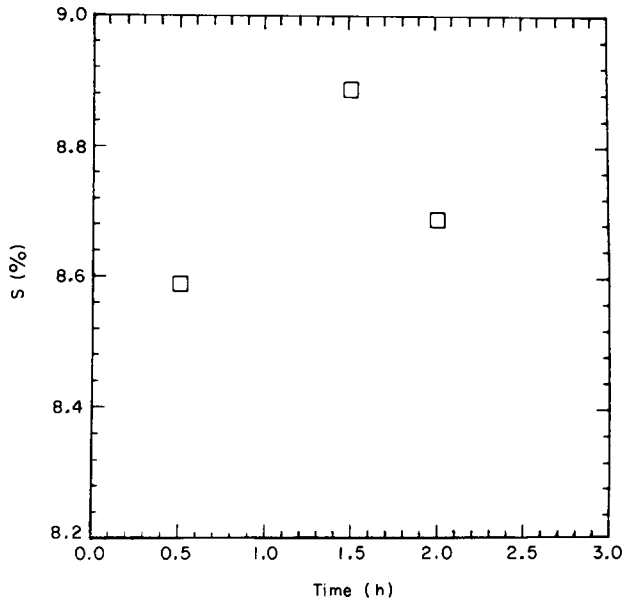
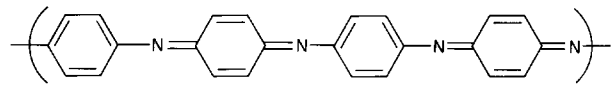


Figure 3 Sulphur content as a function of sulphonation time for polymers synthesized by route 2 starting with EB (see text)

excess sulphonation and consequent protonation of amine nitrogen would convert some of the amine to $-(NH_2^+)-$ groups and hence destabilize the polymer by reducing the extent of its π conjugation. Therefore, it is reasonable to sulphonate pernigraniline, which has fully oxidized repeat imine units, to increase the sulphonation level.

Figure 3 shows the sulphur level in the polymer chain as a function of the sulphonation time in the presence of $(NH_4)_2S_2O_8$ which can oxidize the polymer from the emeraldine oxidation state to the pernigraniline oxidation state in concentrated sulphuric acid[12]. The sulphonation level changes little and the sulphur content is not as high as those obtained in route 1. This can be explained by the fact that quinoid structures undergo hydrolysis more easily, as mentioned for route 1; also sulphonation is an electrophilic reaction, hence the presence of more quinoid units deactivates the sulphonation process. The contribution of the latter cause can be verified by the sulphonation of pernigraniline



directly in ~30% fuming sulphuric acid. *Table 2* gives the elemental analyses for the sulphonation of EB for 0.5 h in the presence of $(NH_4)_2S_2O_8$ and of pernigraniline for 1 h. Even though the sulphonation level for pernigraniline is higher than that of EB in the presence of $(NH_4)_2S_2O_8$, it is not as high as that of EB sulphonated in the absence of $(NH_4)_2S_2O_8$ utilizing route 1 (see *Table 1*). This supports the argument that the presence of quinoid units is not in favour of the sulphonation. Emeraldine is the most stable oxidation state of the polyaniline family[9] in acidic media. Pernigraniline in ~30% fuming sulphuric acid, independent of its origin via *in situ* oxidation of EB in the sulphonation agent solution or from other presynthesized routes, has a tendency to be reduced to the emeraldine oxidation state. The pure pernigraniline is more easily reduced to the emeraldine oxidation state in fuming sulphuric acid since the strong oxidant, $(NH_4)_2S_2O_8$, is absent from the sulphonation solution. Consequently, it has a higher sulphonation level than that of EB sulphonated in the presence of $(NH_4)_2S_2O_8$ because in the latter case the strong oxidant keeps the polymer in the pernigraniline oxidation state.

Figure 4 shows the conductivity as a function of sulphonation time for EB in ~30% fuming sulphuric acid with $(NH_4)_2S_2O_8$. Even though the 1.5 h sulphonation gives the highest protonation level (*Figure 3*) the conductivity of the 1.5 h sample does not show higher conductivity than that of the 0.5 h sample in which the sulphur level is only ~8.6 wt% (S/N = 0.38). This is probably because the prolonged sulphonation process shortens the chain length of the polymer due to the hydrolysis of quinoid structures. This is supported by 2 h sulphonation giving an even lower

Table 2 Elemental analyses for EB sulphonated in fuming sulphuric acid in the presence of ammonium persulphate

Sample	Time (h)	C	H	N	S	O[a]	S:N	Formula
EB	0.5	54.66	4.48	9.72	8.59	22.55	0.38	$C_{12}H_{11.8}N_{1.84}S_{0.70}O_{3.8}$
PN	1	55.65	3.81	10.34	10.64	19.56	0.45	$C_{12}H_{9.8}N_{1.92}S_{0.86}O_{3.2}$

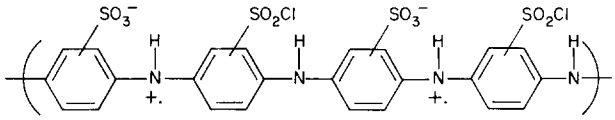
[a] By difference

conductivity. Therefore, the sulphonation of polyaniline in the pernigraniline oxidation state in ~30% fuming sulphuric acid is not an effective method to synthesize SPAN.

As for the samples made in route 1, the comparison of the atomic ratio of oxygen and sulphur for samples synthesized by this route again gives higher values (*Table 2*) than the expected 3. Again, the probable explanation is the presence of water molecules associated with the polymer chain. The polymers synthesized by route 2 have similar solubilities as those made by route 1.

Route 3

Figure 5 shows the *FT*i.r. spectrum of EB sulphonated in $ClSO_3H$ at 100°C for 1 h. Absorption peaks at 1080, 700 and 620 cm^{-1} are consistent with the presence of $-SO_3^-$ groups attached to the phenyl rings[13]; similarly the 1180 cm^{-1} peak is in accord with the substitution of $-SO_2Cl$ on the phenyl rings[13]. Absorption maxima at 820 and 870 cm^{-1} are indicative of 1,2,4-trisubstituents on the phenyl rings. Combining elemental analyses (*Table 3*) the average structure of SPAN made at 100°C for 1 h can be depicted approximately as



The polymers synthesized at two different conditions (room temperature for 72 h and 100°C for 1 h) gave similar conductivities, 3×10^{-3} and 7.5×10^{-3} S cm^{-1}, respectively. However, sulphonation at higher temperature gave a higher sulphonation level of ~83%, i.e. nearly an average of each phenyl ring being substituted by one $-SO_3H$ or $-SO_2Cl$ group; in contrast, only ~50% of the total number of phenyl rings were monosubstituted by $-SO_3^-$ groups for the polymer synthesized in route 1. The higher sulphonation level produced in this route is due to the substitution of not only $-SO_3H$ groups [which converts imine nitrogen sites to polysemiquinone radical cations and amine nitrogen sites to $-(NH_2^+)-$ sites, respectively], but also $-SO_2Cl$ groups. It should be also true for this sulphonation route, as in route 1, that only half the rings need to be substituted by $-SO_3H$ groups in order to produce the stable polysemiquinone form of the polymer. Additional substitution of $-SO_3H$ groups which consequently protonate amine nitrogen atoms would convert some of the $-(NH)-$ to $-(NH_2^+)-$ groups and hence destabilize the polymer by reducing the extent of its π conjugation. Therefore, prolonged sulphonation in this route resulted in primarily an increase in the number of $-SO_2Cl$ groups substituted on the phenyl rings. This accounts for the presence of Cl in samples made by this route and a higher sulphur content than for those samples prepared from the other routes studied.

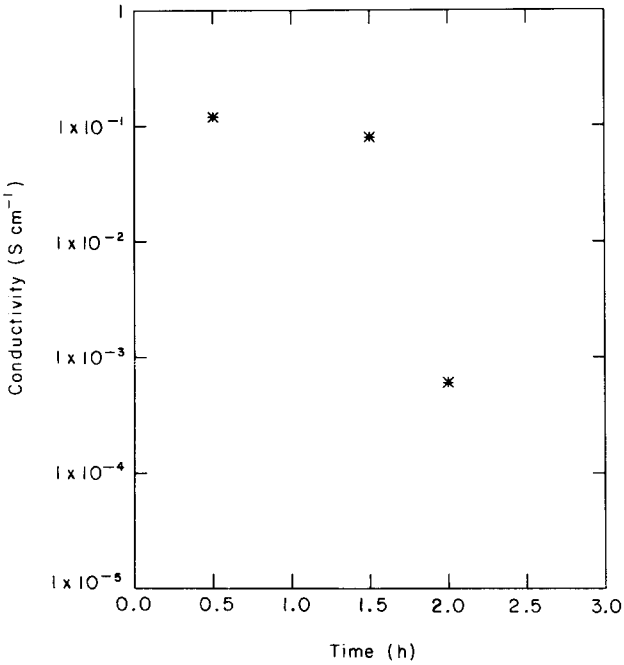


Figure 4 Conductivity as a function of sulphonation time for polymers synthesized by route 2. The samples correspond to those described in *Figure 3*

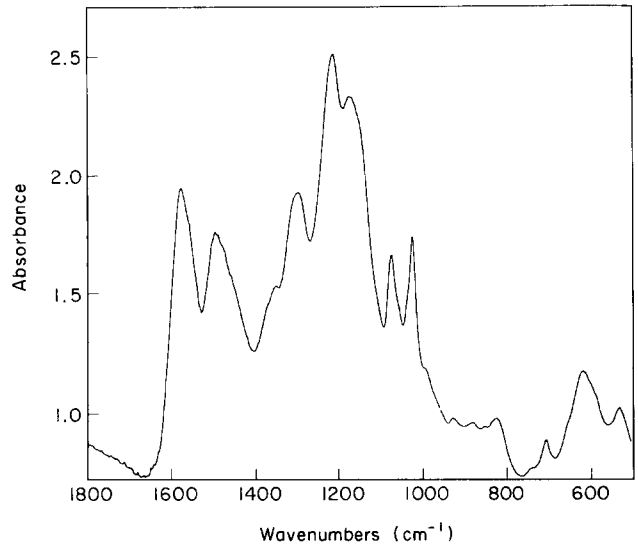
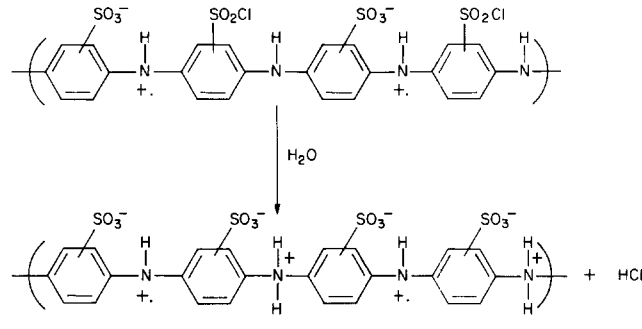


Figure 5 *FT*i.r. spectrum of SPAN synthesized by route 3

The polymers synthesized via route 3 dissolve in 0.1 M NH_4OH showing a blue colour and in dimethylsulphoxide to give a green colour. The polymers do not dissolve in water initially, however, the films cast from 0.1 M NH_4OH do dissolve in water. This is probably due to the conversion of some of the hydrophobic groups ($-SO_2Cl$) into hydrophilic groups ($-SO_3H$) when the polymer dissolves in basic aqueous solutions (*Scheme 11*) which promotes the solubility of the polymer in aqueous solvents.



Scheme 11

A cyclic voltammogram for polymer prepared at 100°C (1 h reaction time) in 1 M HCl is shown in *Figure 6*, contrasted with results for polymers synthesized by route 1. The cyclic voltammogram of the route 3 polymer

Table 3 Elemental analyses for EB sulphonated in chlorosulphonic acid

Time (h)/temp. (°C)	C	H	N	Cl	S	O[a]	S:N	Formula
72/25	41.31	3.46	7.90	7.95	12.54	26.84	0.70	$C_{12}H_{12}N_{1.96}S_{1.37}O_{5.85}Cl_{0.78}$
1/100	38.48	3.27	7.39	8.80	13.88	28.18	0.83	$C_{12}H_{12.1}N_{1.98}S_{1.65}O_{6.58}Cl_{0.93}$

[a] By difference

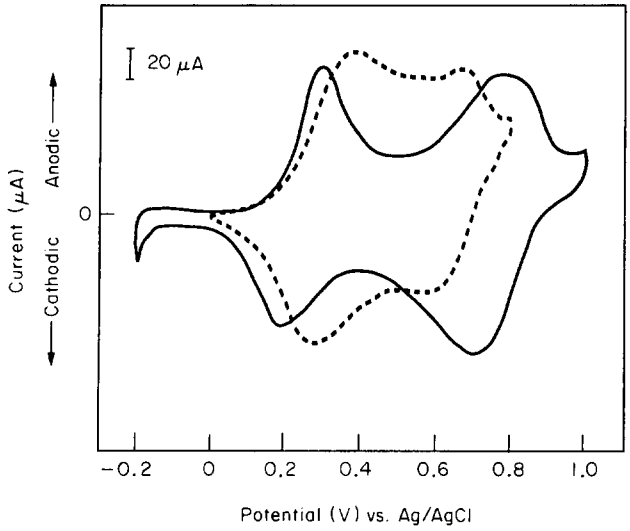


Figure 6 Cyclic voltammograms (50 mV s^{-1}) of sulphonated polyaniline prepared by route 1 (——) and the polymer synthesized by route 3 (– – –) in 1.0 M HCl

consists of two redox peaks: the first peak had an $E_{1/2} = 0.34$ V *versus* Ag/AgCl(sat.) and the second an $E_{1/2} = 0.66$ V. The cyclic voltammogram is essentially identical to that of polymer made in route 1 except that the two sets of redox peaks were closer together[7]. The reason is as follows. Flurscheim first pointed out[14] that all *ortho* substituents reduce the basic strength of the primary aniline bases. This also can be expected for the reduced leucoemeraldine form of SPAN. The higher oxidative potential of the first anodic peak of SPAN obtained via this route (with more substituent groups on the polymer backbone than that from route 1) is not surprising because of the reduced basicity caused by electronic and steric effects of the $-SO_3^-$ groups on the backbone of the polymer. Besides electron withdrawing properties of $-SO_3^-$, the steric effect of short range forces from *ortho*-substituting $-SO_3^-$ changes the basicity of the amine groups. These forces may be (1) steric compression exerted in different degrees in the emeraldine form of the polymer backbone changing the ring and ring nitrogen bond lengths; and (2) a pressure-produced twisting caused by the presence of $-SO_3^-$ groups with a consequent increase of the torsion angle with respect to the –(NH)– plane and decrease of the degree of orbital overlap between the phenyl π electrons and the nitrogen lone pairs.

As a consequence of the steric effect, differential steric compression of $-SO_3^-$ should increase the relative thermodynamic stability of the base, i.e. it should make the base weaker, or their conjugate acids stronger, or, in other words, a higher oxidation potential than that of sulphonated polymer with lower substitution level. Furthermore, introduction of more $-SO_3^-$ groups on phenyl rings and consequent increase in the torsion angle decreases the degree of orbital overlap between the phenyl π electrons and the nitrogen (p_z-like) lone pairs. This makes the reduced leucoemeraldine form more difficult to oxidize to the half-oxidized semiquinone cation radicals[15]. Similar redox properties were observed for poly(*o*-toluidine)[16] which has electron donating groups, $-CH_3$, on the polymer chain. Therefore the steric rather than electronic properties of $-SO_3^-$ are the dominant factors in this redox process. Solvation of $-SO_3^-$ may increase the steric effects in SPAN.

The situation is different at the second anodic process which has $E_{1/2} = 0.66$ V. During this oxidation process the half-oxidized semiquinone cation radicals were further oxidized into the quinonediimine (pernigraniline form) or bipolaron lattice which may be accomplished by the formation of two, fully sp^2-hybridized nitrogen atoms. Some of the steric strain may be relieved by wider C–N=C angles at the quinoid groups than the benzenoid ones[17] to lower the oxidation potential. On the other hand, the better conjugation of lone pair electrons at the nitrogen atoms with π electrons on the phenyl rings as well as with the electron withdrawing groups, $-SO_3^-$, lowers the electron density on the nitrogen atoms and therefore raises the oxidation potential. These effects compete with each other and lead to a lower oxidation potential for the polymer with a higher substitution level[7]. In this process the steric effect again is more dominant than the electronic effect.

Route 4

EB polymers sulphonated at room temperature by dispersing them in 1,2-dichloroethane with 4/1 sulphur trioxide/triethyl phosphate complex as the sulphonation agent[6], have compositions ranging from 0–0.2 sulphonic groups per aniline repeat unit depending on the sulphonation time.

Sulphur trioxide/triethyl phosphate complex was used as the sulphonation complex since the high reactivity of the trioxide can be conveniently controlled by varying the sulphur trioxide/triethyl phosphate ratio. However, since EB was dispersed rather than dissolved in the sulphonation agent, the sulphonation likely occurred on the surface of the polymer powder only.

Table 4 gives the elemental analyses for EB sulphonated using this route. It is important to notice that even though the polymer was washed with 1,2-dichloroethane, there was still some hydrogen sulphate, HSO_4^-, present in the polymer as dopant. Therefore, both conductivity and sulphur content are higher for the dried polymers which were not washed with water to remove sulphuric acid before the measurement. From the table it can be seen that both the conductivity and sulphur level dropped as the polymer was washed with water. Before the wash, the sulphur comes from both sulphonic groups, SO_3^-, and HSO_4^- groups. After the polymer is washed with water,

Table 4 Elemental analyses and conductivities for SPAN synthesized using the sulphur trioxide/triethyl phosphate complex as the sulphonation agent

Time (h)/temp. (°C)	S (%)[a]	S:N[a]	σ^a (S cm^{-1})	S (%)[b]	S:N[b]	O:S[b]	σ^b (S cm^{-1})
1/23	15.40	1.2	2.6	6.56	0.26	5.2	0.46
24/23	12.42	1.2	0.61	6.43	0.25	5.4	0.027

[a] The measurement was done before the sample was washed with water
[b] The measurement was done after the sample was washed with water

Table 5 Elemental analyses and conductivities for SPAN synthesized via solid state sulphonation

Time (h)/temp. (°C)	S (%)[a]	S:N[a]	σ^a (S cm^{-1})	S (%)[b]	S:N[b]	O:S[b]	σ^b (S cm^{-1})
42/120	12.77	0.70	2.7	7.60	0.33	6.6	0.07
48/130	13.35	0.73	0.2	7.61	0.32	6.1	0.03

[a] The measurement was done before the sample was washed with water
[b] The measurement was done after the sample was washed with water

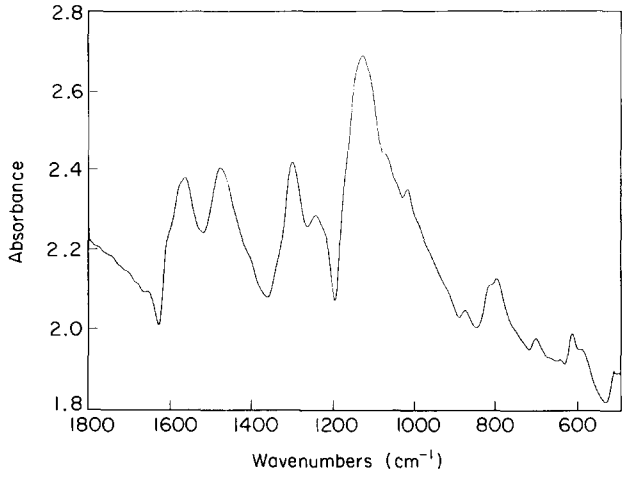


Figure 7 *FT*i.r. spectrum of sulphonated polyaniline synthesized by route 5

the sulphur content is only due to covalently bonded sulphonic groups.

The sulphonation level for the polymer washed with water is ~25%. The sulphonation level is not increased upon increasing the sulphonation time to 24 h. However, the conductivity decreases (from 0.46 to 0.027 S cm^{-1}) more than one order of magnitude below that of the polymer sulphonated for only 1 h, probably due to degradation of the polymer.

The sulphonated polymers made from this route do not dissolve in basic aqueous solutions in contrast to the solubility of the polymers synthesized in the previous routes. This is due to the low sulphonation level.

Route 5

SPAN can also be obtained by solid state sulphonation. *Table 5* gives elemental analyses of SPAN synthesized by route 5 at different temperatures and for different periods. The measurements on the dry samples were done before and after the polymer was washed with water in order to differentiate the effect of the excess hydrogen sulphate groups from that of covalently bonded sulphonic groups.

Figure 7 gives the i.r. spectrum for the polymer sulphonated at 130°C for 48 h. It has almost identical features to the polymers made from route 1[18]. Absorption peaks at 1070, 704 and 610 cm^{-1} are consistent with the presence of $-SO_3^-$ groups substituted on the phenyl rings[13]. Absorption maxima at 820 and 870 cm^{-1} are indicative of 1,2,4-trisubstituents on the phenyl rings. It is noticed that, as in route 4, there are some hydrogen sulphate groups associated with the polymer backbone as the dopant in this route. Therefore, both conductivity and sulphur content are higher for the polymers which were not washed with water. In this case the sulphur in elemental analyses comes from both sulphonic and hydrogen sulphate groups. From *Table 5* it is seen that both conductivity and sulphur levels dropped as the polymer was washed with water, which removed sulphuric acid (leading to the decrease in the sulphur content) and decreased the doping level (leading to the lower conductivity). After the polymer was washed with water, the detected sulphur is due only to sulphonic groups.

The sulphonation level for the washed polymer is only ~33%, insensitive to the conversion temperature and time. However, the conductivity decreased by a factor of ~2 when the sulphonation time and temperature increased, i.e. from 0.07 S cm^{-1} for the polymer sulphonated at 120°C for 42 h to 0.03 S cm^{-1} for one synthesized at 130°C for 48 h. The final polymers do not dissolve in basic aqueous solutions and any common organic solvents. The atomic ratios of oxygen to sulphur are higher than ideal values, as observed for the previous routes (*Table 5*) due to the association of water molecules with the polymer. Even though the conductivity and solubility properties of the polymer made from this route are not at the level for polymers sulphonated via route 1, it does demonstrate that solid state sulphonation can be achieved.

CONCLUSIONS

Comparison of the different synthetic routes shows that route 1 gave better conductivity and higher sulphonation levels than the other routes. As far as solubility is concerned, as-synthesized polymers from routes 4 and 5 did not dissolve in basic aqueous solutions due to lower sulphonation levels. It was found that in order for SPAN to dissolve in a basic aqueous solution, the sulphur content must exceed 8 wt% or a sulphur to nitrogen atomic ratio of 0.38 is needed.

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