

## Electrochemical Oligomerization of Sulfonanilides onto Copper Sheet Anodes

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### SUMMARY:

Methanesulfonanilide and benzenesulfonanilide, salified by a suitable amine were electrolyzed with Cu sheets as anodes in water/organic solvent medium. Coherent insulating coatings on the Cu sheets were thus obtained, which on the basis of various analytical tests resulted to have an oligomeric structure. One electron oxidation of the anilide anions and carbonium-nitrogen coupling of the intermediate free radicals are suggested as the main steps of anilides oligomerization.

### Introduction

The formation of thick poly(oxyphenylene) protective films onto metal sheets has been lately achieved by anodic oxidation of phenols salified with suitable amines in water/methanol medium<sup>1,2</sup>.

One electron oxidation of phenoxide anions and carbonium-oxygen coupling of the radical intermediates are, as for the chemical synthesis of poly(oxyphenylene)s<sup>3</sup>, the alternating steps of the electrolytic polymerization<sup>2,4,5</sup>. However, this route may result more advantageous than the chemical one for obtaining protective coatings since both synthesis and application of the polymer are directly accomplished onto the substrate by only one stage.

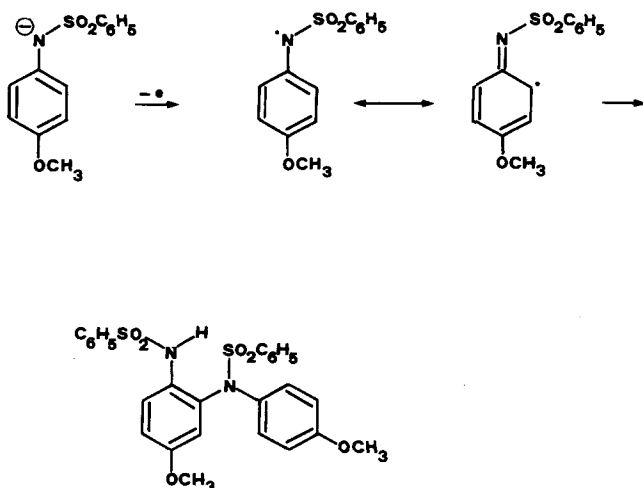
The "in situ" electropolymerization may indeed be a reliable technique for achieving a coherent coating on a metal article working as an electrode, when the monomer system fulfils (as in the case of phenols) the following requirements<sup>6</sup>:

— There is a preferential storage at the electrode surface of the monomer, which does not desorb when an overpotential is applied. (In water medium this condition is approached by monomers bearing a suitable charge.)

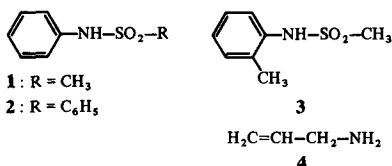
— The polymerization leads to insoluble networks, which possibly do not require any additional curing.

The anilides of strong acids bear many similarities with phenols. Sulfonanilides, e.g., are easily salified by amines and do not suffer hydrolysis in water medium<sup>7</sup>. The chemical literature furthermore gives evidences that 4-substituted sulfonanilides undergo anode oxidation in alkaline solvent through two one electron steps<sup>8,9</sup>: the first one likely corresponds to the formation of a free radical intermediate, as indicated in Scheme 1. Eventually it must be mentioned that in some instances anode passivation by filming occurred during the electrolysis of such compounds<sup>8,9</sup>.

Scheme 1:



Therefore, although no data are so far available on chemical polymerization of anilide anions, these compounds might be suitable, like phenoxides, of anodic coupling polymerization: the present work deals with the results obtained in such direction by anodizing methanesulfonanilide (1), benzenesulfonanilide (2) and *N*-(2-methylphenyl)methanesulfonamide (3) at copper sheet anodes.



1: R = CH<sub>3</sub>

2: R = C<sub>6</sub>H<sub>5</sub>

3

H<sub>2</sub>C=CH-CH<sub>2</sub>-NH<sub>2</sub>

4

## Experimental Part

**Chemicals:** The sulfonanilides 1, 2 and 3 were synthesized according to literature methods<sup>10, 11</sup>. The other chemicals were commercially available reagent grade. Water/methanol mixtures (1 : 1 to 1 : 2 by vol.) were generally used as the solvent for the electrolytic runs; in other cases also water/DMSO<sup>a)</sup> mixtures (1 : 1,5 by vol.) were utilized. The metal samples were cut from baked sheets of copper: their standard dimensions were 23 × 2,5 × 0,05 cm, but the surface dipping in the electrolytic cell and then coated generally was ca. 22 cm<sup>2</sup>. Before use the sheets were washed in succession by diluted HCl, deionized water and acetone.

**Apparatus and procedure:** The coating runs were performed in an uncompartmented cell already described<sup>2)</sup> consisting of a simple glass cylinder which was generally filled by 100 ml of the solution under examination. The sheet sample, placed in the centre of the cylinder, constituted the anode, while a Pt coil rolled around the glass wall was the cathode. The

<sup>a)</sup> DMSO = dimethyl sulfoxide.

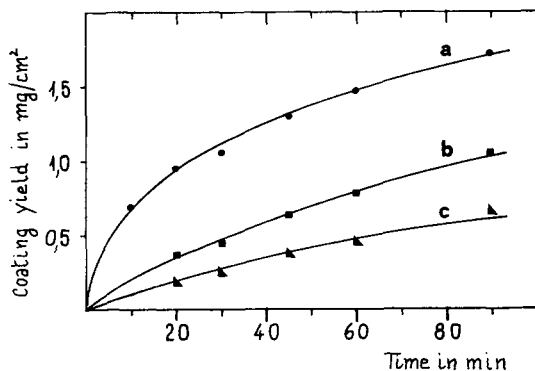
electrolyses were carried out by applying a constant voltage between these electrodes, the current transients being monitored by an ammeter. Having anodized the metal sample for the required time, once withdrawn from the cell it was rinsed by water/methanol and then dried at room temperature or cured in oven at 100–120°C for 15–30 min. Voltammetric measurements were carried out in a compartmented cell equipped with a Cu or Pt working microelectrode (area ca. 0,2 cm<sup>2</sup>), a Standard Calomel Electrode as reference and a Pt coil as counter electrode. Structural analysis of the coatings was carried out by pyrolysis-mass spectrometry<sup>12</sup>, through direct introduction of purified samples into the ionic source of a Hitachi-Perkin Elmer RMU6 mass spectrometer.

## Results and Discussion

### Coating formation

On electrolyzing by voltages in the range of 1 to 5 V a water/methanol solution containing 0,7 mol/l **1** and 0,5 mol/l KOH, the initial current density ( $\leq 50$  mA/cm<sup>2</sup>) dropped to a negligible value in a few seconds, since the Cu sheet anode was passivated by insoluble oxides. On the contrary, when a suitable amine (allylamine (**4**) gave the best results) was added to the solution of **1**, thus substituting in part or totally the alkaline base, the electrolysis current decreased much more slowly and a coherent organic coating formed on the Cu anode. The coating thickness (in mg/cm<sup>2</sup>) grows with the time of electrolysis, but at a rate slowing down according to the current decrease: the current yield steadily ranges between 0,27 and 0,33 mg/C. An example of the kinetics of coating formation during the constant voltage electrolysis is shown in Fig. 1, curve a.

Fig. 1. Kinetics of coating formation. Curve a: 0,50 mol/l methanesulfonanilide (**1**); 0,67 mol/l allylamine (**4**); water/methanol 1 : 1 (by vol.). Curve b: 0,30 mol/l benzenesulfonanilide (**2**); 0,45 mol/l allylamine (**4**); water/DMSO 1 : 1,5 (by vol.). Curve c: 0,21 mol/l benzenesulfonanilide (**2**); 0,38 mol/l allylamine (**4**); water/methanol 1 : 2 (by vol.). 4,0 V applied



The monomer concentration strongly affects the deposition rate: Fig. 2 in fact shows that on increasing the concentration of **1**, while keeping fixed the 1 : 4 concentration ratio, the coating efficiency (coating thickness in mg/cm<sup>2</sup> after a fixed time) grows linearly. The fact is easily explained when considering that any increase of the concentrations of **1** and **4** diminishes the resistance of the system: thus at fixed voltage

applied higher current amounts are transferred, which result in the formation of a larger quantity of deposit. For the same reason, on keeping constant the concentration of 1 and varying that of 4 the deposition rate increases by increasing the concentration of 4. During these experiments the coulombic yield of the coatings was steadily about 0,3 mg/C.

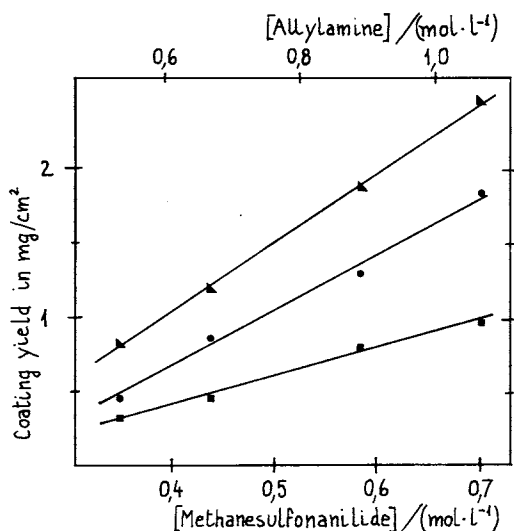


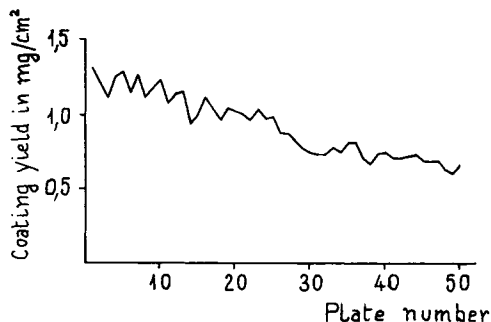
Fig. 2. Coating yield obtained for increasing concentrations of 1 and 4 after three electrolysis times with 4,0 V applied. ■: 15 min; ●: 30 min; ▲: 60 min

The kinetics of film formation from the electrolysis of 2 salified by 4 are shown by curves b and c in Fig. 1, which were respectively obtained in water/DMSO and water/methanol mixtures. The coating rate was higher in water/DMSO than in water/methanol: in fact, not only the coulombic yield was higher in the first solvent (0,3 mg/C as against 0,2 mg/C) but also larger concentrations of 2, with rate increase, could be dissolved in water/DMSO. However, when the concentration of 2 in water/DMSO was increased over 0,4 mol/l, the coatings were degraded and most of the solid anodic products were dispersed into the solution.

#### *Stoichiometry of the anodic process*

With reference to the anodic polymerization of phenols<sup>2,3</sup>, the oxidative coupling of the anions of either 1 and 2 should involve two electron transfers for each addition step: as against the current yields seen above (ca. 0,3 mg/C) are much below the theoretical values which respectively are 0,87 for 1 and 1,20 for 2. Therefore, for a deeper investigation on the stoichiometry of the process the following experiment was carried out: 50 numbered Cu sheets were anodized one after the other in one and the same solution of 1 for 30 min, thus determining for each one both the weight of the deposit and the related coulombic yield. Fig. 3 shows how the weight of coating varies with the progressive number of the sheet: there is a slight efficiency decrease which,

Fig. 3. Coating yield as a function of the progressive number of the coated sheet from a water/methanol (1 : 1 by vol.) solution containing 0,59 mol/l methanesulfonanilide (1) and 0,80 mol/l allylamine (4)



however, is not paralleled by either degradation of coating morphology or coulombic yield loss. When the experiment was stopped, 4670 C had been transferred with the total formation of 1,55 g of coating, corresponding to a 0,33 mg/C average current yield. The film formed onto the sheets was not the only solid product of the electrolytic process since other 0,65 g of a material having the same composition of the film (by IR and MS) were recovered at the bottom of the cell. Furthermore, after having extracted (by  $\text{CHCl}_3$ ) 11,36 g of unreacted 1 (75,6% of the initial amount), the water/methanol phase was found to contain 0,13 g of copper ions and another product from the oxidation of 1. The amount of this latter was about 1,02 g (by sulfur determination) and it probably was an anilide oligomer which could not be eluted on thin layer chromatography by the common organic solvents. Therefore, on adding the weight of all the products obtained from the electrolysis of 1 (3,35 g, corresponding to 22,4% of initial 1) and correcting the current amount of copper dissolution, the true coulombic yield was 0,749 mg/C. In other words 1 is oxidized at the Cu anode with the transfer of 2,36 Faraday/mol, not far from the stoichiometry of phenol anodic coupling polymerization.

It must be eventually mentioned that the current yield depends strongly on the water/methanol ratio: this fact can be easily seen in Fig. 4 for coatings obtained from 1. At low water content the anode process is mainly supported by Cu oxidation to  $\text{Cu}^{\text{I}}$ : such oxidation stoichiometry for Cu is due to the presence of the anilide which probably complexes  $\text{Cu}^{\text{I}}$ . On increasing the water content of the medium film formation takes place, and the coulombic yield soon reaches  $\approx 0,3$  mg/C.

### Voltammetric runs

Fig. 5 illustrates the current-potential curves obtained at a Cu microanode in water/methanol medium either in the absence or in the presence of sulfonanilide. These curves have been plotted by points, on recording for each point the (pseudo)-steady-state current attained after 3 min of potentiostatic electrolysis. Curve a, referring to water/methanol with KOH as background electrolyte, shows that the electrode suffers from some passivation (the current attains a relatively low value).

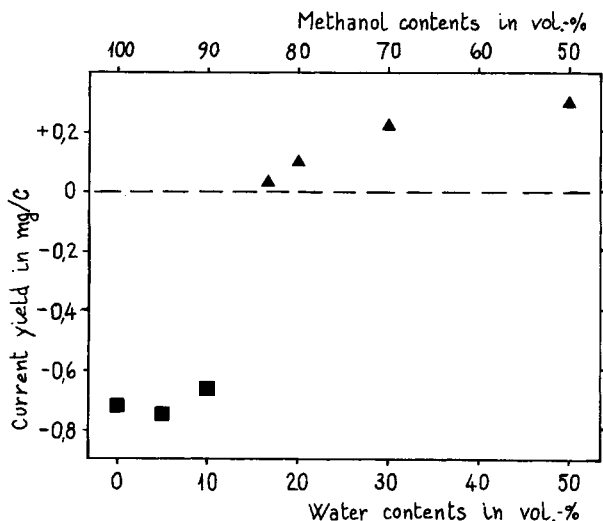


Fig. 4. Current yields obtained by electrolyzing (4,0 V applied) a solution containing 0,47 mol/l methanesulfonanilide (1) and allylamine (4) in water/methanol mixtures of different contents. ■: weight loss due to copper dissolution; ▲: weight increase due to film formation. Dashed line denotes the borderline between copper dissolution and polymer film formation

Curve b shows that in the presence of 4 the electrode is somehow depolarized, especially at high potentials. Curve c emphasizes the extensive passivation of the anode caused by film formation when a solution containing 1 and 4 is electrolyzed. The direct oxidation of 1, however, could not be detected at a Cu anode, not even by using faster voltammetric techniques. Conversely at a Pt anode a well defined oxidation wave of 1 could be evidenced as shown in Fig. 6: the current-potential curves were here recorded potentiodynamically at a rotating disc electrode. It is clear that the oxidation of 1 was evident at Pt only, for two main reasons: a) no other electrode reaction (e.g. metal dissolution) takes place at Pt for a wide potential range; b) extensive passivation of Pt does not occur (neither during long macroscale electrolyses) as oil products, rather than adhering insulating films, are generally produced. This second fact is accounted by some specific intervention of the metal electrode (probably not occurring with Pt) in polyanilides network building up.

### Characterization of the products

#### a) Molecular weights

The coatings obtained from water/methanol solutions of either 1 or 2, when dried at room temperature, have a good solubility in many organic solvents such as *N,N*-dimethylformamide (DMF), DMSO,  $\text{CF}_3\text{COOH}$ ; as against the coatings formed from 2 in water/DMSO are far less soluble. A thermal curing under the very mild conditions previously mentioned leads to complete insolubility of any type of film.

The products obtained from water/methanol medium, once purified by dissolution and precipitation, gave (by vapour pressure osmometry in DMF at 80°C) number average molecular weights  $\bar{M}_n = 850$  (product from 1) and  $\bar{M}_n = 1200$  (product from 2) respectively.

Fig. 5. (Pseudo)-steady-state current potential curves obtained at Cu electrodes. Curve a: water/methanol 1 : 1 (by vol.); 0,1 mol/l KOH; Curve b: as a with 0,67 mol/l allylamine (4); Curve c: as b with 0,47 mol/l methanesulfonanilide (1). (S.C.E. = Standard calomel electrode)

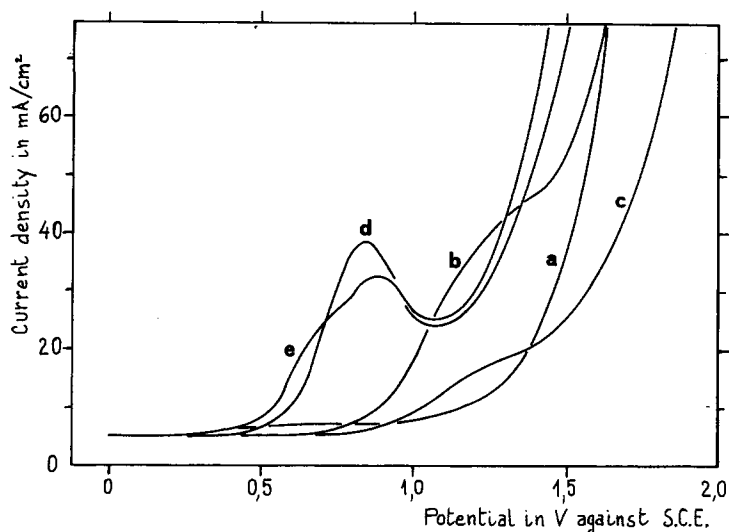
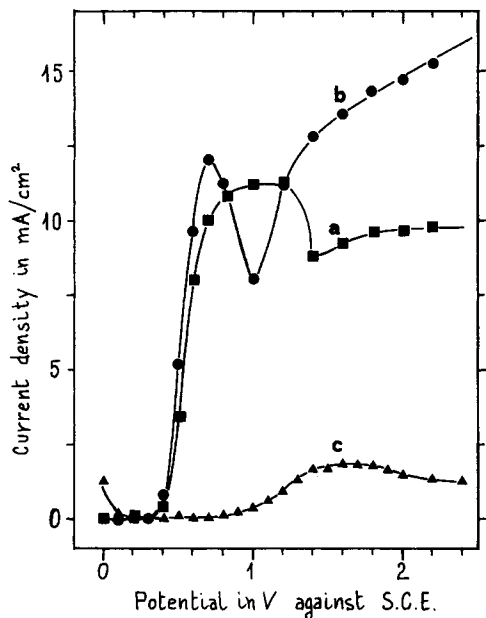


Fig. 6. Voltammetric current-potential curves obtained at a Pt rotating disc electrode in water/methanol (1 : 1 by vol.) solution by a potential sweep = 33 mV/s. Curve a: the solvent with 0,2 mol/l  $\text{NaClO}_4$  as background electrolyte; curve b: as a with 0,01 mol/l KOH; curve c: as a with 0,01 mol/l allylamine (4); curve d: as c with 0,01 mol/l methanesulfonanilide (1); curve e: as b with 0,01 mol/l methanesulfonanilide (1)

### b) Elemental analysis

Tab. 1 resumes the C, H, N elemental analysis data of the oligomers. The experimental values are compared with the theoretical ones, which have been computed from the monomers on assuming a head-to-tail coupling with the loss of two hydrogen atoms for each unit.

Tab. 1. Data of elemental analyses of the products from electrochemical oligomerizations of methanesulfonanilide (1) and benzenesulfonanilide (2), respectively

Monomer	Elemental analysis of the resulting oligomer				Formula [Molecular weight]
1	Calc.	C 49,69	H 4,17	N 8,28	$(C_7H_7NO_2S)_n [(169,2)_n]$
	Found	C 49,54	H 4,19	N 8,19	
2	Calc.	C 62,32	H 3,92	N 6,06	$(C_{12}H_9NO_2S)_n [(213,3)_n]$
	Found	C 61,45	H 4,12	N 6,85	

### c) Infrared spectra

The most striking feature of the IR patterns of the oligomeric products, when compared with the spectra of the corresponding monomers, is given by the absence of the bands at  $3400\text{ cm}^{-1}$  and  $1395\text{ cm}^{-1}$  which may be ascribed to stretching and respectively bending of the N—H bond. The products still keep the typical bands of the S—O bond at  $1330$ ,  $1155$  and  $520\text{--}580\text{ cm}^{-1}$ , thus indicating that sulfonic groups have not been lost during the polymerization.

For the products obtained from 1 an out-of-plane vibration at  $825\text{ cm}^{-1}$ , absent in the monomer spectrum, which might be ascribed to *para*-substitution was eventually noted.

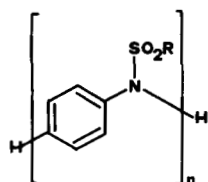
### d) Mass spectrometry data

Pyrolysis/mass spectrometry analysis carried out at  $320^\circ\text{C}$  by a 70 eV electron beam energy on the products from 1 gave the pattern shown in Fig. 7.

The most significant peaks progressively increase by a repetitive unit having  $m/e = 91$  which corresponds to the  $C_6H_4NH$  group. Such view is confirmed by Fig. 8, in which the spectrum of the products obtained from the electrolysis of 3 emphasizes a repetitive unit having  $m/e = 105$  ( $C_7H_7NH$ ).

Since mass spectrometry fragmentation of sulfonanilides (monomers) emphasizes the very easy cleavage of the N—S bond with loss of  $SO_2R$  and “ $SO_2H$ ” moieties<sup>(13)</sup>, the absence of sulfonic groups from the repetitive units above is not surprising. It must be noted, however, that in such units the sulfonic groups are substituted by hydrogen atoms and this reaction cannot be due to electronic impact. Therefore, the product of the electrolytic process has very likely the following structure:





This product, however, undergoes intermolecular hydrogen transfer and cleavage of N—S bonds by pyrolysis<sup>a)</sup> before vaporizing. The different volatility of the pyrolysis products causes a decrease of the intensities of the peaks for increasing  $m/e$

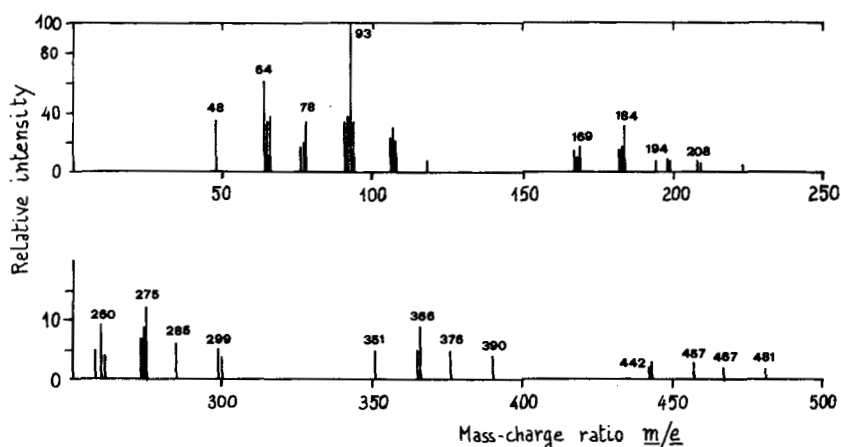


Fig. 7. Mass spectrum of the electrolysis product of 1, recorded at 70 eV and 320°C

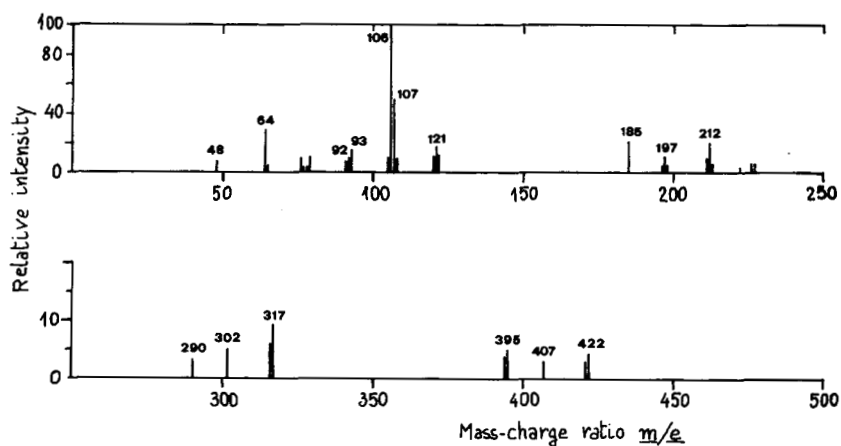
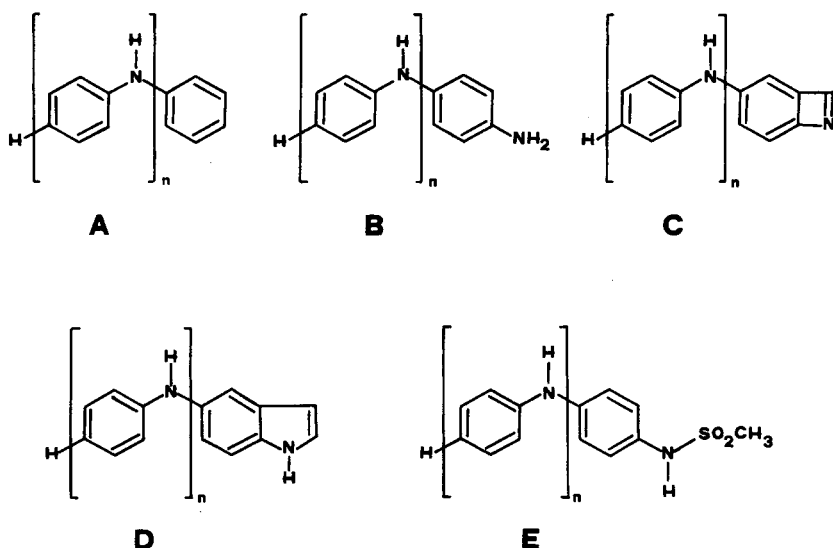


Fig. 8. Mass spectrum of the electrolysis product of 3, recorded at 30 eV and 250°C

values, according to the similar behaviour of poly(oxyphenylene)s<sup>14)</sup> and poly-benzyls<sup>15)</sup>. With respect to a more detailed discussion of the mass spectra of Fig. 7, the higher intensity peaks may be identified by structures **A** and **B** of Scheme 2 and Tab. 2: pyrolysis products which have been ionized without fragmentation would be involved here. Also the fragments having  $m/e = \mathbf{B} + 10$  and  $\mathbf{B} + 24$ , respectively, although their identification is less easy, probably are formed by the same pathway: in fact their intensity relative to the one of structures **B** is independent of the electron beam energy, in the range 30 to 70 eV. Structures **C** and **D** may reasonably be suggested for such fragments.

Scheme 2:



The mass spectrum of the electrolysis product of **1** carried out by 30 eV outlines strong intensity peaks at  $m/e = 171, 262, 353$ , and  $444$  which may be likely identified with structure **E** of Scheme 2: such fragments are far less important in the patterns obtained with higher energy (70 eV), owing to the loss of  $\text{SO}_2\text{R}$  residual groups. In this case ions having  $m/e = \mathbf{B} - 1$  are formed. The strong intensity peaks having  $m/e = 48$  and  $m/e = 64$  are eventually ascribed to  $\text{SO}$  and  $\text{SO}_2$ .

<sup>a)</sup> The pyrolysis/mass spectrometry of a polymeric trifluoroacetanilide sample prepared electrochemically showed again the  $\text{C}_6\text{H}_4\text{NH}$  repetitive unit: since no hydrogen might come in this case from the acid moiety ( $\text{CF}_3\text{CO}-$ ), hydrogen transfers have to occur intermolecularly at the pyrolytic stage.

Tab. 2. Pyrolysis/mass spectrometry fragmentation data of the coatings obtained from methanesulfonanilide (1)

Structure in Scheme 2	<i>m/e</i> values for increasing values of <i>n</i> (cf. Scheme 2)				
	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4
<b>A</b>	78	169	260	351	442
<b>B</b>	93	184	275	366	457
<b>C</b>		194	285	376	467
<b>D</b>		208	299	390	481
<b>E</b>	171	262	353	444	

The pyrolysis/mass spectrometry patterns of coatings obtained from **2** are similar to those of **1**, the main difference being due to the presence of a strong peak at *m/e* = 77, which is clearly related to benzenesulfonic moiety fragmentation.

### Physical properties

The coatings described so far, especially when cured in an oven, exhibit a very fine gloss and coherence, their colour varying from yellow to brown.

Some of the physical properties of samples obtained under different conditions are reported in Tab. 3: such properties are indeed interesting. It must be eventually noted that the coating shows a fair resistance to salt fog corrosion tests performed according to ASTM method B 117: neither corrosion nor blisters appeared on unscratched samples for 120 h, at least.

Tab. 3. Physical properties of coatings from electrochemical oligomerization of methanesulfonanilide (1) and benzenesulfonanilide (2) salified with allylamine (4)

System compositions concs. in mol/l	Thickness in $\mu\text{m}$	Hardness <sup>a)</sup>	Film porosity <sup>b)</sup> in pores/ $\text{cm}^2$	Cross cut adhesion <sup>c)</sup>
[1] = 0,47; [4] = 0,75; volume ratio water/methanol 1 : 1	8	4 H	5	good
Idem	10	4 H	0	good
Idem	12	3 H	0	good
[2] = 0,21; [4] = 0,38; volume ratio water/methanol 1 : 2	4	4 H	45	good
Idem	5	5 H	25	good
Idem	7	4 H	20	good
[2] = 0,30; [4] = 0,45; volume ratio water/DMSO 1 : 1,5	6	4 H	40	good
Idem	8	3 H	55	good
Idem	10	4 H	110	good

a) Determined by graphite standards.

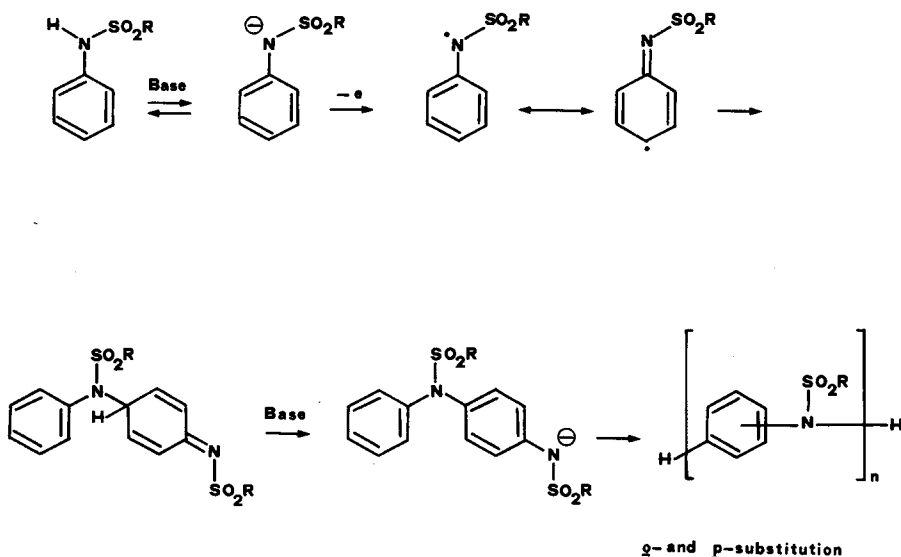
b) Film porosity was tested by an electrographic method.

c) Cross cut adhesion was performed by making a series of parallel cuts in one direction and a second series at right angle to the first, applying an adhesive tape and stripping.

### Conclusive Remarks

The results discussed above unambiguously suggest that the oligomerization of sulfonanilides occurs by a mechanism similar to the oxidative coupling polymerization of phenols: one has only to substitute C—N for C—O coupling according to Scheme 3.

Scheme 3:



With respect to the termination step, which strongly limits the number-average molecular weight  $\bar{M}_n$  of the products from either **1** or **2**, an N—N coupling reaction cannot be disregarded. However, the literature data give no evidence for the formation of N—N coupling products (hydrazobenzenediamides) from the oxidation of 4-substituted sulfonanilides<sup>8,9</sup>. As against, the heterogeneity of the process is likely to be a more important chain limitation step: as soon as polysulfonanilide anions become insoluble and precipitate on the electrode, the anionic ends are no longer suitable of anodic oxidation and chain growth is consequently stopped. When the medium is a better solvent for the oligomers the polymerization degree may increase: this seems to be the case for the products obtained from **2** in water/DMSO solvent. The importance of both amine and water for polymerizing sulfonanilides onto Cu sheet anodes needs some comments. It was previously seen that when anilide is salified by an alkaline base, passivating oxides are formed on the anode. As against in the presence of amine, which likely absorbs on Cu, the formation of oxides is inhibited: therefore some Cu may still dissolve (as a soluble species) but also sulfonanilide oxidation takes place at the same potential. At this point, when a first

polymer layer forms on the bare metal, Cu dissolution is hindered, and sulfonanilide supplies the electrode reaction till the resistance of a thickened coating stops the current passage.

With respect to the influence of water, it is probably much related to precipitation and adhesion onto the anode of the first oligomer layer, whose formation is essential for shifting the electrode process in favour of polymerization.

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