AD-A259 662

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REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

REPORT DATE
June 29, 1992

3. REPORT TYPE AND DATES COVERED
Technical — 5/31/91 – 6/30/92

4. TITLE AND SUBTITLE
"COMPARISON OF DIFFERENT SYNTHETIC ROUTES FOR SULFONATION OF POLYANILINE"

5. FUNDING NUMBERS
G—N00014-90-J-1559

6. AUTHOR(S)
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JAN 22 1993
S B D

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Pennsylvania
Department of Chemistry
Philadelphia, PA 19104-6323

8. PERFORMING ORGANIZATION REPORT NUMBER
1992-48

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Sponsoring Agency:
DARPA
3701 N. Fairfax Drive
Arlington, VA 22203-1714

Monitoring Agency:
ONR
800 N. Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Unlimited

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

93-01170

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14. SUBJECT TERMS

93 1 2 8

15. NUMBER OF PAGES
31

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
UL

OFFICE OF NAVAL RESEARCH

GRANT NO.: N00014-90-J-1559

R & T CODE NO.: A400004DF3

TECHNICAL REPORT NO.: 1992-48

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by

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Accepted for Publication in
Polymer, (1992)

University of Pennsylvania
Department of Chemistry
Philadelphia, PA 19104-6323

July 1, 1992

92-48

Polymer, in press

November 7, 1991

COMPARISON OF DIFFERENT SYNTHETIC ROUTES FOR SULFONATION OF POLYANILINE

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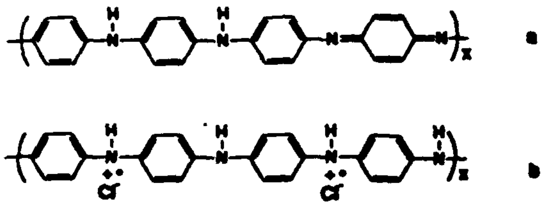
ABSTRACT

Polyanilines containing sulfonic groups covalently bonded to the backbone were synthesized from parent polyaniline via sulfonation of the polymer utilizing differing sulfonation agents and differing means. The sulfonation conditions were studied as a function of several parameters including sulfonation time, starting forms of the precursor polymer, presence of oxidizer, ($(NH_4)_2S_2O_8$), and temperature. The sulfonated polyanilines were characterized by FTIR, elemental analyses, DC conductivity and electrochemical methods. It was found that using fuming sulfuric acid as the sulfonation agent gave both higher conductivity and higher sulfonation level for sulfonated polyaniline than implementation of other sulfonation agents and means.

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 I(a).[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 I(b) (polysemiquinone or polaron lattice form).



Scheme I

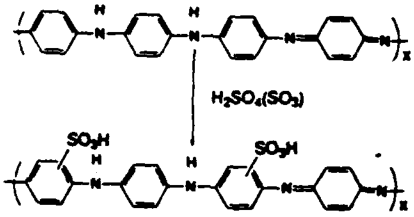
Recently sulfonated polyaniline (SPAN), the first self protonic acid doped polyaniline, was reported.[4] In order to establish the relationships between a variety of synthesis variables and characteristics of this interesting polymer, we present results on the effects of the type of sulfonation agents,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

EXPERIMENT

Several sulfonation methods can be applied to synthesize SPAN. The synthetic routes listed below have been practiced in this laboratory.

Route I. – Sulfonation of Solutions of Emeraldine Base in Fuming Sulfuric Acid.

Emeraldine base (EB) was synthesized by using a previously described method.[5] The self protonic acid doped polyaniline was synthesized by sulfonation of EB in fuming sulfuric acid.[4] In a typical procedure, 0.5 g of EB was sulfonated by dissolving EB powder in 40 ml of ~30% fuming sulfuric acid which was previously cooled to approximately 5 °C with constant stirring in ice water, Scheme II.



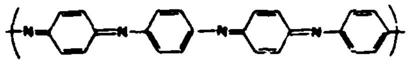
Scheme II

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 continuing to stir (~5–10 min). The color of the solution changed from dark purple to dark blue during ~0.5 hours at room temperature. The solution was then slowly added during ~20 minutes to 200 ml of methanol to precipitate most of the product, the temperature during this step being held between 10 ~ 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 approximately 10 minutes; the filter cake then is 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.

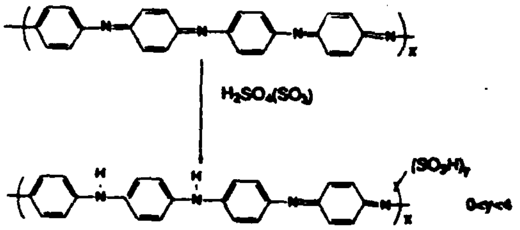
The above procedure was repeated at room temperature exactly except for differing periods of sulfonation time to determine optimum sulfonation conditions.

Route II. –Sulfonation of Solutions of Pernigraniline Base and Salt in Fuming Sulfuric Acid.

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

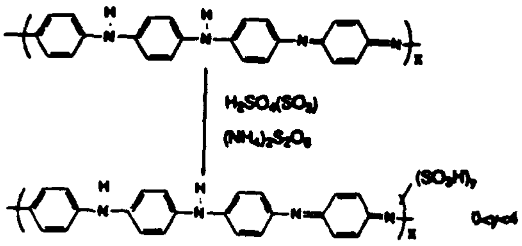


was either used directly (as was EB in Route I), Scheme III,



Scheme III

or alternatively, pernigraniline salt was used as the starting material for sulfonation, being obtained by converting emeraldine salt in ~30% fuming sulfuric acid in the presence of strong oxidizer such as ammonium persulfate, $(NH_4)_2S_2O_8$, Scheme IV.

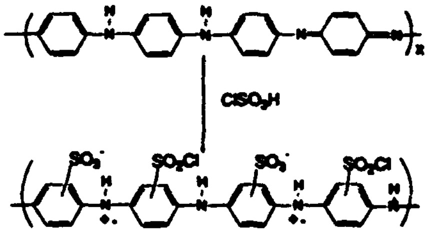


Scheme IV

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

Route III. –Sulfonation of Solutions *of Emeraldine* Base Using Chlorosulfonic Acid.

Besides using of fuming sulfuric acid as a sulfonation agent, EB also can be sulfonated by dissolving it in chlorosulfonic acid, $ClSO_3H$. 0.2 g of fine ground EB powder was dissolved in 2 ml of $ClSO_3H$.

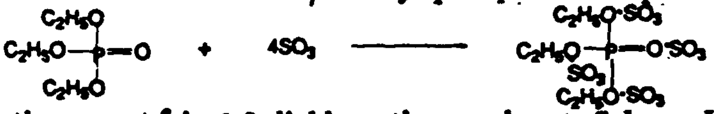


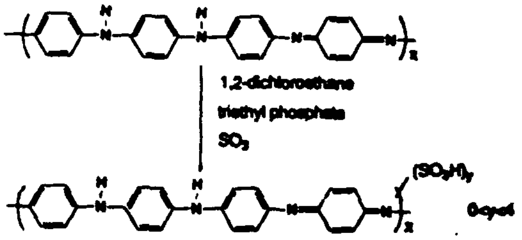
Scheme V

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

Route IV. –Sulfonation of Dispersion of Emeraldine Base.

Another known sulfonation method[6] is to disperse powders of the precursor polymer in a suitable solvent which contains a sulfonation agent. For example, a typical sulfonation procedure for synthesizing SPAN utilizing this method is to use a sulfur trioxide/triethyl phosphate complex as a sulfonation agent,[6] in 1,2-dichloroethane solvent, Scheme VI.



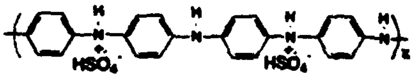


Scheme VI

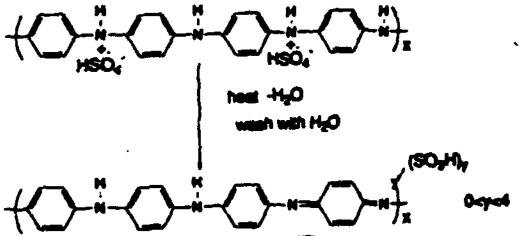
A 4/1 $SO_3/(C_2H_5O)_3PO$ complex in 1,2-dichloroethane solution was prepared by adding 2 ml (3.8 g; 0.048 mol) of sulfur trioxide to a solution of 2 ml (2.2 g; 0.012 mol) of triethyl phosphate in 20 ml of 1,2-dichloroethane. The temperature of the solution was kept below 25 °C by adding the SO_3 slowly and by cooling the solution with an ice bath. Meanwhile, 1.0 g of EB powder was dispersed in 40 ml of 1,2-dichloroethane. The sulfonation solution was then dropwise added 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 hr.

Route V. –Sulfonation via Heating of Emeraldine Sulfate Salt.

Since EB can be doped by a protonic acid to form emeraldine salt, ES, one can achieve sulfonation of EB by heating the salt of emeraldine hydrogen sulfate,



which is EB doped by sulfuric acid, under N_2, Scheme VII.



Scheme VII

1 g of emeraldine hydrogen sulfate was placed into an oven which was preheated to 120 °C or 130 °C. The flow rate of N_2 was set to be 1.4 l/min. 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 I. It is very important to wash H_2SO_4 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 H_2SO_4 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]

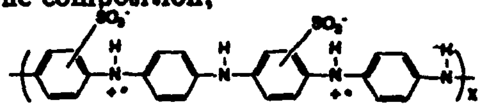
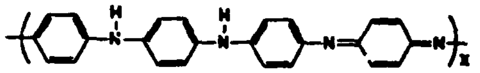


Table 1 gives elemental analyses data for SPAN prepared via Route I using differing sulfonation times. Formulas given are those which best fit the analytical data.

For all samples the atomic ratio of oxygen to sulfur is higher than the expected value of 3. The most likely explanation is the presence of H_2O molecules associated with the polymer chain. This is consistent with our XPS studies[8] where we observed excess oxygen per two ring repeat unit in SPAN, presumably present as H_2O.

Elemental analyses for hydrogen are not sufficiently accurate enough 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 sulfur 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 sulfur is ~2, in other words, ~50% of the total number of nitrogen atoms present in the polymer are protonated.

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

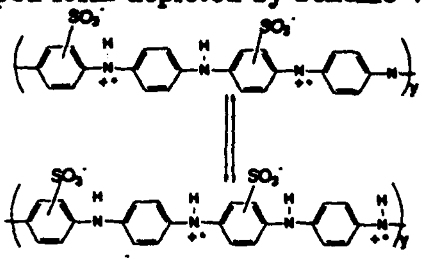


which are protonated is 50 ± 2%. However, Fig. 1 shows that the maximum conductivity was observed at a sulfonation time of 1 ~ 2 hr; decreased conductivities were found beyond this time. These results indicate that the sulfonation occurred relatively rapidly and was essentially finished within 2 hr. Prolonged sulfonation periods seemed to cause a slow hydrolysis of EB in fuming sulfuric 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 sulfonated. This is consistent with the fact that only half the rings need to be sulfonated in order to produce the stable polysemiquinone form of the polymer. Indeed, additional sulfonation 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.

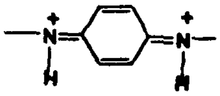
Figure 2 reveals that the yield of SPAN, calculated according to Scheme II, was sensitive to the sulfonation time. The yield decreased almost linearly with increasing of the sulfonation time likely because fuming sulfuric acid, which is a strong oxidant, promoted decomposition/depolymerization of SPAN 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 doped form depicted by Scheme VIII.

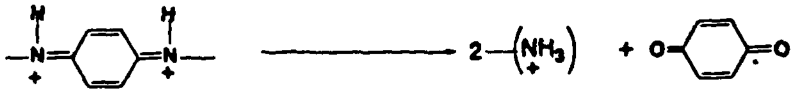


Scheme VIII

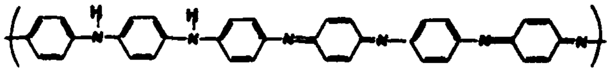
The resonance between the oxidized and reduced repeat units permitted in the protonated emeraldine oxidation state (*i.e.* the polysemiquinone radical cation), derived from equal numbers of oxidized and reduced repeat units, eliminates the presence of the



groups which are known to hydrolyze readily in aqueous acid[10, 11] viz.

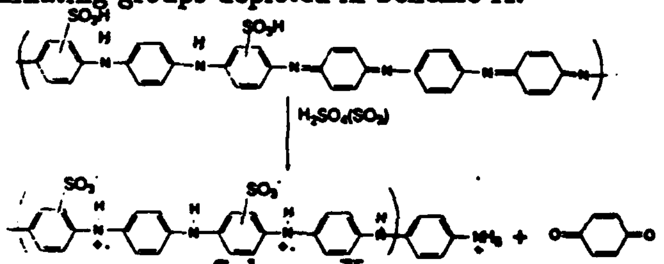


However, in addition to being a *sulfonation agent*, fuming sulfuric acid is also a strong oxidant. Prolonged sulfonation time may raise the oxidation state of emeraldine to higher levels causing the polymer to more readily hydrolyze. By way of an example, two oxidized repeat units are placed adjacent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



Scheme IX

to represent an excess of the oxidized 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 picture, 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 depicted in Scheme X.



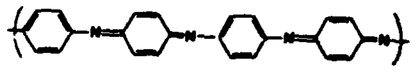
Scheme X

This accounts for the yield of the sulfonation product decreasing as the sulfonation time is increased.

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

Route II. Since only half the rings of EB need to be sulfonated in order to produce the stable polysemiquinone form, excess sulfonation and consequent protonation of amine nitrogen atoms 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 sulfonate pernigraniline, which has fully oxidized repeat imine units, to increase the sulfonation level.

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



directly in ~30% fuming sulfuric acid. Table 2 gives the elemental analyses for the sulfonation of EB 0.5 hr in the presence of $(NH_4)_2S_2O_8$ and pernigraniline for 1 hour. Even though the sulfonation level for pernigraniline is higher than that of EB in the presence of $(NH_4)_2S_2O_8$, it is not as high as

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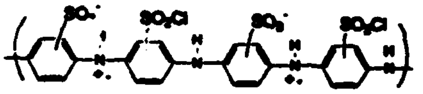
values (Table 2) than the expected 3. Again, the probable explanation is the presence of H_2O molecules associated with the polymer chain. The polymers synthesized by Route II have similar solubilities as those made in Route I.

Route III. Figure 5 shows the FTIR spectrum of EB sulfonated in $ClSO_3H$ at 100 °C for 1 hr. 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 trisubstitutents on the phenyl rings. Combining elemental analyses (Table 3) the average structure of SPAN made from 100 °C for 1 hr can be depicted approximately as



The polymers synthesized at two different conditions (room temperature for 72 hr and 100 °C for 1 hr) gave similar conductivities, 3×10^{-3} S/cm and 7.5×10^{-3} S/cm, respectively. However, sulfonation at higher temperature gave higher sulfonation level ~83%, *i.e.,* nearly an average of each phenyl ring being substituted by one $-SO_3H$ or $-SO_2Cl$ group, in contrast that only ~50% of the total number of phenyl rings were mono-substituted by $-SO_3^-$ groups for the polymer synthesized in Route I. The higher sulfonation 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 sulfonation route, as in Route I, that only

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mer consists of two redox peaks: the first peak had an $E_{1/2} = 0.34$ V vs 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 I[7] except that the two sets of redox peaks were closer together. 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 of from Route I) 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 (A) steric compression exerted in different degrees in the emeraldine form of the polymer backbone changing the ring and ring-nitrogen bond lengths; and (B) a pressure-produced twisting caused by the presence of the -SO_3^- groups with a consequent increase of the torsion angle with respect to the -(NH)- plane and decrease the degree of orbital overlap between the phenyl π-electrons and the nitrogen lone pairs.

As a consequence of the steric effect (A), 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 sulfonated 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 IV. EB polymers sulfonated at room temperature by dispersing it in 1,2-dichloroethane with 4/1 sulfur trioxide/triethyl phosphate complex as the sulfonation agent,[6] have compositions ranging from 0 ~ 0.2 sulfonic groups per aniline repeat unit depending the sulfonation time.

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

Table 4 gives the elemental analyses for EB sulfonated in this route. It is important to notice that even though the polymer was washed with 1,2-dichloroethane, there were still some hydrogen sulfate, HSO_4^-, present in the polymer as the dopant. Therefore, both conductivity and sulfur content are higher for the dried polymers which were not washed with water to remove sulfuric acid before the measurement. From the table we can see that both conductivity and sulfur level drops as the polymer was washed with water. Before the wash, the sulfur comes from both sulfonic groups, SO_3^-, and hydrogen sulfate groups. After the polymer is washed with water, the sulfur content is only due to covalently bounded sulfonic groups.

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

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

Route V. SPAN can be also obtained by solid state sulfonation. Table 5 gives elemental analyses of SPAN synthesized by Route V at different temperatures and 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 sulfate groups from that of covalently bonded sulfonic groups.

Figure 7 gives the IR spectrum for the polymer sulfonated at 130 °C for 48 hr. It has almost identical features as those of polymers made from Route I.[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 trisubstitutents on the phenyl rings. It is noticed that, as in the Route IV, there are some hydrogen sulfate groups, associated with the polymer backbone as the dopant in this route. Therefore, both conductivity and sulfur content are higher for the polymers which were not washed with water. In this case the sulfur in elemental analyses comes from both sulfonic and hydrogen sulfate groups. From Table 5 it is seen that both conductivity and sulfur levels drop as the polymer was washed with water, which removed H_2SO_4 (leading to the decrease in the sulfur content) and decreased the doping level (leading to the lower conductivity). After the polymer was washed with water, the detected sulfur is due only to sulfonic groups.

The sulfonation level for the washed polymer is only about ~33%, insensitive to the conversion temperature and time. However, the conductivity decreased by a factor of ~2 when the sulfonation time and temperature increased, *i.e.*, from 0.07 S/cm for the polymer sulfonated at 120 °C for 42 hr to 0.03 S/cm for one synthesized at 130 °C, 48 hr. The final polymers do not dissolve in basic aqueous solutions and any common organic solvents. The atomic ratios of oxygen to sulfur 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 of polymers sulfonated via Route I, it does demonstrate that solid state sulfonation can be achieved.

CONCLUSIONS

Comparison of the different synthetic routes shows that Route I gave better conductivity and higher sulfonation levels than the others. As far as solubility is concerned, as-synthesized polymers from Routes IV and V did not dissolve in basic aqueous solutions due to lower sulfonation levels. It was found that in order for SPAN to dissolve in a basic aqueous solution, the sulfur content must exceed 8 weight percent or a sulfur to nitrogen atomic ratio of 0.38 is needed.

Acknowledgment. This research has been supported in part by the Defense Advanced Research Projects Agency through a contract monitored by the U.S. Office of Naval Research.

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I. Figure Captions And Figures

Figure 1. Conductivity as a function of sulfonation time for polymers synthesized using Route I.

Figure 2. Yield as a function of sulfonation time for polymers synthesized in Route I.

Figure 3. Sulfur content as a function of sulfonation time for polymers synthesized in Route II starting with EB, see text.

Figure 4. Conductivity as a function of sulfonation time for polymers synthesized in Route II. The samples correspond to those described in Fig. 3.

Figure 5. FTIR spectrum of sulfonated polyaniline synthesizd in Route III (in wave numbers, cm^{-1}).

Figure 6. Cyclic voltammograms (50 mV/s) of sulfonated polyaniline prepared in Route I (——) and the polymer synthesized in Route III (- - - - - -) in 1.0 M HCl.

Figure 7. FTIR spectrum of sulfonated polyaniline synthesizd in Route V (in wave numbers, cm^{-1}).

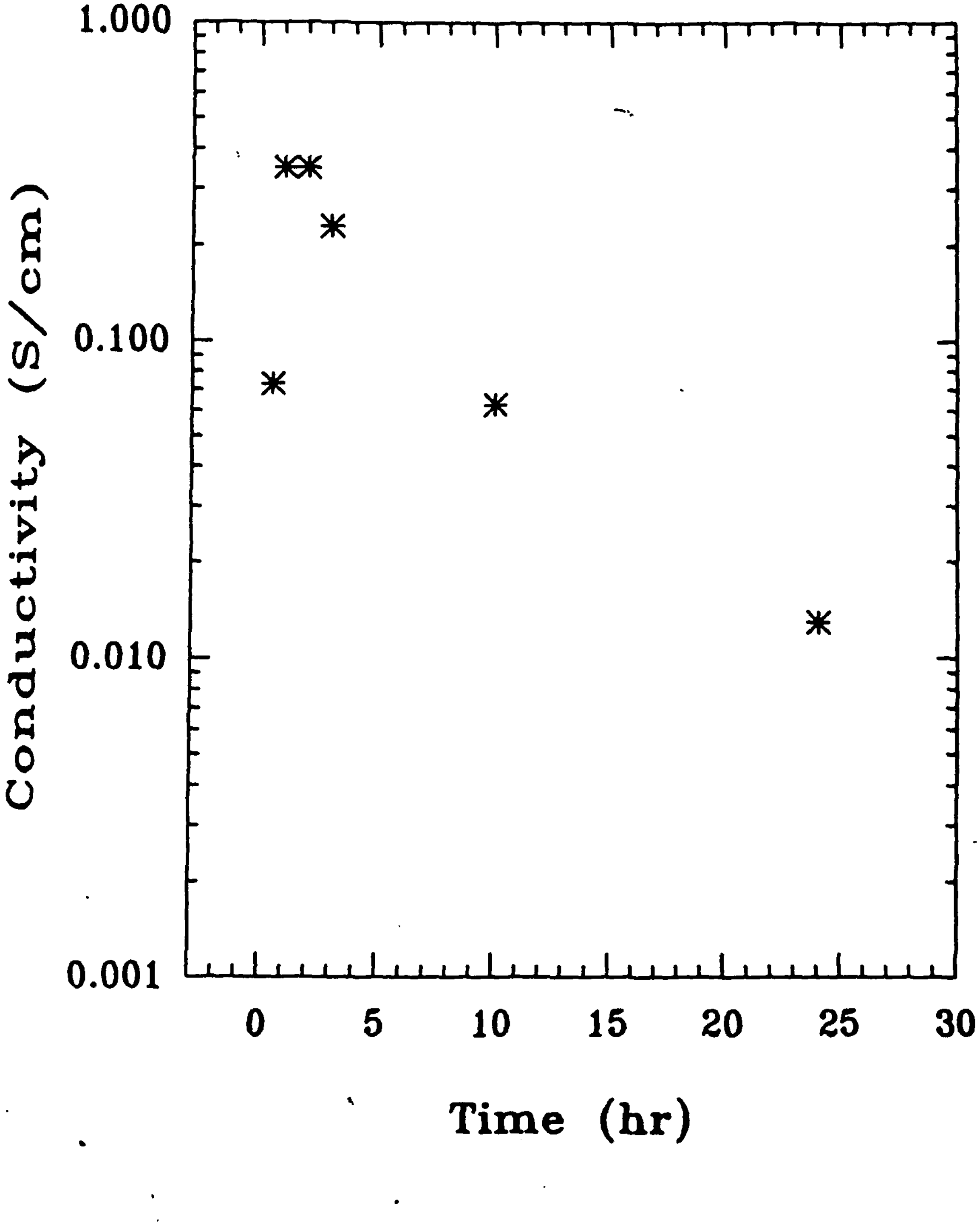

Figure 1. Yue, et al.

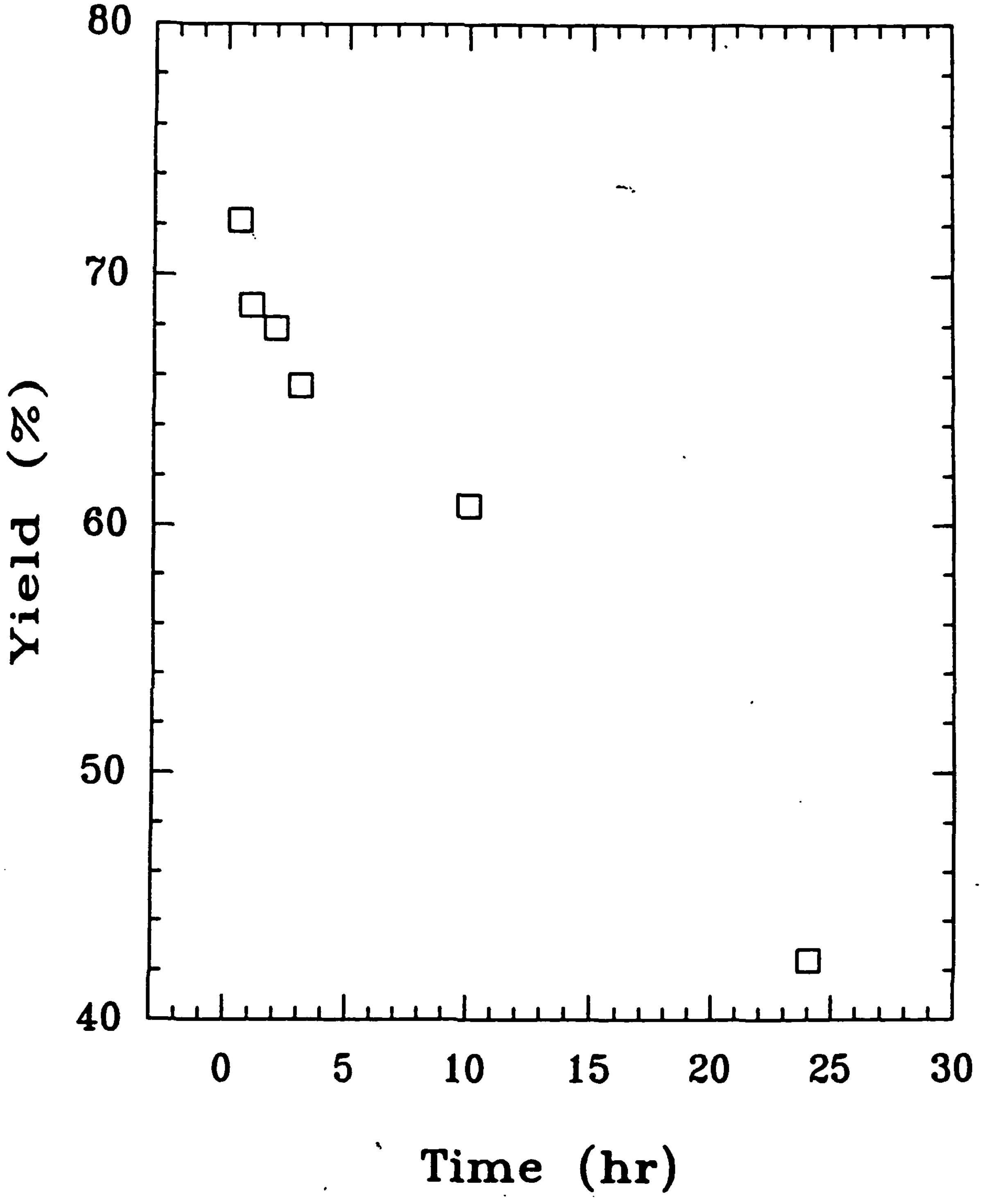

Figure 2. Yue, et al.

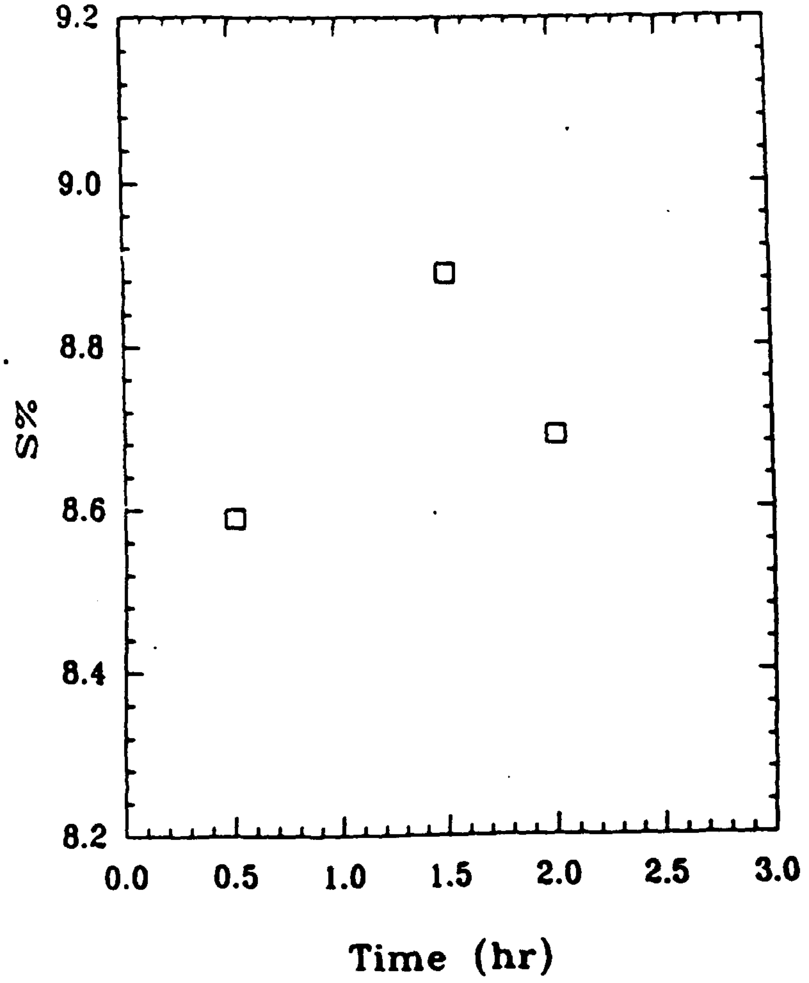

Figure 3. Yue, et al.

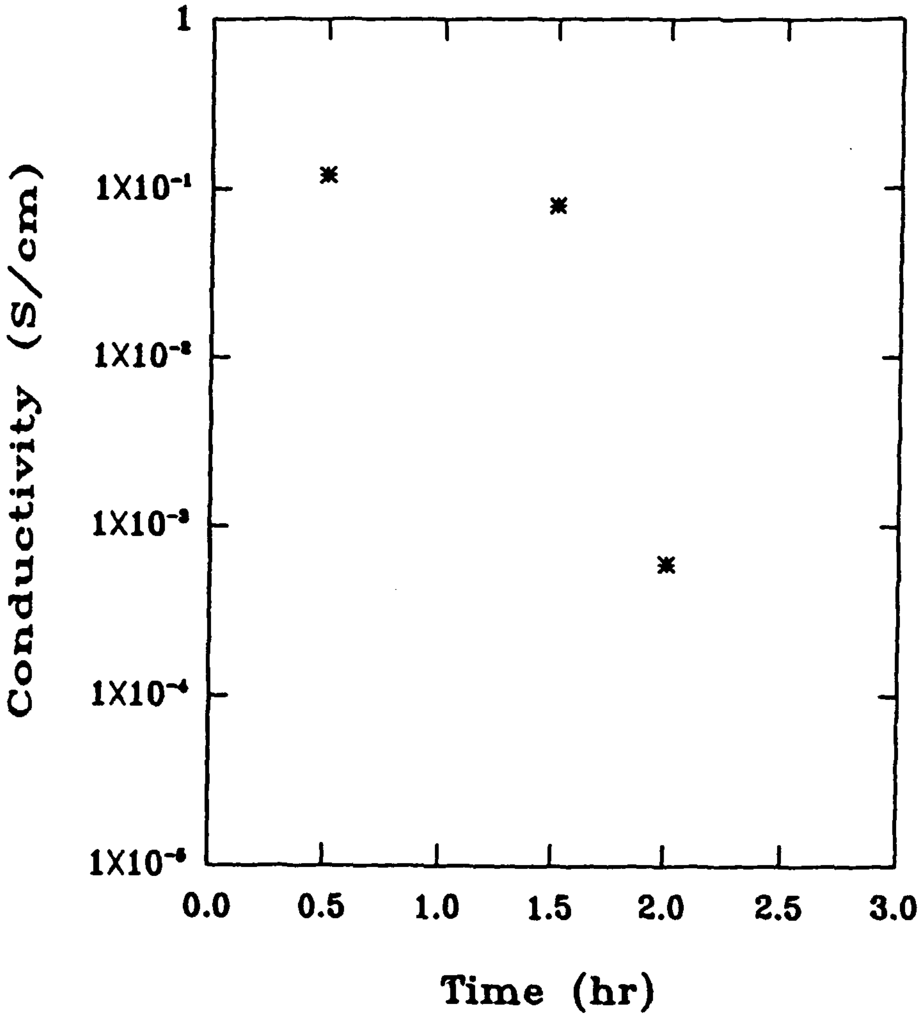

Figure 4. Yue, et al.

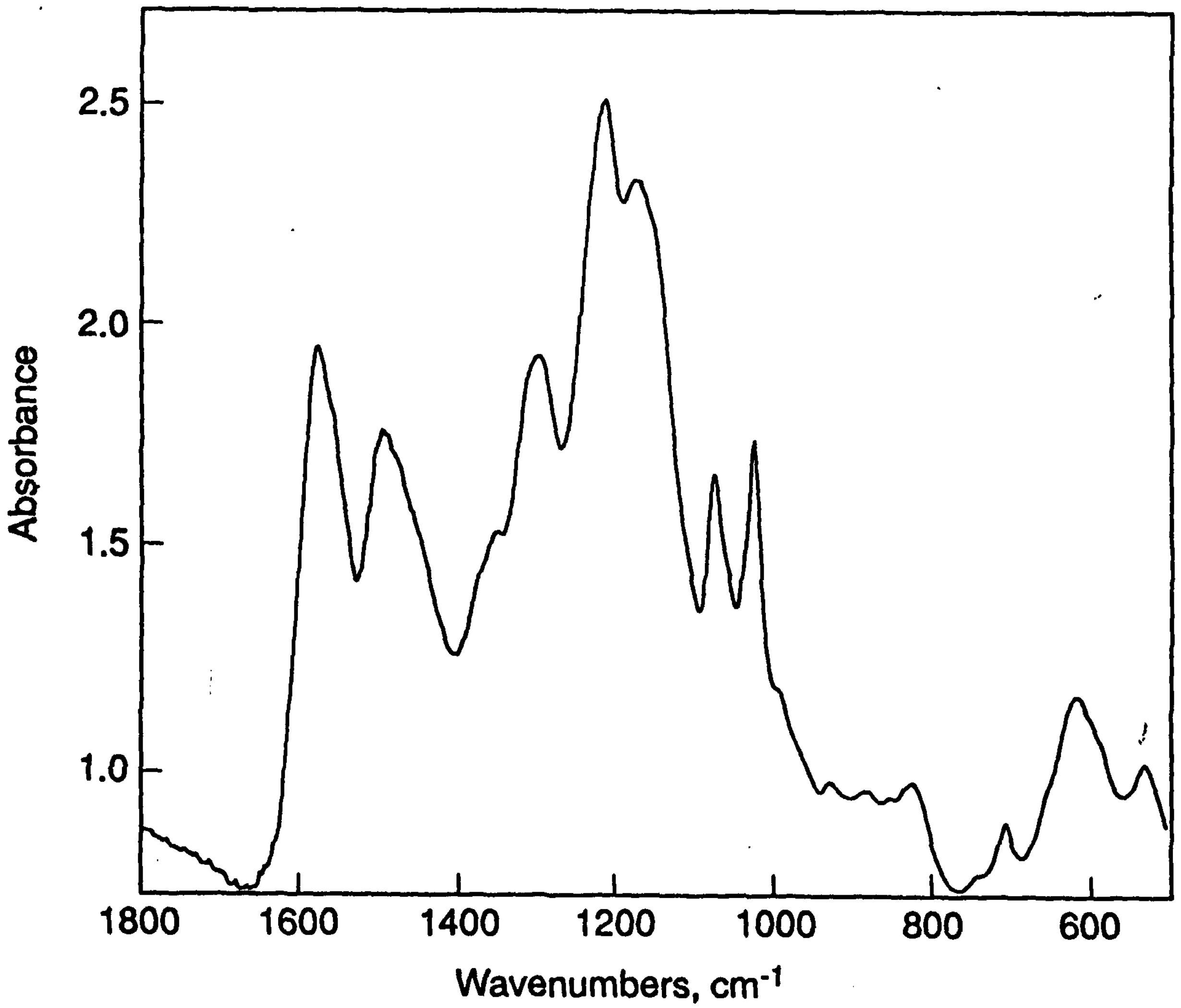

Figure 5. Yue, et al.

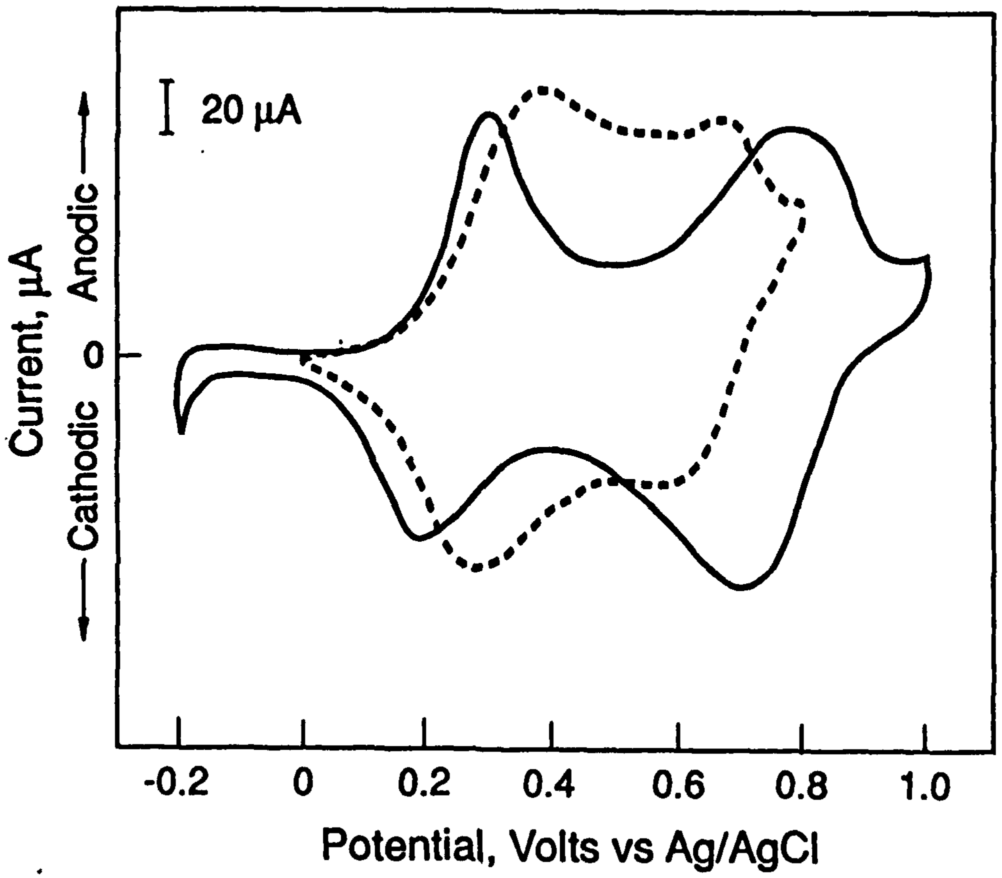

Figure 6. Yue, et al.

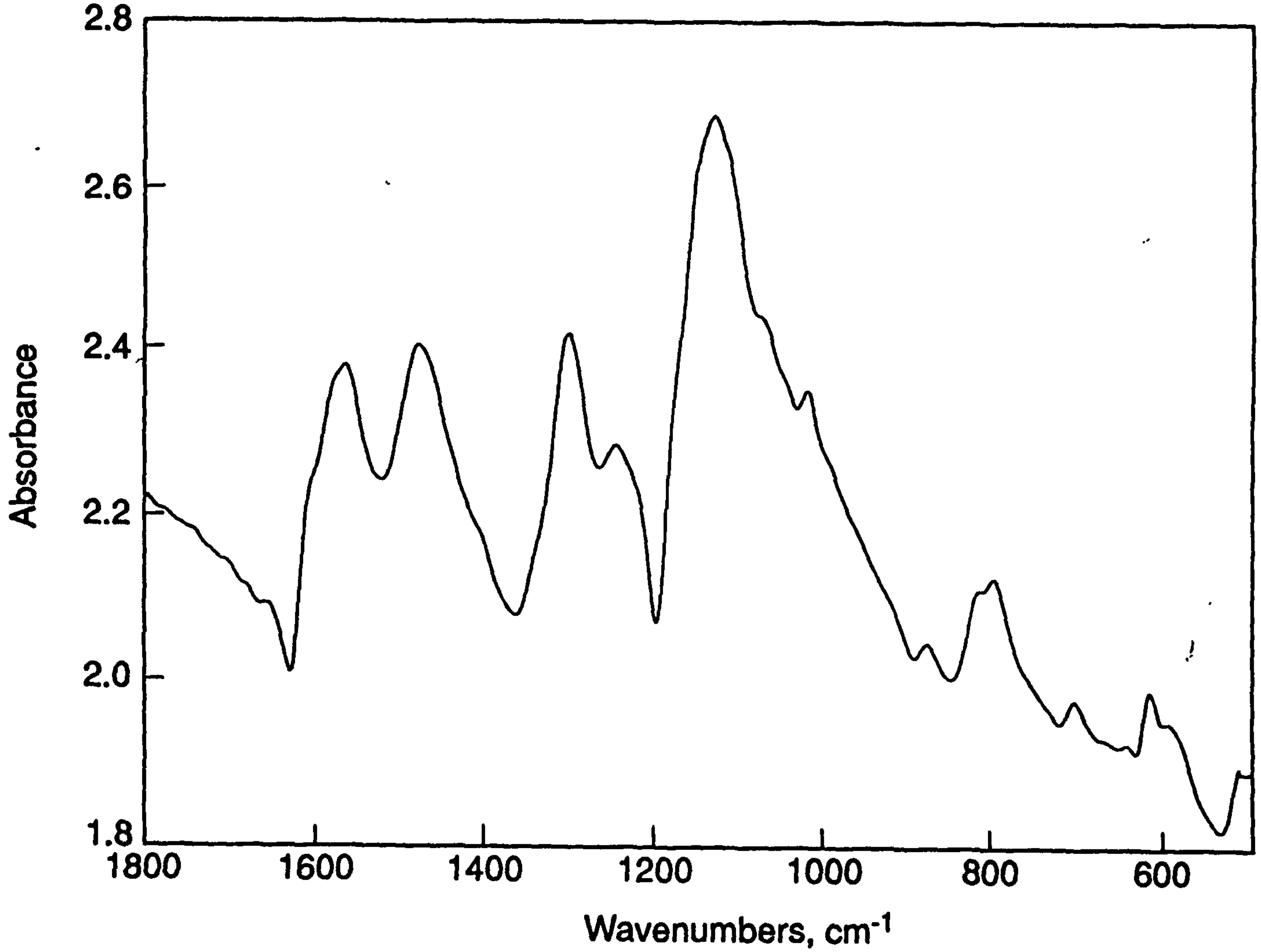

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Figure 7. Yue, et al.

Table I: Elemental analyses for emeraldine base sulfonated in fuming sulfuric acid

time (hr)	C	H	N	S	O^a	S:N	Formula
——^{b}	51.61	3.94	10.04	11.47	22.94	0.50	$C_{12}H_9N_2SO_3(H_2O)$ (cal.)
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: Content of oxygen is by difference.

b: Caculated for $C_{12}H_9N_2SO_3(H_2O)$.

Table II: Elemental analyses for emeraldine base sulfonated in fuming sulfuric acid under the presence of ammonium persulfate

sample	time (hr)	C	H	N	S	O^*	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	$C_{12}H_{9.8}N_{1.92}S_{0.86}O_{3.2}$

* Content of oxygen is by difference.

Table III: Elemental analyses for emeraldine base sulfonated in chlorosulfonic acid

time(hr)/^{0}C	C	H	N	Cl	S	O^*	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	$C_{12}H_{12.1}N_{1.98}S_{1.65}O_{6.58}Cl_{0.93}$

* Content of oxygen is by difference.

Table IV: Elemental analyses and conductivities for sulfonated polyaniline synthesized by using sulfur trioxide/triethyl phosphate complex as the sulfonation agent

time(hr)/temp(°C)	S%^{a}	S:N^a	σ^a(S/cm)	S%^{b}	S:N^b	O:S^b	σ^b(S/cm)
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

* Content of oxygen is by difference.

a: the measurement was done before the sample washed with water

b: the measurement was done after the sample washed with water

Table V: Elemental analyses and conductivities for sulfonated polyaniline synthesized via solid state sulfonation

time(hr)/temp(°C)	S%^{a}	S:N^a	σ^a(S/cm)	S%^{b}	S:N^b	O:S^b	σ^b(S/cm)
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

* Content of oxygen is by difference.

a: the measurement was done before the sample washed with water

b: the measurement was done after the sample washed with water