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# Chemical modification of polyaniline powders by surface graft copolymerization

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## Abstract

Chemical modification of emeraldine (EM) based powders via thermally induced surface graft copolymerization with acrylic acid (AAc), 4-styrenesulfonic acid (SSAc) and amphoteric $N,N'$-dimethyl(methacryloylethyl)ammonium propanesulfonate (DMAPS) was carried out in aqueous media. The effects of temperature on graft copolymerization and Mohr's salt on homopolymerization were also studied. The chemical composition and structure of the graft-copolymerized powders were studied by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. In all cases, the graft yield increased with the monomer concentration and the temperature used for graft copolymerization. Certain Mohr's salts effectively inhibited the production of the homopolymers. Graft copolymerization with AAc and SSAc readily gave rise to self-protonated and semi-conductive EM powders, with the conductivity increasing with the extent of grafting. However, steric hindrance and spatial configuration of the grafted chains had substantially limited the extent of protonation of the EM substrate by the protonic acid functional groups of these chains. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Polyaniline; Graft copolymerization; Powders

## 1. Introduction

During the past two decades, the synthesis and characterization of electroactive polymers have become one of the most important areas of research in polymer and materials science [1–4]. Among the electroactive polymers, the century-old aniline polymers [5,6] have been of particular interest because of their environmental stability [7–10], controllable electrical conductivity [11,12], and interesting redox properties associated with the chain nitrogen [13–15]. Aniline polymers have the general formula $[(\text{–B–NH–B–NH})_y(\text{B–N=Q=N})_{1-y}]_x$, where B represents a benzenoid ring and Q a quinonoid ring. The intrinsic oxidation state of the polymer can be varied from the fully reduced leucoemeraldine state (LM, $y = 1$) through the 50% intrinsically oxidized emeraldine state (EM, $y = 0.5$) to the fully oxidized pernigraniline state (PNA, $y = 0$). The 75% intrinsically oxidized polymer has been termed nigraniline (NA, $y = 0.75$) [5,6]. Aniline polymers also exhibit crystallinity [16,17] and solution- or counterion-induced processability [18–24]. Further, the electrical properties of aniline polymers can be substantially improved through secondary doping [25]. The excellent processability and the presence of a number of intrinsic redox states have substantially enhanced the potential of the aniline polymers in practical applications, such as in corrosion protection of metals [26,27], light-emitting devices [28–30], and materials for catalysts, electrodes and sensors [31–33]. However, with respect to practical applications, materials modification and functionalization, in particular those aiming at the surface and interface, will be necessary. The general methods of chemical modification of polymer surfaces have been reviewed recently [34]. It has also been demonstrated that surface modifications can be performed through graft copolymerization under mild conditions for a number of conventional polymers, such as polyethylene, poly(ethylene terephthalate), poly(viny chloride), Nylons, polypropylene, etc. when their surfaces are pretreated with high-energy radiation, glow discharge, corona discharge, ozone exposure or UV irradiation [35–38]. Further, protein and enzyme immobilizations on the surface-modified polymer substrates have also been of great interest [39].

Because electroactive polymer substrates may provide an

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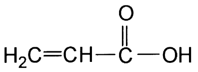
added advantage over conventional polymer substrates, it should be interesting to extend the study to the surface-modified and functionalized electroactive polymers [40]. Graft copolymerization of vinyl monomers may be considered a convenient method for modifying the chemical and physical properties of electroactive polymer surfaces [41]. For surface modification of conventional polymers via graft copolymerization, the role of Mohr's salts in reducing the homopolymer formation has been reported by several investigators [42,43]. Most of the former studies on the surface modifications of polyaniline (PANI) by graft copolymerization involved film samples [40,44,45]. The present study investigates the chemical modifications of pristine EM base powders, which have a much larger specific surface area than the film samples, by surface graft copolymerization with acrylic acid (AAc), 4-styrenesulfonic acid (SSAc) and the amphoteric *N*,*N*′-dimethyl(methacryloylethyl)ammonium propanesulfonate (DMAPS). The effects of monomer concentration and temperature used during graft copolymerization on the copolymer composition and chemical structure were studied by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. The graft-modified PANI powders were also characterized by measuring the graft yield and the electrical conductivity. The action of Mohr's salts in inhibiting the homopolymer production, and thus facilitating the isolation of the copolymer powders produced, was also studied. Because of the reactive and somewhat oxidized nature of the conjugated polymer surfaces, as well as the thermal stability of EM base (stable up to 150°C) [10], the graft copolymerization can be accomplished thermally and in the absence of any surface pretreatment or preactivation of the PANI powders. Common pretreatment methods, such as ozone and Ar plasma pretreatment, have been known to result in over-oxidization and structural alteration of the PANI chains at the film surface [46,47].

## 2. Experimental

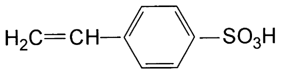
### 2.1. Materials

PANI powders in its EM salt form were prepared via oxidative polymerization of aniline by ammonium persulfate in 0.5 M $H_2SO_4$ according to the method reported in the literature [48]. It was then converted to the neutral EM base by treatment with excess 0.5 M NaOH. The monomers used for graft copolymerization, such as AAc, sodium salt of SSAc (NaSS), were obtained from Wako Pure Chemical Industries Ltd of Tokyo, Japan. The SSAc monomer was prepared by the reaction of equal molar amount of NaSS and HCl. The *N*,*N*′-DMAPS amphoteric monomer was prepared according to the method reported earlier [49]. The chemical structures of the monomers used for graft copolymerization are shown below:

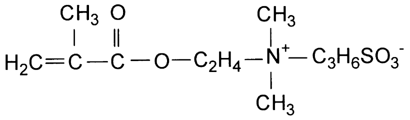


$H_2C{=}CH{-}C({=}O){-}OH$

AAc



SSAc



$H_2C{=}C(CH_3){-}C({=}O){-}O{-}C_2H_4{-}N^+(CH_3)_2{-}C_3H_6SO_3^-$

DMAPS

Mohr's salts were obtained from Nacalal Tesque Inc. of Kyoto, Japan. The solvents and other reagents were of reagent grade and were used without further purification.

### 2.2. Graft copolymerization

About 0.3 g of EM base powders were used in each graft copolymerization experiment. The EM powders, the water-soluble monomer, and the Mohr's salt, if used, were placed in a 50 ml conical flask containing 20 ml of distilled water. The reaction mixture was purged thoroughly with purified argon for at least 40 min and subsequently sealed with a ground stopper. The reaction temperature and time for graft copolymerization with different concentrations of AAc monomer was 90°C and 30 min; for graft copolymerization with AAc in the simultaneous presence a Mohr's salt was 80°C and 110 min; for graft copolymerization with SSAc and DMAPS was 90°C and 6 h. For graft copolymerization with AAc at different temperatures, the polymerization time was about 30 min. After each graft copolymerization experiment, the EM powders were washed thoroughly by vigorous stirring in an excess amount of doubly distilled water at 55°C before being recovered by centrifugation. The washing and centrifugation processes were repeated at least six times to ensure the complete removal of the homopolymer and the physically adsorbed polymer. Finally, the graft-modified EM powders were dried by pumping under reduced pressure until a constant weight was reached.

### 2.3. Material characterization after graft copolymerization

The EM powders after graft copolymerization were characterized by graft yield determination, conductivity measurement, transmission FTIR spectroscopy and XPS. The graft yield was calculated as follows:

$$\%\text{Graft yield} = 100\%(W_2 - W_1)/W_2, \tag{1}$$

where $W_1$ is the initial weight of the EM powders (0.3 g in this study) and $W_2$ is the weight of the graft-modified EM powders. The conductivity of each sample was measured by the two-probe method in the form of compressed pellets. The FTIR spectra were measured on a Bio-Rad FTS 135 spectrophotometer.

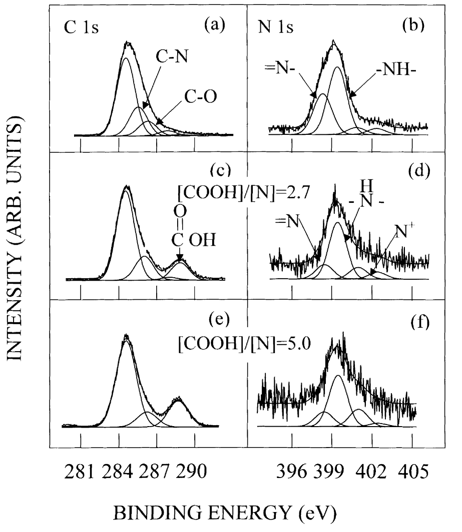


Fig. 1. C 1s and N 1s core-level spectra, obtained at $\alpha = 75°$ of (a) and (b) pristine EM powders, of EM powders after been subjected to graft copolymerization in (c) and (d) 2.5 vol.% AAc solution, and (e) and (f) 10 vol.% AAc solution at 90°C.

XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg Kα X-ray source (1253.6 eV photons). The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The EM powders were mounted on the standard VG sample studs by means of double-sided adhesive tape. The core-level spectra were obtained at the photoelectron take-off angle of 75°. The pressure in the analysis chamber was maintained at $10^{-8}$ mbar or lower during each measurement. To compensate for surface charging effects, all binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV. In peak synthesis, the line width (full width at half maximum or FWHM) of Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak area ratios, corrected with the experimentally determined sensitivity factors, and were accurate to within ±5%. The elemental sensitivity factors were calibrated using binary compounds of well-defined stoichiometries. The surface graft concentration is defined as the number of repeat units of the graft chains per repeat unit of the substrate EM base. Thus, the concentrations of surface-grafted AAc and SSAc polymers are expressed as the XPS-derived [COOH]/[N] and [S]/[N] mole ratios, as reported previously for the UV-induced graft copolymerization of EM films [40]. The surface concentration of the grafted DMAPS polymer, on the other hand, is expressed as the $[N^+]/([=N–] + [–NH–])$ ratio and derived from the component area ratio of the curve-fitted N 1s core-level spectrum.

## 3. Results and discussion

Recent studies [50–52] have demonstrated that the quinonoid imine (=N– structure), benzenoid amine (–NH– structure), and positively charged nitrogen ($N^+$ structure) in a PANI complex correspond, respectively, to peak components with BEs at about 398.2, 399.4, and >400 eV in the properly curve-fitted N 1s core-level spectrum. Fig. 1(a) and (b) shows, respectively, the C 1s and N 1s core-level spectra of the pristine EM powder used in this work. The powder consists of about equal amounts of imine and amine nitrogen, consistent with the intrinsic redox state of the EM base. The residual high BE components above 400 eV in the N 1s core-level spectrum may have resulted, at least in part, from surface oxidation products or weakly charge-transfer complexed oxygen [50]. These assignments are supported by the presence of a fairly strong O 1s signal in the pristine EM base powders. This conclusion is also consistent with the more reactive nature of the conjugated polymer surfaces [53], in comparison with the surfaces of the polymers with saturated backbones. The charge transfer interaction between the conjugated backbone and the oxygen in air will result in an ‘oxidized’ EM surface. Some of the oxidized species, such as the peroxides and hydroperoxides, can be subsequently used in the thermally induced surface vinyl graft copolymerization. The peroxides and hydroperoxides initiated mechanism has generally been proposed for the thermally or UV-induced surface graft copolymerization of vinyl monomers on conventional polymer substrates [34,35,40]. The reactive nature of the conjugated polymer surfaces in initiating surface vinyl graft copolymerization has also been reported in a number of recent studies [44–46]. In the case of the AAc graft-copolymerized EM surface, the bonding of AAc units to the amine units of the EM base via amide linkages may have also occurred to some extent, as indicated by the appearance of a weak absorption band at 1656 $cm^{-1}$ in the IR absorption spectra (see Fig. 3, later). In all of the graft-copolymerized samples, the physically adsorbed homopolymers on EM powders must have been completely removed by the exhaustive washing procedures employed (see Section 2), as all of them are readily soluble in the water.

### 3.1. Chemical modification by surface graft copolymerization with AAc

#### 3.1.1. Effect of monomer concentration

Fig. 1(c)–(f) shows the respective C 1s and N 1s core-level spectra of EM powders after having been subjected to thermal graft copolymerization in 2.5 vol.% AAc solution (see (c) and (d)) and 10 vol.% AAc solution (see (e) and (f)) at 90°C. The small but distinct high-BE C 1s component at 288.7 eV is characteristic of the carboxylic acid group of the grafted AAc polymer [54]. The presence of self-protonation is indicated by the reduction in intensity of the imine component and the appearance of the high-BE tail in the N 1s core-level spectrum. The extent of surface grafting in each case can also be determined from the corrected area ratio of the C 1s peak component at 288.7 eV and the total N 1s area. The concentration of surface grafting can thus be

Table 1
XPS-derived surface redox states and compositions of the various EM powder samples with the surface grafted AAc polymer

| Sample no. | AAc monomer concentration (vol.%) | Graft concentration [COOH]/[N][a] | Proportion[b] of | | |
|---|---|---|---|---|---|
| | | | =N– | –NH– | $N^+$ |
| 1 | 0.3 | 0.16 | 0.30 | 0.57 | 0.13 |
| 2 | 0.8 | 0.18 | 0.25 | 0.61 | 0.14 |
| 3 | 1.5 | 0.84 | 0.22 | 0.61 | 0.17 |
| 4 | 2.5 | 2.70 | 0.21 | 0.58 | 0.21 |
| 5 | 5.0 | 3.91 | 0.18 | 0.59 | 0.23 |
| 6 | 7.5 | 4.18 | 0.17 | 0.59 | 0.24 |
| 7 | 10 | 5.03 | 0.17 | 0.59 | 0.24 |
| 8 | 12.5 | 5.54 | 0.16 | 0.59 | 0.25 |
| 9 | 15 | 6.08 | 0.15 | 0.59 | 0.26 |

[a] Based on the corrected area ratios of a C 1s component at 288.6 eV and the total N 1s spectrum.

[b] Determined from the curve-fitted N 1s core-level spectra.

expressed as the number of repeat units of the graft AAc polymer per EM repeat unit, or the [COOH]/[N] ratio. The [COOH]/[N] ratio and the proportions of the various nitrogen species of the EM powders as a function of graft concentration are summarized in Table 1. For all samples, the protonation levels, or the proportions of the $N^+$ species, in the surface region are substantially below the expected value of 0.5 for the fully protonated EM base, despite the fact that the [COOH]/[N] ratios for the more heavily grafted EM powders are well above 0.5. This observation readily suggests that steric hindrance and spatial configuration of the grafted AAc chains must have played an important role in controlling the extent of protonation of the EM substrates. Protonation, in most cases, must have been limited to the outer-most surface layer of the EM substrate, which is less than the probing depth of the XPS technique.

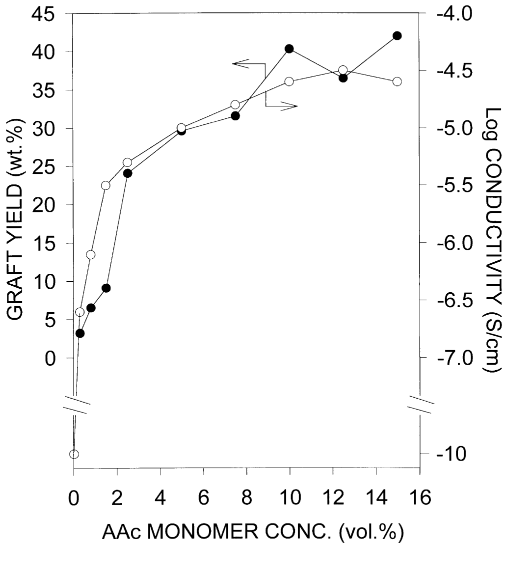


Fig. 2. Effect of AAc monomer concentration on the graft yield and the electrical conductivity of the graft-modified EM powders for graft copolymerization carried out at 90°C.

Fig. 2 shows the graft yield of the AAc polymer and the corresponding electrical conductivity of the graft-modified EM powders as a function of AAc monomer concentration used during thermal graft copolymerization at 90°C. In general, the grafted yield of the AAc polymer increases with increasing monomer concentration in the reaction media, with the most significant increase being observed for AAc concentrations between 0 and 4 vol.%. It can be expected that graft copolymerization of EM powders with AAc will also result in a self-doped or self-protonated surface structure. The electrical conductivity of the EM powders grafted with AAc polymer increases with monomer concentration in a manner similar to that of the graft yield. This result is consistent with the increase in the extent of self-protonation as a result of the increase in graft yield. However, at AAc concentration above 10 vol.%, the graft yield does not seem to increase significantly. This phenomenon is probably associated with the complete coverage of the EM powder surface by the grafted AAc polymer. As a result, the electrical conductivity ceases to increase also for samples graft copolymerized in AAc concentration above 10 vol.%. The increase in conductivity of the graft-modified powders is also indicated by the change in color of the EM powders from violet to green, characteristic of the protonated EM. It is further confirmed by the decrease in the =N– component intensity and the corresponding increase in the proportion of the positive charge nitrogen in the N 1s core-level spectra of the graft-copolymerized samples (Fig. 1(d) and (f)). Though the changes in color and the N 1s line shape are similar to those of EM powders protonated by an external protonic acid, such as HCl, there are some fundamental differences between the two materials. When the compressed EM–HCl pellet was soaked in an excess amount of distilled water, the electrical conductivity decreased from about $10^{-2}$ to about $10^{-3}$ S/cm in 36 h, and to about $10^{-4}$ S/cm in 132 h. An even more drastic decrease in electrical conductivity was observed when the EM–HCl salt in its free powder form was equilibrated in water. The observations suggest that the EM powders protonated by HCl readily undergo deprotonation when exposed to an aqueous medium, as protonation/deprotonation of EM is an equilibrium process [13–15]. On the contrary, the grafted AAc polymer molecules are covalently tethered to the substract chains, and they cannot be easily removed from the EM powders. The conclusion is readily supported by the fact that the conductivity of the EM powders from graft copolymerization in 15 vol.% AAc, for example, remains constant at $2.4 \times 10^{-5}$ S/cm even after the exhaustive washing and soaking in water for over 2 weeks.

The presence of a surface-graft copolymerization and self-protonated EM structure is also revealed by FTIR spectroscopy. Fig. 3(a) shows the transmission of FTIR spectrum of the pristine EM powders, which consists of absorption bands of about equal intensities at 1500 and 1600 $cm^{-1}$,

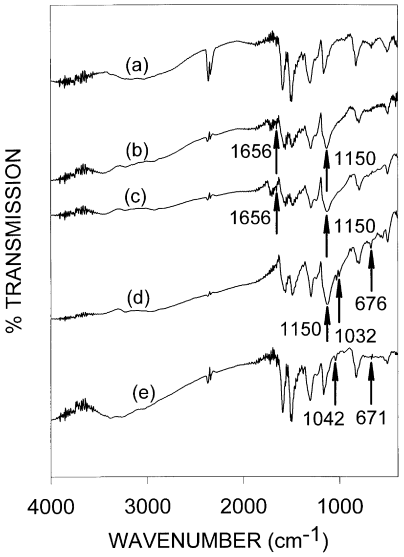


Fig. 3. FTIR absorption spectra of (a) pristine EM powders and EM powders after graft copolymerization in (b) 2.5 vol.% AAc; (c)15 vol.% AAc; (d) 5 wt.% SSAc; and (e) 5 wt.% DMAPS.

attributable to the benzenoid and quinonoid units, respectively [55]. Fig. 3(b) and (c) shows the corresponding FTIR absorption spectra of the samples after graft copolymerization in 2.5 vol.% AAc and 15 vol% AAc solutions. The characteristic feature of the graft-copolymerized and self-protonated EM powders is the presence of a strong and broad absorption band at about 1150 $cm^{-1}$, which has been associated with the electrical conductivity and a high degree of electron delocalization in PANI [56]. The broadening of the absorption band in Fig. 3(c) further suggests the presence of a higher extent of protonation in this sample compared to that of the sample in Fig. 3(b). The weak absorption band at 1656 $cm^{-1}$ is suggestive of the formation of some amide linkages. Finally, it should be emphasized that the self-protonation phenomenon observed must have resulted predominantly from the grafted AAc chains. The protonation by the homopolymer can be ruled out even through the latter, if present, will have a strong tendency to protonate the EM base. All the water-soluble and physically adsorbed homopolymer must have been removed by the exhaustive washing procedure employed (see Section 2), as protonation/deprotonation of the EM base is an equilibrium process [11]. Thus, the contribution of the doped homopolymer to the graft yield can be neglected.

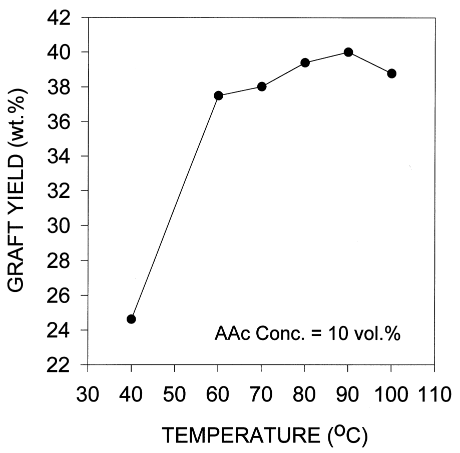


Fig. 4. Effect of temperature on the graft yield for EM powders graft copolymerization in 10 vol.% AAc.

### 3.1.2. Effect of graft copolymerization temperature

As the graft copolymerization in this study was accomplished thermally, the effect of temperature on graft yield was also investigated. The rate of initiation and the rate of monomer diffusion on the surface of the polymer powders are expected to be sensitive to temperature. Fig. 4 shows the effect of reaction temperature on the graft copolymerization yield for graft copolymerization carried out in 10 vol.% AAc solution The graft yield increases with increasing temperature, with the most significant increase occurring in the temperature range between 40 and 60°C. At temperatures above 60°C, the graft yield approaches an asymptotic value. This saturation phenomenon in graft yield again suggests the complete coverage of the powder particles by the grafted AAc chains. From the data in Fig. 4, it is observed that the optimum temperature range for the graft copolymerization EM powders with AAc is between 60 and 90°C. An optimum graft yield of close to 40 wt.% can be achieved.

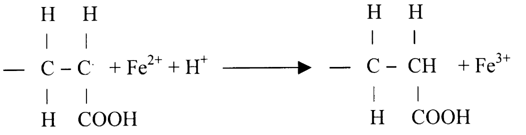
### 3.1.3. Effect of Mohr's salts

Surface graft copolymerization is always accompanied by homopolymerization. In many cases, the removal of the viscous, and sometimes crosslinked, homopolymer is extremely tedious. Some Mohr's salts have been used with great success in the inhibition of homopolymerization during the radiation-induced graft copolymerization [42,43]. The effect of certain transition metal compounds in inhibiting the homopolymerization are investigated in the present work and the results are shown in Table 2. Ferrous sulfate ($FeSO_4$) and copper sulfate ($CuSO_4$) exhibit some degree of inhibiting effect on the homopolymerization. The other salts are not effective in preventing homopolymerization as they are probably not good radical scavengers. Fig. 5 shows the graft yield of the AAc polymer as a function of ferrous sulfate and copper sulfate concentration for graft copolymerization carried out in 25 vol.% AAc solution at 80°C. The graft yield in each case is also affected by the presence of the metal compound and decreases with increasing concentration of Mohr's salt. This phenomenon is also revealed by the XPS data in Fig. 6. Fig. 6(a) and (b) shows the corresponding C 1s and N 1s core-level spectra of the EM sample graft copolymerized at 80°C in 25 vol.% AAc solution containing 0.02 M $FeSO_4$. Fig. 6(c) and (d), on the other hand, shows the corresponding C 1s and N 1s core-level spectra of the EM sample when the $FeSO_4$ concentration is increased to 0.06 M during graft copolymerization.

Table 2
List of compounds used to inhibit the AAc homopolymerization during surface-graft copolymerization of EM powders with AAc

| Compound | Compound concentration (M) | Homopolymer | Yield (wt.%) | Conductivity (S/cm, $\times 10^{-3}$) |
|---|---|---|---|---|
| Magnesium sulfate ($MgSO_4$) | 1.0 | Present | 33.92 | 0.010 |
| Zinc sulfate ($ZnSO_4$) | 1.0 | Present | 34.35 | 0.30 |
| Manganese sulfate ($MnSO_4$) | 1.0 | Present | 36.58 | 0.25 |
| Cobalt sulfate ($CoSO_4$) | 1.0 | Present | 36.31 | 0.18 |
| Potassium titanium oxalate ($K_2TiO(C_2O_4)_2$) | 1.0 | Present | 44.5 | 0.066 |
| Nickel sulfate ($NiSO_4$) | 1.0 | Present | 34.07 | 0.024 |
| Copper sulfate ($CuSO_4$) | 0.08 | Trace | 21.05 | 0.020 |
| Ferrous sulfate ($FeSO_4$) | 0.08 | Trace | 20.42 | 0.024 |

The graft concentration, expressed as the [COOH]/[N] ratio, decreases with increasing concentration of the metal salt. The phenomenon can be explained by assuming that the $Fe^{2+}$ ions present in the grafted layer of the copolymer take part in chain termination reactions as shown below [57]:



$$-\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}-\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}^{\cdot}\\|\\\mathrm{COOH}\end{array} + Fe^{2+} + H^{+} \longrightarrow -\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}-\begin{array}{c}\mathrm{H}\\|\\\mathrm{CH}\\|\\\mathrm{COOH}\end{array} + Fe^{3+} \qquad (2)$$

Further, the lower graft concentration, or lower [COOH]/[N] ratio at higher metal salt concentration leads to a higher =N– peak intensity in Fig. 6(d) compared with that in Fig. 6(b). Finally, no Fe or Cu signal is discernible in the XPS wide-scan spectra of both samples, suggesting the complete removal of the metal compounds after the graft copolymerization process.

### *3.2. Chemical modification by surface graft copolymerization SSAc*

Fig. 7 shows the graft yield and electrical conductivity of EM powders graft copolymerized with SSAc as a function of the SSAc monomer concentration. The graft yield of the SSAc polymer increases with increasing monomer concentration in the reaction media, with the most significant increase being observed at SSAc concentrations between 0 and 2 wt.%. It can be expected that graft copolymerization of EM powders with SSAc will also result in a self-doped or self-protonated surface structure, and thus electrically conductive powders. The conductivity of EM powders grafted with SSAc polymer increases with increasing monomer concentration, with the most significant increase in conductivity been observed between 0 and 2 wt.% SSAc. This result is consistent with the increase in the extent of self-protonation as a result of the increase in graft yield. However, at SSAc concentration above 2 wt.%, the conductivity does not seem to increase substantially. This phenomenon is probably associated with the steric hindrance and spatial configuration of the grafted SSAc polymer chains in interacting with the EM powder surfaces, especially at high graft concentration.

Fig. 8(a)–(f) shows the corresponding C 1s, N 1s and S 2p core-level spectra for pristine EM powders after having been subjected to surface graft copolymerization in 5 wt.% SSAc solution (see (a)–(c)) and 10 wt.% SSAc

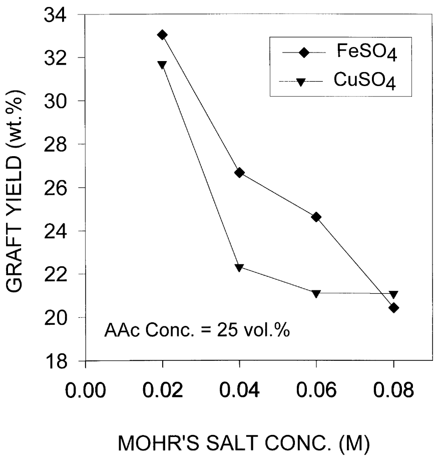


Fig. 5. Effect of Mohr's salts concentration on the graft yield of the AAc polymers for graft copolymerization carried out in 25 vol.% AAc solution at 80°C.

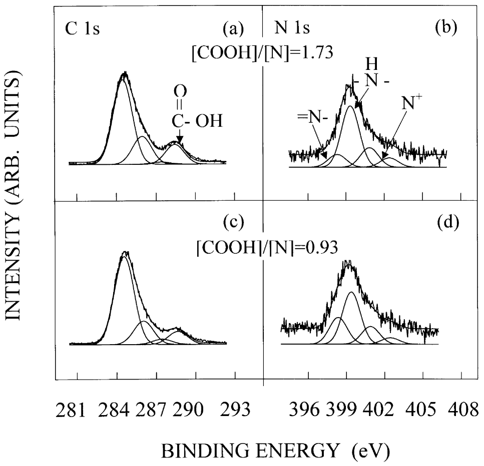


Fig. 6. C 1s and N 1s core-level spectra, obtained at $\alpha = 75°$, for pristine EM powders after having been subjected to graft polymerization at 80°C in 25 vol.% AAc solution containing (a) and (b) 0.02 M $FeSO_4$ and (c) and (d) 0.06 M $FeSO_4$.

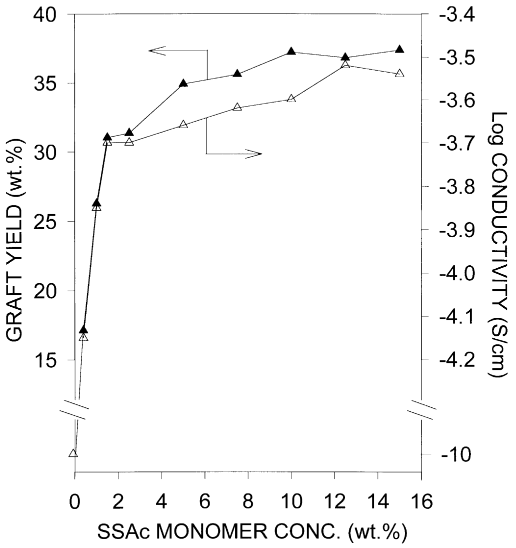


Fig. 7. Effect of SSAc monomer concentration on the graft yield and electrical conductivity of EM powders for graft copolymerization carried out at 90°C.

solution (see (d)–(f)) at 90°C. The presence of a surface-grafted SSAc polymer is readily suggested by the appearance of the S 2p core-level signal at about 168 eV, characteristic of the covalently bonded sulfonic acid group ($-SO_3$) of the SSAc polymer [58]. In this case, the concentration of surface-grafted polymer can be conveniently determined from the sensitivity-factor corrected [S]/[N] spectral area ratios. In comparison with the graft concentration of the AAc polymer prepared under similar condition, the lower [S]/[N] ratios suggest a substantially lower graft copolymerization efficiency for the SSAc monomer. Nevertheless, as in the case of the SSAc graft-copolymerized surface, the N 1s core-level spectra of the SSAc polymer grafted samples all show the presence of a high BE tail above 400 eV, characteristic of the positively charged nitrogens [52,53], and a reduced imine component intensity at 398.2 eV. These results really suggest that the sulfonic acid groups of the grafted SSAc polymer must have also participated in the protonation of the imine nitrogens of the EM powders to give rise to a self-protonated and semiconductive EM surface. In fact, the electrical conductivity of an SSAc graft-copolymerized EM sample is at least one order of magnitude higher than that of its AAc graft-copolymerized counterpart at the similar extent of grafting (compare Fig. 7 with Fig. 2). This phenomenon is consistent with the fact that sulfonic acid is a stronger protonic acid than the carboxylic acid.

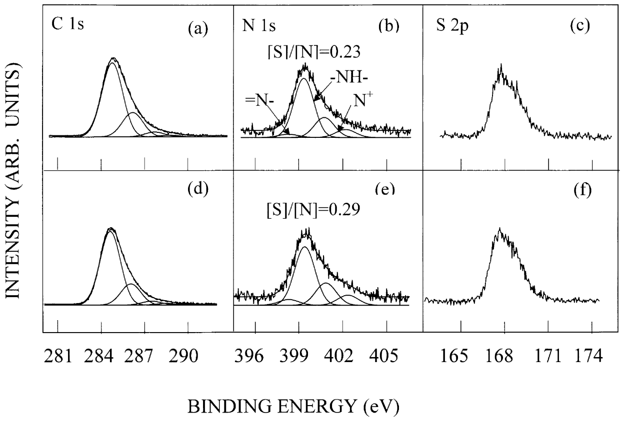


Fig. 8. C 1s, N 1s and S 2p core-level spectra, obtained at $\alpha = 75°$, for pristine EM powders after having been subjected to surface-graft copolymerization in (a)–(c) 5 wt.% SSAc solution and (d)–(f) 10 wt.% SSAc solution at 90°C.

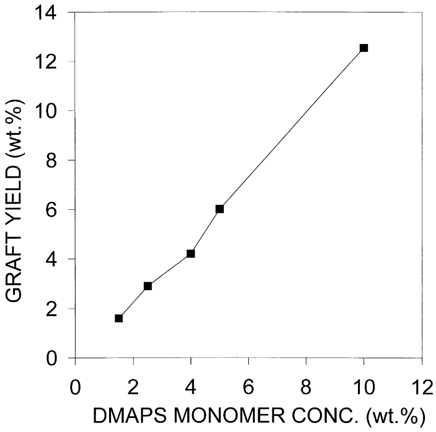


Fig. 9. Effect of DMAPS monomer concentration on the graft yield of EM powders for graft copolymerization carried out at 90°C.

The presence of surface-grafted SSAc polymer is also revealed by the transmission FTIR spectroscopy. Fig. 3(d) is the FTIR transmission spectrum of the EM powders graft copolymerized in 15 wt.% SSAc at 90°C. The absorption bands due to the $-SO_3$ groups are visible between 1000 and 1050 $cm^{-1}$, and at 670 $cm^{-1}$ [59]. Also the enhanced and broadened absorption band at 1150 $cm^{-1}$ is again characteristic of the increase in electrical conductivity of the EM powders grafted with the SSAc polymer.

### *3.3. Chemical modification by surface-graft copolymerization with DMAPS*

Fig. 9 shows the graft yield of the amphoteric DMAPS polymer on EM powders as a function of the monomer concentration for graft copolymerization carried out at 90°C. The graft yield increases with the increasing monomer concentration. A graft yield of 12.5% was obtained at 10 wt.% DMAPS monomer concentration. When the monomer concentration is increased to above 10 wt.%, it is difficult to isolate the graft-modified EM powders because of the presence of excess DMAPS homopolymer and the high viscosity of the reaction mixture. Thus, the concentration of the DMAPS monomer is kept below 10 wt.% for all the graft copolymerization experiments. Graft copolymerization with DMAPS is not accompanied by self-protonation,

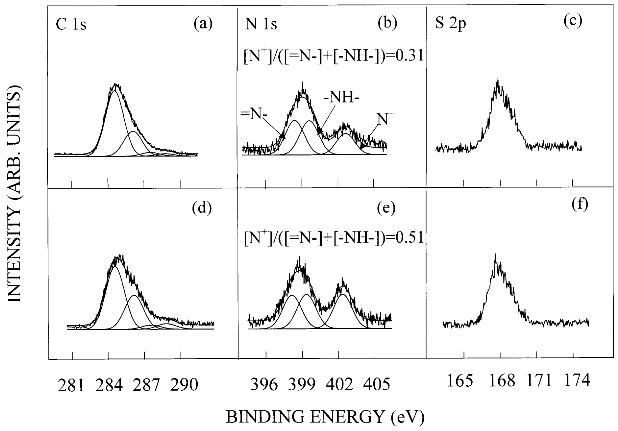


Fig. 10. C 1s, N 1s and S 2p core-level spectra, obtained at $\alpha = 75°$, for pristine EM powders after having been subjected to surface graft copolymerization in (a)–(c) 5 wt.% DMAPS solution, and (d)–(f) 10 wt.% DMAPS solution at 90°C.

and so the EM powders after graft copolymerization remain insulating in nature.

Fig. 10(a)–(f) shows the corresponding C 1s, N 1s and S 2p core-level spectra of EM powders, obtained at a take-off angle of 75°, after thermal-graft copolymerization in 5 wt.% DMAPS solution (see (a)–(c)) and 10 wt.% DMAPS solution (see (d)–(f)). The DMAPS polymer has a C 1s component at the BE of about 287.0 eV, which is attributed to the $-C-N^+$ functional group [60]. Also, the appearance of the S 2p core-level signal at the BE of about 168.0 eV, characteristic of the covalently bonded sulfonic acid group ($-SO_3$) of the DMAPS polymer, is consistent with the presence of surface-grafted DMAPS polymer. In the case of the N 1s spectrum, the $-C-N^+$ groups of the grafted DMAPS polymer give rise to a distinct $N^+$ nitrogen component at the BE of about 401.7 eV. The amount of the grafted DMAPS polymer on the EM substrate can thus be determined from the N 1s core-level spectral component areas and expressed as the $[N^+]/([=N-] + [-NH-])$ ratio. The ratio of $[N^+]/([=N-] + [-NH-])$ for EM powders graft copolymerized in 5 wt.% DMAPS solution is 0.31. The ratio increases to 0.51 for graft copolymerization carried out in 10 wt.% DMAPS solution. The graft copolymerization of DMAPS onto EM powder surfaces is further confirmed by the FTIR transmission in Fig. 3(e), where the EM powders were graft copolymerized in 5 wt.% DMAPS solution at 90°C. The absorption bands between 1000 and 1050 cm$^{-1}$ and at 670 cm$^{-1}$ are again characteristic of the $-SO_3^-$ group.

## 4. Conclusion

Because of the reactive nature of the conjugated polymer surface, EM powders are readily susceptible to surface modification via thermal graft copolymerization with hydrophilic functional monomers, such as AAc, SSAc and DMAPS, in the absence of any surface pretreatment. Graft yields were determined as weight ratios and conductivities of the relevant graft-modified EM powders were measured. XPS and FTIR were used to elucidate the surface microstructure and chemical composition of the EM powders after thermal graft copolymerization. In all cases, the graft yields increase with the monomer concentration and temperature. It was found that graft copolymerization with AAc and SSAc also gave rise to a self-protonated and semi-conductive EM surface structure. However, steric hindrance and spatial configuration of the graft chains had substantially limited the extent of protonation in the surface region of the EM substrate. The covalently tethered graft chains on the EM powder surfaces remained intact even after prolonged exposure in an aqueous medium. Certain Mohr's salts, such as $FeSO_4$ and $CuSO_4$, were found to be effective in inhibiting homopolymerization.

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