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Sulfonated Polyaniline: Influence of Sulfonation Routes on its Thermal and Structural Characteristics

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In order to study the influence of different sulfonation routes on its thermal and structural properties sulfonated polyaniline (SPAni) was prepared. FT-IR revealed that the formation of PAni salt or ring sulfonation depends on the route. UV-visible spectra pointed out that the level of the PAni protonation was dependent on the sulfonation route. A new approach was given for TG/DTG and DSC results correlating different energy levels with the distinguished sulfonation routes. The TG/DTG degradation steps and the amount of the released material corroborated the structural differences of the polyanilines. For each DSC first regime of heating, a broad and intense peak (from –30 to 250 °C) with different level of energy was noticed. That peak could be ascribed to the multiple relaxations and breaking of the PAni intra and inter hydrogen bonds after sulfonation.

Keywords: *SPAni, TG/DTG, DSC, FT-IR, UV-vis*

1. Introduction

Target polymer materials have been receiving extensive research due to their unique physical properties and potential applications in micro/nanoelectronics, electromagnetics and biomedical devices. Among these polymers, a great number of researches have been addressed to polyaniline (PAni). Similar to metals, it owns unusual electronic, magnetic, electrochemical and optical properties jointly with high environmental stability, easy polymerization and low cost of monomer. However, its processability by melting is not practical since the polymer decomposes at temperatures below its softening or melting point[1-4]. Basically, in the previous published articles, the presence, absence and type of dopant agent besides the thermal treatment on its behavior have been highlighted. Due to its cation exchange properties, voltammetric analysis of metals in water was performed by Fungaro[5] using sulfonated polyaniline coated mercury film electrodes. As PAni is considered a material with poor mechanical properties, Lenz et al.[6] prepared its blend with low density polyethylene (LDPE) in order to match the unusual conductive characteristics and the remarkable mechanical resistance intrinsic of each polymer. In recent study, MacDiarmid and collaborators[7] showed that conductometric devices integrated with HCl-doped PAni nanofibers and subject to different thermal treatments could exhibit different transduction behaviors when exposed to 1% hydrogen carried by nitrogen. According to them, the controversy in hydrogen storage studies, involving conducting polymers, may be related to the ambiguous thermal treatments on HCl-treated PAni samples. In their investigation on PAA/PAni blends, Chen and co-authors[8] registered the drop of PAni conductivity in the glass transition region correlating this behavior to its partial deprotonation. Microwave absorbing sheet was achieved by Folgueras et al.[9] when blended doped polyaniline with silicone rubber. Thermal stability and glass transition temperature were found to be dependent on the type and amount of the inorganic nanoparticles in composites containing aluminium oxide and multi-walled carbon nanotube[10-12]. PAni nanofibers doped with several inorganic/organic acids were synthesized by interfacial polymerization being the morphology, thermal stability and electrical conductivity dependent on the dopant chemical nature[13]. Dendrimers modified polyaniline nanotubes as biosensor for detecting glucose at low voltage was prepared by Queiroz and his group[14]. This research deals with the sulfonation of PAni-EB at different time and temperature conditions. Structural changes due to the aromatic ring sulfonation and formation of the emeraldine salt were monitored by FT-IR, UV-vis., TG/DTG and DSC. The presence of sulfonic group as acid or ion, sulfonation degree, degradation steps, thermal stability and the correlation of DSC endothermic peak with level of sulfonation were assessed.

2. Experimental

2.1. Materials

Aniline was distilled twice under vacuum and stored in a refrigerator. Analytical grade chloridric acid [HCl] (37% - 10 M), ammonium peroxydisulfate [$(NH_4)_2S_2O_8$], ammonium hydroxide [NH_4OH] (28% - 8 M), concentrated sulfuric acid [H_2SO_4] (98% - 10 M) and fuming sulfuric acid (SO_3 content = 20%) were used without purification.

2.2. PAni and sulfonated PAni syntheses

The PAni hydrochloride powder was synthesized by the oxidative polymerization of aniline in 1M aqueous HCl with $(NH4)_2S_2O_8$ as oxidant, as described in a previous work[15]. The powder was converted to PAni-EB (emeraldine base) by treatment with 0.3 M aqueous NH_4OH followed by drying under dynamic vacuum, until constant weight.

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In a glass flask, 40 mL of concentrated sulfuric acid was cooled to 5 °C and 0.5 g of PAni-EB was added, kept for 15 minutes, under magnetic stirring. After that, the flask was removed from the cooled bath, heated to 100 °C and maintained under stirring, for 24 hours. In the next step, the resultant solution was slowly poured into a cooled methanol bath (10 °C) being the precipitate filtered and washed with distilled water until neutral pH. Finally, the solid was dried in vacuum oven, until constant weight. The same procedure was performed to sulfonate PAni-EB at 150 °C. The synthesis of sulfonated PAni with fuming sulfuric acid followed the above procedure with some alterations. The reactional temperature was kept at 25 °C and the reaction times were 1/2, 1 and 2 hours. The reaction products and their acronyms were arranged in Table 1.

2.3. *Fourier-transform infrared spectroscopy (FTIR)*

The effect of the sulfonation conditions on the PAni-EB were monitored with a Varian FT-IR spectrophotometer model Excalibur 3100, using KBr disk of each sample. The spectra were recorded from 4000 to 400 cm^{-1}, with 20 scans at a resolution of 4 cm^{-1}.

2.4. *Ultraviolet and visible spectroscopy (UV-vis)*

In order to check the effect of the sulfonic group on the PAni iminequinoid and benzenoid groups, a Varian UV-visible spectrophotometer, model Cary 100 was used. The dimetilformamide and ammonium hydroxide were the solvents for emeraldine base and sulfonated PAni, respectively. The UV-vis. spectra were recorded between 200-900 nm from solution concentration in the range of 0.005 to 0.01% (w/v).

2.5. *Thermogravimetry/derivative thermogravimetry (TG/DTG)*

Thermal stability of the PAni-EB and sulfonated PAni was conducted in a TA thermogravimetric analyser model Q500, in the range of 30-700 °C, at 10 °C /min, under nitrogen atmosphere. The onset temperature (T_{onset}), maximum degradation temperature (T_{max}), end temperature (T_{end}) and residue content were determined.

2.6. *Differential scanning calorimetry (DSC)*

The calorimetric parameters were assessed using a TA calorimeter model Q1000. Three scans were performed. The first scan was concerned with heating from –80 to 250 °C, at 10 °C /min, being the sample kept for two minutes at 250 °C in order to eliminate the thermal history; after that, the sample was cooled (2nd scan) from 250 to –80 °C, at 200 °C/min. Finally, the sample was re-heated (3rd) at the same protocol used for the first scan.

3. Results and Discussion

3.1. *Fourier-transform infrared spectroscopy (FTIR)*

The FT-IR spectra of the PAni - emeraldine base (EB) - and polyaniline synthesized with both acids are arranged in Figure 1. In the PAni-EB spectrum, the region of 4000-3000 cm^{-1} showed poor resolution and the N-H and C-H stretching of the aminebenzenoid rings were not assigned with reliability. The characteristic bands around 1591 and 1500 cm^{-1} were ascribed to C=N and C=C stretching vibration of iminequinoid and benzenoid rings, respectively, also detected by Su et al.[13,16]. The C-N stretching vibration of aromatic secondary amines was pointed out at 1309 and 1253 cm^{-1}, according to Colthup[17]. Similarly to mentioned by Chen et al.[8], there is a peak at 1147 cm^{-1} which was associated to the electronic-like absorption of N=Q=N where Q denotes the iminequinoid rings. The vibration bands situated around 829 and 507 cm^{-1} were attributed to the benzenoid rings 1,4 disubstituted C-H and N-H out of plane bending, respectively. The FT-IR spectrum of SPAniF2 showed two bands around – 3390 and 3250 cm^{-1} - which, according to Colthup[17] and Pretsch[18], could be attributed to N-H stretching of the benzenoid rings and O-H stretching of the sulfonic acid group [O=S(=O)-OH]. Their assignment, as free or hydrogen bonds, is not easy to estabilish. For SPAniF½ and SPAniF1, those bands merged as a unique and broad band. It is interesting to notice that all PAni produced with fuming acid showed two very weak peaks around 2600 and 2500 cm^{-1} which could be emerged from intra and inter H-bonded between O=S(=O)-OH and amine groups[17]. In the spectral region of 2000-500 cm^{-1} the spectra resembled each other. All of them showed C=N and C=C sharp and defined bands around 1600 and 1500 cm^{-1} which could be assigned to the stretching of the benzenoid and iminequinoid rings, respectively, as reported by Lenz et al.[6] in an article on blends of polyaniline synthesized with dodecil benzenesulfonic acid (DBSA) and camphorsulfonic acid (CSA). A band around of 1290 cm^{-1} and a shoulder in the vicinity of 1230 cm^{-1} were concerned with the stretching of the C-N bond[16]. The sulfonyl (O=S=O) asymmetric and symmetric stretching of the sulfonic group linked to the benzenoid ring[16] were detected around 1320 and 1178 cm^{-1}. The sulfonic group as protonation agent ($HSO_4^- \leftrightarrow OH\text{-}SO_3^-$ ion) showed the sulfonyl asymmetric and symmetric stretching at 1170 and 1010 cm^{-1} while the S-O-H stretching appeared as a sharp and intense band around 850 cm^{-1} all of them associated to the emeraldine salt[17]. Meanwhile the band nearby of 820-830 cm^{-1} concerned with the C-H 1,4 disubstituted

Table 1. Reaction products and their acronyms.

Reaction product	Acronym
PAni – emeraldine base	SPAni - EB
PAni – sulfonated with concentrate acid at 100 °C	SPAniC100
PAni – sulfonated with concentrate acid at 150 °C	SPAniC150
PAni – sulfonated with fuming acid, 25 °C, 1/2 hour	SPAniF1/2
PAni – sulfonated with fuming acid, 25 °C, 1 hour	SPAniF1
PAni – sulfonated with fuming acid, 25 °C, 2 hours	SPAniF2

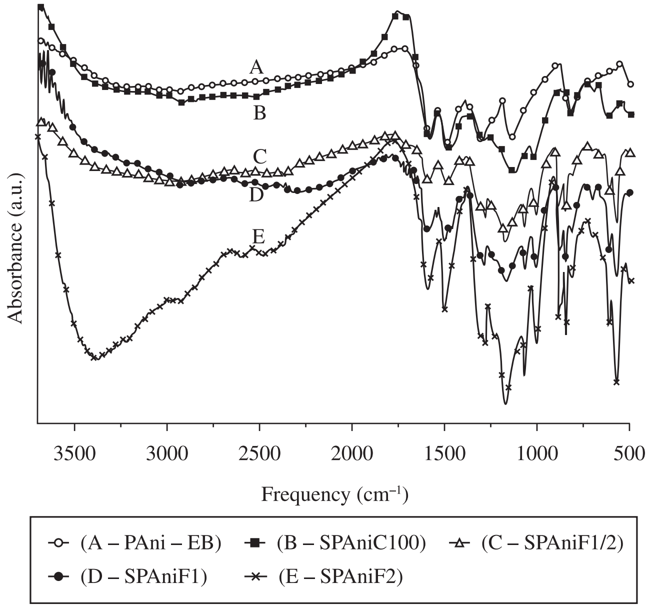

Figure 1. PAni-EB and PAni synthesized with both acids FT-IR spectra.

aromatic ring stretching decreased its intensity the vibrations at 887 cm^{-1} – C-S-OH stretching – and around 700 cm^{-1} – C-S stretching - emerged on account of the ring sulfonation reaction[17,19]. Two strong, sharp and intense peaks around 615 and 576 cm^{-1} came out in the sulfonated polyanilines. Using Raman resonance spectroscopy, Temperini et al.[20] detected these bands in redox process of polyaniline secondarily doped with camphorsulfonic but their attribution was not estabilished sharply. Herein, these bands could be ascribed to the formation of the emeraldine salt along the backbone of the PAni chains and could be associated to additional vibrational modes of the nitrogen-hydrogen and oxygen-hydrogen bonds of the sulfonic and amine groups. The IR spectrum of polyaniline yielded with 10 M concentrated H_2SO_4 (SPAniC100) were similar to that of the PAni-EB but some absorptions were shifted. The band ascribed to the C=N vibration was shifted to higher wavenumber (1598 cm^{-1}) while that of the C=C stretching was dislocated to lower wavenumber (1490 cm^{-1}). The C-N vibrational mode appeared at lower wavenumbers (1303 and 1222 cm^{-1}). The absorption of the iminequinoid rings (N=Q=N) was shifted to higher wavenumber (1153 cm^{-1}). The vibration band at 829 cm^{-1} remained indicating that the aromatic ring sulfonation did not occur. A new band was detected at 1024 cm^{-1} which was attributed to the vibrational mode of the sulfonyl group in its ionic form (HSO_4^- ↔ $OH\text{-}SO_3^-$). The shift of the PAni absorptions was reported in a study on polyaniline nanofibers doped with acids[13] such as HAc, $HClO_4$, H_3PO_4 and HCl. It might conclude that the unsuccessful attempt of sulfonating PAni-EB with 10M concentrated H_2SO_4 could be correlated with a probable reversibility of the reaction. The activation energy for the ring desulfonation could be lower than its sulfonation due to the extreme reactional conditions[21]. Nevertheless, the new band at 1028 cm^{-1} indicated that the emeraldine salt was achieved.

3.2. Ultraviolet and visible spectroscopy (UV-vis)

Figure 2 shows the UV-vis spectra of the PAni-EB and those yielded with both acids. There are two well sharp and defined absorption peaks around 323 and 610 nm in the PAni-EB UV-visible spectrum which were ascribed to the π–π* transition of the aminebenzenoid rings and the exciton absorption of the iminequinoid rings, respectively. It is expected that when the imine groups are doped by acids they are protonated; the nitrogen atom and its neighboring iminequinoid ring become a semiquinoid radical cation and the exciton absorption band intensity decreases. For fully protonated imine groups, the exciton absorption band of the PAni tends to disappear[8]. It can be noticed that in the spectrum of our PAni yielded at 100 °C both absorptions shifted to lower wavenumbers which means that both the aminic and iminic nitrogens would be protonated. The acid dopant action seems to be greater in the PAni synthesized at 150 °C since the exciton absorption band effectively vanished while that one attributed to the aminebenzenoid rings seems to be decreasing its intensity. The spectra of the PAni prepared with fuming acid showed the same features. As the reaction time increased the absorption peaks moved towards lower wavenumbers. For the highest time, the exciton absorption peak practically disappeared. All PAni yielded with both acids showed a band around 280 nm which could be correlated with the partial formation of the oxidized PAni base – pernigraniline – reported by Kang et al.[22] using NMP as solvent. The results were corroborated by those found in FT-IR section.

3.3. Differential scanning calorymetry (DSC)

The DSC curves of the PAni-EB and those synthesized with both acids are arranged in Figure 3. Those yielded with concentrated acid showed the similar pattern to that of the PAni-EB and it is in accordance with Lenz et al.[6]. A broad and intense peak which started around –30 °C and finished nearby 230 °C was noticed showing a maximum at the vicinity of 130 °C. The calorimetric curves of the PAni synthesized with fuming acid presented two peaks with the same pattern regardless of the reaction time. The first one occurred between 70-120 °C and appeared as a broad and weak peak. The second one started immediately after the end of the previous peak and finished around 230 °C but with remarkable intensity. It is noteworthy that the maximum of the DTG peak shifted to higher temperature for the sample sulfonated at ½ hour and decreased progressively with the increase of the sulfonation time. Akcelrud et al.[23] published a comprehensive article on polyaniline DMTA thermal transitions from NMP cast films. Multiple relaxations were detected in the temperature range from –150 to 250 °C and, for annealed samples,

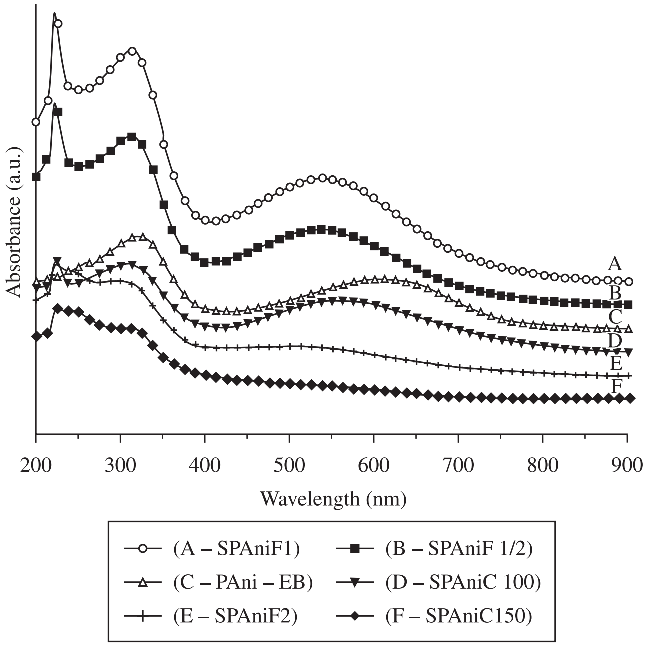

Figure 2. PAni-EB and PAni synthesized with both acids UV-Vis. Spectra.

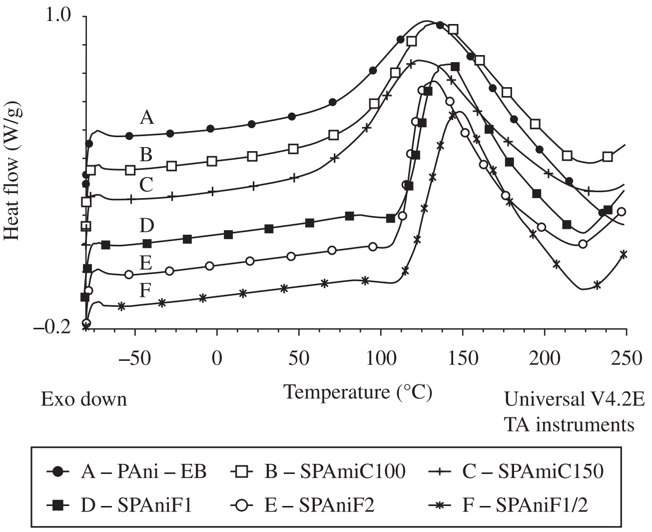

Figure 3. PAni-EB and PAni synthesized with both acids DSC curves.

a transition immediately preceding the glass transition temperature (T_g) was reported. They guessed that its origin is correlated with a particular water/NMP composition, but its nature is still unknown. We could conjecture that the broad peak observed in all DSC curves is considered to be polyanilne T_g and some sub-T_g transitions. For comparing, the peak area of each calorimetric curve was calculated in order to evaluate the effect of the sulfonation routes on the thermal behavior of each sample (Table 2). Pani-EB exhibited the highest value of energy. Besides the T_g and sub-T_g transitions, in this amount of energy, could be included that necessary to breaking the intra and inter hydrogen bond between the aminic and iminic nitrogens during the first regime of heating. For polyalnilines synthesized with concentrated acid, the energy dropped on account of the emeraldine salt decreased the amount of iminic nitrogens available to lead intra and inter hydrogen bonds along the PAni backbone. The lowest energy values were noticed for polyanilines prepared with fuming acid. This behavior could be taken into consideration the combined decreasing effect of the free iminic nitrogens and the steric hindrance of the sulfonic group attached to the aminebenzenoid rings. Both playing together could release the segmental mobility of the molecules through the increasing of the free volume among the polymer chains. For all samples, the second regime of heating did not show any change of the DSC baseline which could reflect the chains crosslinking during the heating process as approached by Espe et al.[24] in their article on the effect of elevated temperature on the reactivity and structure of polyaniline. The results are in agreement with those found in the structural analyses.

Table 2. Polyanilines peak temperature and area.

Reactional condition			Peak temperature (ºC)	Peak area (J.g^{-1})
H_2SO_4	Reaction temperature (ºC)	Reaction time (h)		
Concentrated	100	24	134	286.6
	150		127	269.3
Fuming	25	1/2	148	258.1
		1	141	254.6
		2	131	213.0
PAni-EB	–	–	131	427.1

3.4. *Thermogravimetry/derivative thermogravimetry (TG/DTG)*

Figures 4 and 5 show the TG and DTG curves of the undoped and polyanilines obtained by acids. In Table 3 are arranged the onset temperature (T_{onset}), maximum degradation temperature (T_{max}), end temperature (T_{end}), residue content for all samples. The undoped PAni TG/DTG curves showed that its loss of mass happened in two steps. The first one occurred before 100 °C concerning the release of water (8%). The second one started around 440 °C, reached a maximum at 586 °C and burned continuously until 700 °C representing the degradation of the polymer backbone (56%). A coal (36%) remained which needs further heating to burn completely. Regarding the TG/DTG curves of the polyanilines synthesized with concentrated acid, they presented similar patterns and three degradation steps as was reported by Ansari and collaborators[1]. That step below 100 °C was related to the loss of water (9 and 11%). The intermediate one was located between 250 and 400 °C with maximum around 290 °C which might be associated to the sulfonic groups release (19 and 16%) of the emeraldine salt and PAni low molar mass. Around 400 °C, the curve dropped progressively with temperature until 700 °C which was regarded as the degradation of the PAni backbone (22%). At the end, a residue (50%), which consists of coal and sulfate ion, was left. The polyanilines synthesized with fuming acid also exhibited TG/DTG curves similar to each other and three decays of degradation, although different from those obtained by concentrated acid. There is a peak below 100 °C which was also attributed to the release of water ($\approx$10% for all). The second peak, started around 240 °C, reached a maximum at 280 °C and ended around 400 °C. That decay might be also correlated with the loss of the sulfonic group attached to the aminebenzenoid ring, the sulfonic ion of the emeraldine salt and PAni molar mass which percentages were 24, 20 and 19% for sulfonation time of ½, 1 and 2 hours, respectively. It is interesting to notice that the content of sulfonic group has been decreasing as the reaction time increased. This could be attributed to the changes of the planarity (aromatic ring sulfonation) and the conformation of the PAni chains both making difficult the access of the sulfonic group to the reaction sites. The third decay was detected around 400-700 °C. Su et al.[12] observed the shift of the T_{max} to lower temperature in their work on HCl-doped polyaniline. Herein, we noticed that the maximum degradation temperature has been decreasing as the sulfonation

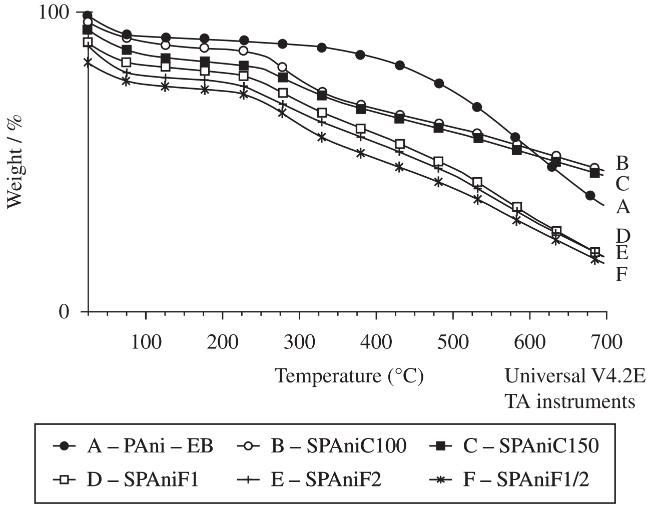

Figure 4. PAni-EB and PAni synthesized with both acids TG curves.

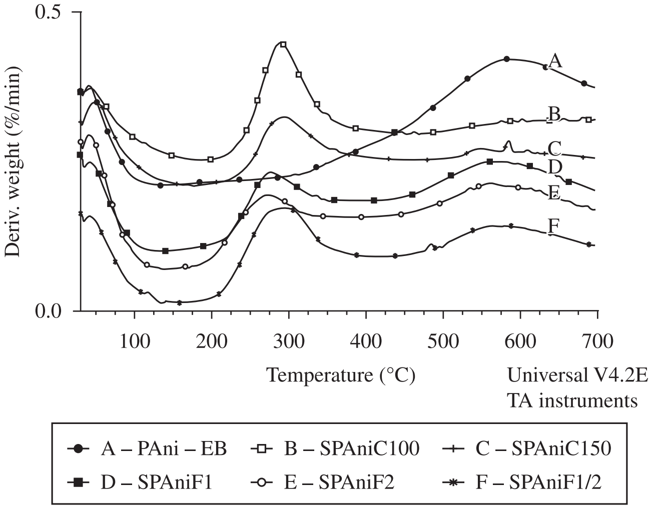

Figure 5. PAni-EB and PAni synthesized with both acids DTG curves.

Table 3. Polyanilines thermal parameters.

Reactional condition			T_{onset} (°C)			T_{max} (°C)			T_{end} (°C)	Residue (%)
H_2SO_4	Reaction temperature (°C)	Reaction time (h)	Step			Step				
			1st	2nd	3rd	1st	2nd	3rd		
Concentrated	100	24	30	255	425	45	286	–	700	50
	150		30	255	425	56	293	552	700	51
Fuming	25	1/2	30	239	425	43	285	564	700	33
		1	30	238	400	44	279	560	700	29
		2	30	225	400	45	277	556	700	30
PAni-EB	–	–	30	449	–	46	586	–	700	36

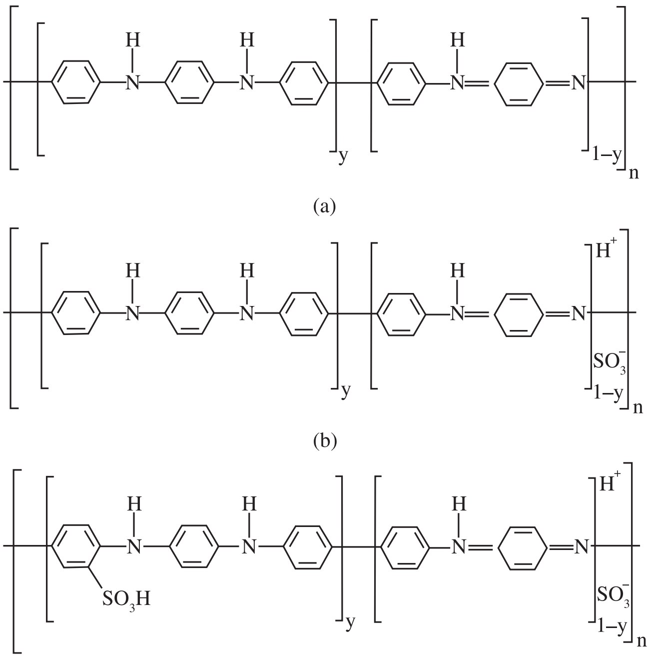

Figure 6. Schematic representation of the suggested structure for: a) PAni-EB; b) protonated PAni; and c) protonated and sulfonated PAni.

time increased. The losses concerning the polymer backbone were 34, 41 and 38% according to the increase of the sulfonation time. The amount of residue was 33, 29 and 30% and followed the duration of the sulfonation. The percentage polymer backbone degradation and residue of the synthesized polyaniline with fuming acid was lower than that of the parent PAni. It could suggest that for PAni synthesized with the acids the intermediate degradation step comprises both the release of the sulfonic group and the degradation of some PAni low molar mass. Then, the thermal analysis was fitted for confirming structural changes of the PAni using distinguished sulfonation routes.

The results indicated that the concentrated acid mainly played a role as protonating agent of the imine groups of the PAni. Additionally, the fuming acid also acted as a sulfonating agent of the amine groups. The suggested structures are showed in Figure 6.

4. Conclusions

A systematic study of sulfonation of PAni was performed with concentrated and fuming sulfuric acid. The type of acid and reaction routes regulated the changes along the PAni chains. FT-IR and UV-Visible analyses showed that both acids were able to form salt of PAni. The benzene ring sulfonation was only achieved with fuming acid. On account of the amount of sulfonic groups as a salt and/or as a group attached to the amine ring the intra and intermolecular hydrogen bonds between aminic and iminic nitrogens decreased leading to the drop of the energy at the glass transition region and different degradation steps.

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