

Study of the Polymerization Ability of a Novel Type of Aniline Monomer, 2-(*m*-Aminophenylbenzothiazole)

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Received 29 December 2000; accepted 5 February 2003

ABSTRACT: The oxidation process of the aniline derivative [2-(*m*-aminophenylbenzothiazole)] was studied, and the products obtained from its oxidation and the coreaction with different ratios of aniline were characterized in structure and properties. IR, NMR, and MALDI-TOF spectrometries demonstrate the actual polymerization of the monomer, whereas DSC, TGA, and conductivity measurements show their good

thermal and electrical properties when combined with aniline. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 497–504, 2003

Key words: conducting polymers; polyaniline; MALDI; thermal properties; structure

INTRODUCTION

A field that has attracted major interest and effort in chemical research during the last few decades is the study of conducting polymers. Their important properties ensure a number of useful applications now and in the future. Such applications are related to very different fields, some of which are conducting coatings, organic batteries, and sensors.¹

However, the development of such applications is not easy because there are still a number of drawbacks in presently available polymers. Normally, these polymers are excellent conductors but they are not processable.^{2,3} Regarding their electric behavior, some of them are excellent conductors but are not stable enough to withstand the doping–dedoping cycles⁴ and have short lifetimes. No conducting polymer has yet been found that also simultaneously exhibits good chemical, thermal, and mechanical properties.

There are some groups studying alternative structures to find polymers that are characterized by all these property requirements. A great deal of investigation has been focusing on compounds that contain sulfur atoms in their structure.^{5–7} The polythiophenes have shown good conductivities, and their ambient stability is much greater than that of polyanilines or polypyrroles. The presence of sulfur atoms affects the complexation of conjugated compounds with metal ions (as has been shown, for example, with the bis(ethylenedithio)tetrathiafulvalene (BEDT)–tetrathiaful-

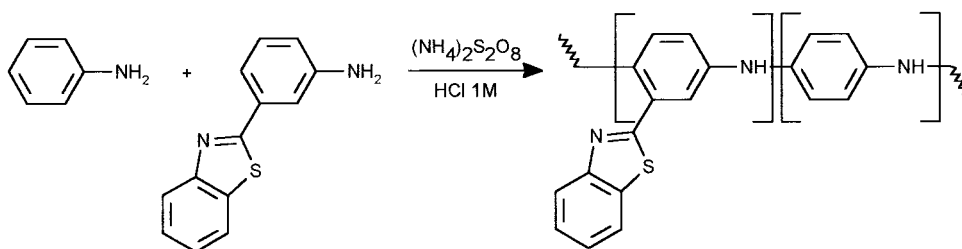
valene (TTF)–Cu systems⁸) and thus improves the conductivity of the system.

Furthermore, these kinds of polymers are expected to be used as anticorrosion protection for metals (because of the strength of the metal–sulfur bonds) without losing the conductive properties of the metal pieces, as was shown to occur with polyaniline⁹ and polypyrrole.

Prompted by these findings, Abdel-Azzem and co-workers^{10,11} performed some studies on the electrochemical copolymerization of aniline and 2-(4-aminophenyl)-6-methylbenzothiazole. They reported the formation of organic films during electrooxidation of the initial solution and the formation of an azeotropic copolymer with aniline. However, the presence of the benzothiazole group in the *para*-position with respect to the amine group in the 2-(4-aminophenyl)-6-methylbenzothiazole prevents delocalization of the radical cation formed in the final amino group to a favorable position for polymerization. They report the link of the benzothiazole derivative at the end of polyaniline chains (it somehow acts as an end capper).

Following the idea of the inclusion in the polymers of a benzothiazole unit, our work has thus focused on 2-(3-aminophenylbenzothiazole) (mAFBT) (see Scheme 1). It can be seen as a modified aniline molecule, and because of its free *para*-position, its polymerization behavior may be expected to be the same as that of aniline. In any case, the presence of the benzothiazole group may affect the spatial distribution of the polymer, causing a steric inhibition of the polymerization. That steric inhibition may lead to the formation of shorter chains than in the case of aniline monomer, or to the formation of helicoidal chains that allow the uniform distribution of the benzothiazole units in the

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Scheme 1

space. In both cases, the protonation of the aminic nitrogens of the obtained polymer, and thus the conductivity, may be decreased.

All these potential problems regarding the steric inhibition of the molecule may be partially solved by the addition of aniline to the mAFBT solution before polymerization is performed. The introduction of some aniline groups between the mAFBT units may allow an increase in both the molecular weight and the protonation (and thus conductivity) of the polymers obtained.

On the other hand, the copolymerization of aniline with small amounts of mAFBT may lead to polyanilines with better properties regarding their ambient stability, thermal resistance, and sensing capabilities for metal ions because of the presence of the sulfur atoms.

The present study describes the results obtained from our work in this field, and the improvements achieved in the characteristics of this kind of polymers.

EXPERIMENTAL

The monomer mAFBT was synthesized according to the procedure described previously by Hasebe.¹²

Chemical polymerizations were performed by oxidizing monomer solutions containing 0.025M in mAFBT, and aniline concentrations varying from 0 to 0.25M. The oxidizing agent used in all experiments was ammonium peroxodisulfate, in a concentration equal to that of the joint monomers, that is, 1 mol of ammonium peroxodisulfate for every mol of monomer (this has been described as the best concentration for the polymerization of aniline¹³). The products obtained were dedoped when needed by treatment in 1M NH₃ for 12 h (see Scheme 2).

The thermal behavior of all the compounds obtained was studied by the weight losses observed in the polymers while the temperature was increased by thermogravimetric analysis (TGA). TGA was performed by heating from 30 to 900°C in a nitrogen atmosphere at a rate of 10°C/min.

Molecular weight determination was assayed by matrix-assisted laser desorption/ionization–time-of-flight (MALDI-TOF) mass spectrometry (MS) under conditions described in a previous study published by

our research group.¹⁴ Furthermore, the products obtained were also pyrolyzed under conditions described for polyaniline in previous investigations^{15,16} to study the nature of the bonds formed during the oxidation process.

Conductivity of the different products was studied in a temperature range from 20 to 300 K, measured by the four-point probe method on pressed pellets (~ 13 mm diameter; 2 mm thick), to study the conduction mechanism of the copolymers and relate it to the monomer ratios.

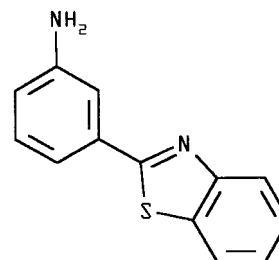
Electrochemical studies were performed in a CAEM ContPDC potentiostat (United Kingdom), using a Pt sheet as the working electrode, a graphite rod as the counterelectrode, and a standard Ag/AgCl/KCl reference electrode. Solutions studied contained 0.005M mAFBT, with and without aniline (0.005M).

RESULTS AND DISCUSSION

Structure determination

Elemental analyses of the dedoped products obtained from the different oxidation reactions were consistent with the initial amounts of each monomer in the reaction mixture.

The infrared spectrum corresponding to the product obtained from the oxidation of the *m*-aminophenylbenzothiazole mainly resembles that of polyaniline, especially in the region 1000–1700 cm⁻¹, although there are also narrower peaks (superimposed on the broad peaks) that are typical from the monomer unit. The presence of these two kinds of combined signals seems to indicate the formation of a compound with a structure related both to polyaniline and to mAFBT,



Scheme 2

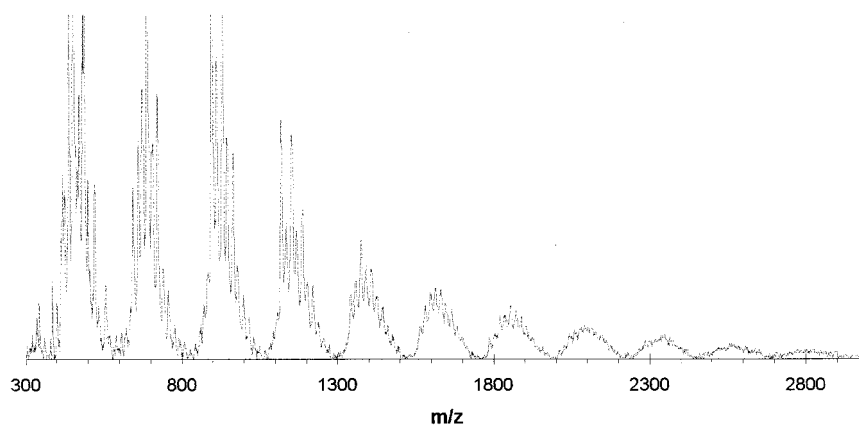


Figure 1 MALDI-TOF mass spectrum corresponding to the poly(mAFBT).

probably the expected polymer described in the introductory section.

Regarding the products obtained from the oxidation of mixtures of aniline and mAFBT, their IR spectra again showed the typical bands corresponding to polyaniline, although the signals attributed to the *m*-aminophenylbenzothiazole part decreased, whereas the amount of aniline increased in the initial mixture. These two features together demonstrate the increasing importance of the polyaniline part. However, these kinds of signals could also be attributable to a mixture of two kinds of compounds, each with one of the structures described earlier, although the following discussion will prove that this is not the case.

The pyrograms obtained from the product of the oxidation of mAFBT show peaks corresponding to the monomer, fractions of higher molecular weights, and also chlorinated monomer units (as identified by mass spectrometry). The oxidation process leads to the formation of Cl_2 in the reaction mixture and, from the molecules identified, this gas is reactive enough to interact with the monomer forming the chlorinated compounds.

The pyrograms obtained from the copolymers of aniline and *m*-aminophenylbenzothiazole show the same peaks as those obtained from the result of the individual oxidation processes of both monomers, but also other undefined peaks appear as a result of the joint polymerization process. These additional peaks are expected to correspond to combinations of both kinds of monomers, although further studies would be required to confirm their nature.

Molecular weight

The MALDI-TOF-MS analysis of the polymer obtained from the oxidation process of *m*-aminophenylbenzothiazole (Fig. 1) generated spectra showing molecules of up to 3000 Da (about 14 monomer units). The presence of groups of peaks at differences of about 224

mass units demonstrates the actual polymerization of the monomer studied. The formation of compounds of such high molecular weights makes evident that the pending benzothiazole groups do not prevent polymerization of the monomer even if they cause some steric difficulties or the polymerization is performed in a different way compared to that of polyaniline.

Furthermore, the mass distribution corresponding to each group of peaks has the same shape as that of polyaniline, showing peaks beside the main one (corresponding to the theoretical mass of the oligomer) at differences of +16 and -16 Da. These differences make evident the presence of final amino groups in the polymer. Furthermore, there are also less intense groups of peaks appearing in the whole mass range, always differing their centers in 14–16 mass units, a characteristic that has already been reported for other polymers derived from polyaniline.^{14,17,18}

All these facts prove that the oxidation of *m*-aminophenylbenzothiazole leads to the formation of a polymer with a main polyaniline chain having pendant benzothiazole groups.

Nonetheless, the real molecular weight of the polymer is not yet clear because of the difficulties when preparing a solution of the sample. The low solubility in the solvents assayed allows a reasonable doubt concerning the representativity of the portion of polymer dissolved. Furthermore, the spectra obtained do not show the typical mass distribution expected from a radical polymerization, with a maximum amount of oligomers with the maximum probability of occurrence and lower amount of greater and smaller oligomers. Instead, in the spectra obtained, the amount of each oligomer is lower than the immediately lower mass oligomer. This behavior has been described for polymers with high polydispersity values.^{19,20}

The MALDI-TOF-MS spectra obtained from the copolymers in the same conditions as polyaniline and poly(*m*-aminophenylbenzothiazole) do not show either the peaks or the distribution of the homopoly-

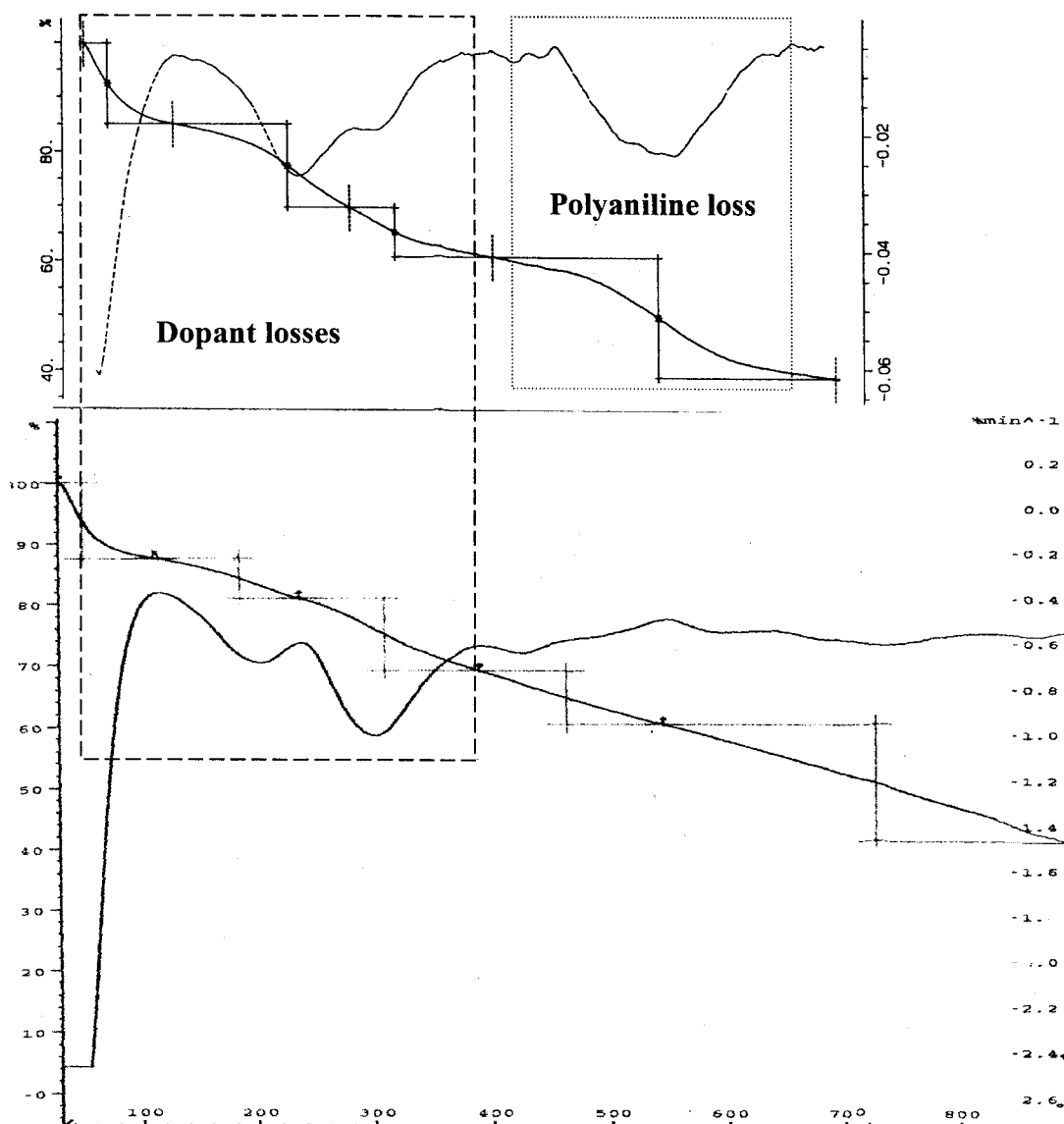


Figure 2 Thermograms obtained from (a) polyaniline and (b) its copolymer 1 : 10 with mAFBT, both doped with hydrochloric acid.

mers, although the peaks' pattern is not yet clear. This fact demonstrates that the product obtained is not a mixture of the two polymers, but has a different structure of its own. Further work is being performed to clarify the structure and molecular weight of such compounds.

Thermal behavior

Thermogravimetric analyses of all the assayed copolymers showed their good thermal stability. The homopolymer shows defined mass losses only at low temperatures, similar to those found in polyaniline, attributed to elimination of the dopant acid.

Regarding the copolymers, all of them experience similar mass losses because of the hydrochloric acid, but, even the copolymer with the highest amount of

aniline (1 : 10 mol ratio) shows a clear difference with respect to polyaniline spectra. Polyaniline has an important mass loss about 550°C, attributed to the main chain, given that it is independent of the dopant, which cannot be observed for any of the copolymers. A comparison of the thermograms corresponding to polyaniline and the copolymer 1 : 10, both doped with hydrochloric acid, is shown in Figure 2. The absence of this defined process shows that the addition of a small amount of mAFBT to the aniline solution leads to the formation of a polymer with a higher stability than that of bare polyaniline.

Conductivity measurements

The conductivity dependency on temperature differs with respect to the conduction mechanism. The mea-

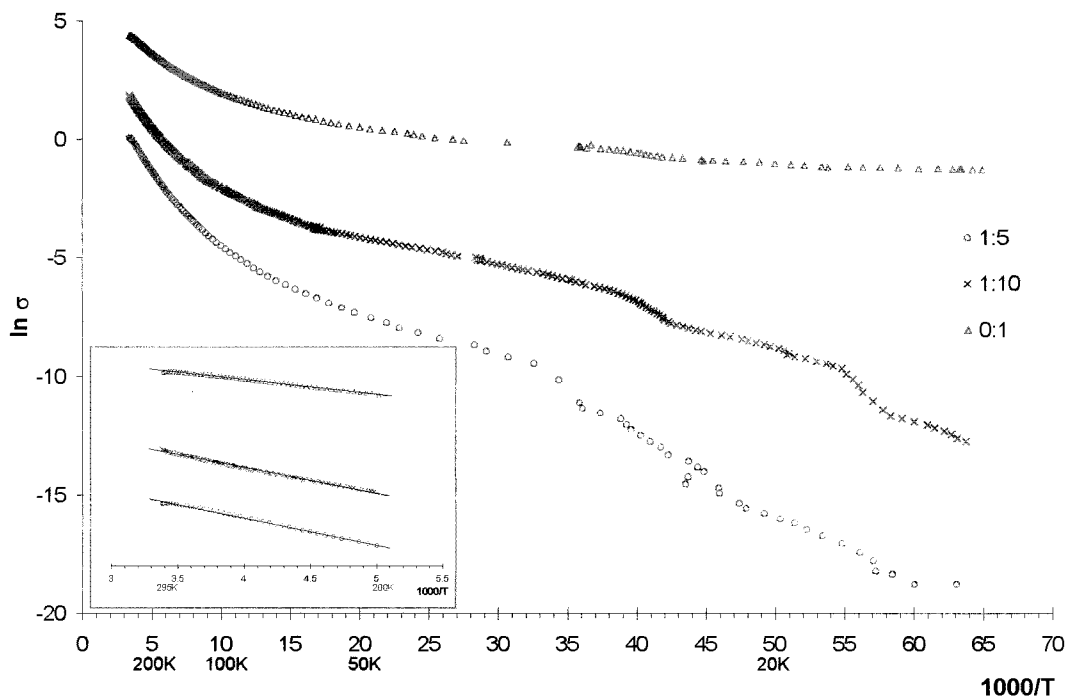


Figure 3 Conductivity values shown as a function of inverse of temperature (showing thermally controlled process). The linear zone is enlarged in the inset.

surement of the conductivity values at different temperatures allows the determination of the mechanism involved in the process.

The conductivity measured for the copolymers prepared with the highest aniline ratios increases with temperature, as expected for semiconducting materials. The conductivity decreases as the ratio of mAFBT in the copolymers increases. At ambient temperature (20°C), polyaniline exhibits good conductivity (80 S cm⁻¹), whereas it decreases when small amounts of mAFBT are added to the reaction mixture. For the 1 : 10 copolymer (9% molar ratio of mAFBT) the conductivity value is 6 S cm⁻¹, and for the 1 : 5 copolymer (17% molar ratio), only around 1 S cm⁻¹. The increase of the amount of mAFBT involved in the reaction to a 50% molar ratio increases drastically the resistance of the pressed pellets to a value higher than 20 MΩ (corresponding to a conductivity lower than 7 × 10⁻⁶ S cm⁻¹). This product and that obtained directly from mAFBT oxidation cannot be considered conducting polymers.

The conductivity dependency on the inverse of temperature is shown in Figure 3, with an enlargement of the linear part of the plot in the inset. This functionality is related to thermally activated processes, and the parameters defined by the linear fit allow calculation of the activation energy. The activation energy depends on the ease of conduction attributed to jumps between adjacent chains,²¹⁻²³ and its calculated values for the copolymers are listed in Table I. The increase of the activation energy when the amount of mAFBT is

increased shows that, as expected (see introductory discussion), *m*-aminophenylbenzothiazole acts as a steric inhibitor, and makes difficult the approach of near chains. The activation energy of bare polyaniline is roughly one half that of the 1 : 5 copolymer (17% mAFBT), whereas the decrease in the ratio of mAFBT to 9% decreases the activation energy only slightly. This demonstrates that the separation between chains is obtained with only a small amount of mAFBT, and an increase of this unit in the copolymer does not separate the chains to any significant degree.

However, a linear function of ln σ versus 1/T can be fit from ambient temperature to only about 200 K, a small range of temperatures. In contrast, the function ln σ versus T^{-1/4} can be fit in a linear range down to about 75 K. This function is related to 3D hopping processes and is shown in Figure 4, with the corresponding inset of the linear range.

The comparison of the two plots reveals that the conductivity mechanism for these copolymers fits best to a 3D hopping process^{24,25} than to a thermally acti-

TABLE I
Activation Energies Calculated for the Different Copolymers from the Thermally Activated Assumption

| Copolymer | mAFBT (mol %) | ΔE_{act} (meV) |
|-----------|---------------|-------------------------------|
| 1 : 5 | 17 | 76.9 |
| 1 : 10 | 9 | 73.2 |
| 0 : 10 | 0 | 41.0 |

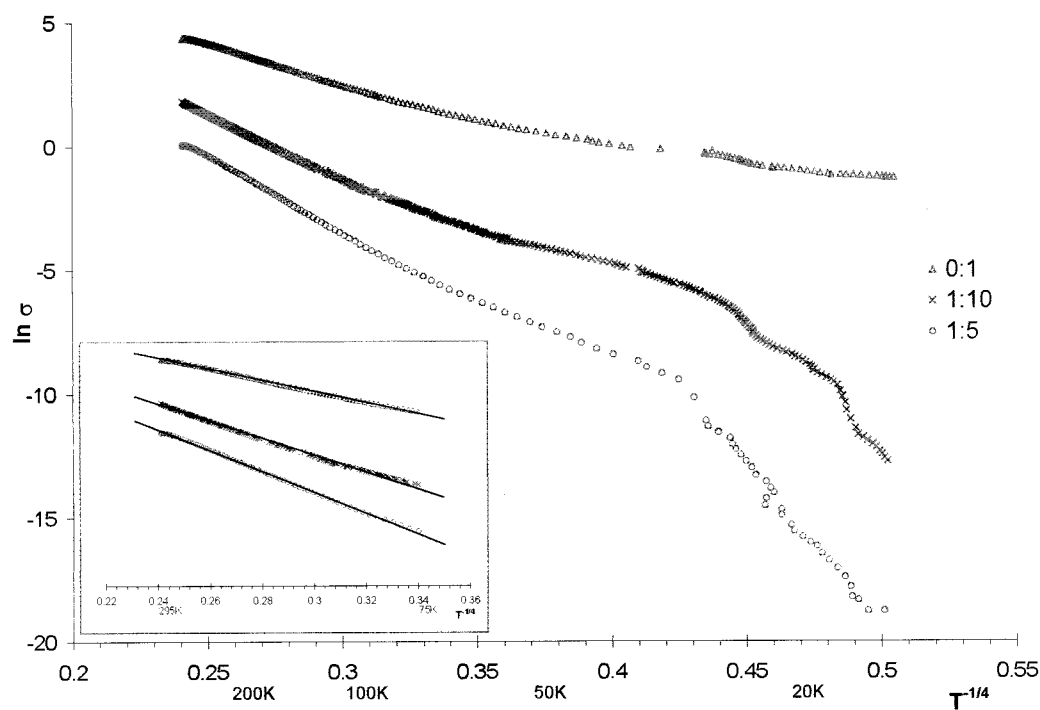


Figure 4 Conductivity values shown as a function of $T^{-1/4}$ (showing 3D hopping processes). The linear zone is enlarged in the inset.

vated process, that is, conduction is more likely because of the three-dimensional process.

The shape of the curves in the lower temperature range shows a different behavior for the copolymers than that for the polyaniline sample. The change in the decreasing ratio shows that the conductivity process involved is different at low temperatures, although this part corresponds to very high resistance values,

probably not accurate enough to be considered. As far as we know, this behavior has not yet been described for any other polymer.

Electrochemical studies

Oxidation of acidic solutions of mAFBT shows a weak oxidation process at about 1200 mV (Fig. 5) and a reduc-

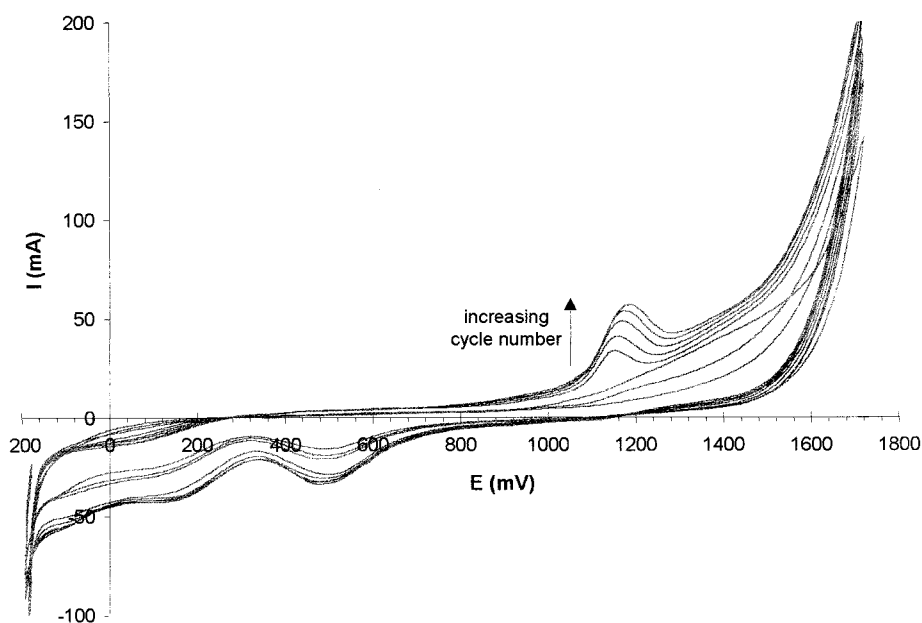


Figure 5 Cyclic voltammogram of a 0.05M mAFBT solution in 0.1M HCl.

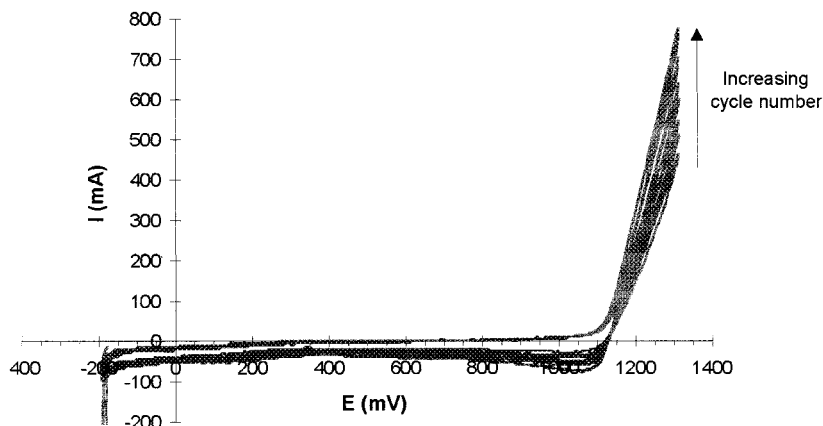


Figure 6 Cyclic voltammogram in 0.1M HCl obtained by cycling the product deposited on the electrode surface from a solution of mAFBT in hydrochloric acid.

tion process at 500 mV. The big difference in potential among these two peaks creates doubt about the reversibility of the processes involved. The slow increase of these peaks at successive oxidation cycles seems to prove the formation of a film on the electrode surface, probably similar in structure to the one observed during aniline oxidation. However, the film obtained from this new aniline monomer does not show the oxidation and reduction processes corresponding to the changes in the oxidation state (leucoemeraldine to emeraldine to pernigraniline) observed in polyaniline. It seems that this film does not show the same conducting properties as those of the polyaniline film.

Reversibility of the redox process has been proved not to occur by cycling the film deposited onto the electrode surface in an acidic solution (1M HCl). The voltammograms obtained from this process (Fig. 6 up to 1300 MV) show the increase in intensity at high potential values observed in successive scans. This increase demonstrates the degradation process of the deposited film, given that solvent oxidation occurs at a higher extent with each scan. Furthermore, no reversible processes are observed in the voltammograms, thus proving that the changes in the oxidation state (if any) are not comparable to those occurring in polyaniline.

On the other hand, addition of aniline to the solution after oxidation of the mAFBT does not lead to the formation of polyaniline on the electrode surface, but on the contrary, the film formed prevents aniline oxidation. Protecting a part of the electrode surface from mAFBT polymerization, and deprotecting it when aniline is added to the solution has proved this fact. In the subsequent cycles, polyaniline is formed only in the newly reacting part of the electrode. The partial polymerization of aniline confirms the insulating character of the film obtained from mAFBT.

Cooxidation of mAFBT with the same concentration of aniline leads to the formation of the same kind of

film as when mAFBT is alone, as observed from the voltammograms obtained. *m*-Aminophenylbenzothiazole seems to act as an inhibitor of electrochemical aniline polymerization, as ascertained from the lack of peaks corresponding to aniline oxidation.

However, the upper potential limit needed to oxidize mAFBT is high enough to cause polyaniline to overoxidize and decompose, and probably the application of such potential to the mixed solution makes the polyaniline part decompose as it is formed.

CONCLUSIONS

The oxidation behavior of *m*-aminophenylbenzothiazole was studied chemically and electrochemically, demonstrating the formation of a polymer with a structure similar to that of polyaniline. Chemical polymerization of a solution containing both mAFBT and aniline leads to products with intermediate structures between both, not attributable to a mixture of the homopolymers, but most likely to a product involving both monomer structures. Furthermore, these products show high thermal resistance and striking conductivity values that make them very important compounds for the development of new applications.

The electrochemical oxidation of mAFBT leads to the formation on the platinum electrode surface of a film that prevents polymerization of aniline on the modified surface. Electrochemical copolymerization of mAFBT and aniline has proved to be difficult because of the inhibition effect caused by the *m*-aminophenylbenzothiazole on the behavior of aniline.

The authors thank Drs. D. B. Amabilino and J. Veciana for the MALDI-TOF-MS measurements and Dr. N. Ferrer and Y. Takhtoukh for the conductivity measurements.

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