High-Throughput Screening Method to Detect Amphiphilic Counterions Able to Solubilize Conducting Polymers

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Inherently conducting polymers have attracted considerable interest since the discovery of doped polyacetylene in 1977.[1] Since then, a large variety of conjugated polymers have been developed, such as polythiophene, polyaniline, poly(phenylenevinylene), and polypyrrol.[2] However, severe practical problems in developing materials were encountered: the stability of the materials is insufficient and they are insoluble in common solvents and not miscible with common polymers (i.e., poorly processable). Among conducting polymers, PANI has received greater attention due to its advantages over other conducting polymers.[3] The simplicity of its preparation from cheap materials, good environmental stability, its conductivity that can be reversibly controlled either electrochemically (by oxidation/reduction) or chemically (by protonation/deprotonation),[4] make it very useful in preparing lightweight batteries, electrochromic devices, sensors and electro-luminescent devices.[5,6]

However, the major problem related to its successful utilization lays in its poor mechanical properties and processability due to its insolubility in common organic solvents.[7] The insulating emeraldine base (EB) form of PANI is soluble in some hydrogen bonding solvents, such as sulphuric acid, 80% acetic acid, 60%−88% formic acid, and N-methylpyrrolidone. The protonated PANI, electrically conducting, is very much less soluble than EB in these solvents.[8] For this reason, the topic of many publications is focused on the improvement of its processability in the past several years. This can be done by substitution of aromatic ring of polyaniline with different functional groups leads to higher solubility in organic solvents and even in water.[9] However, while the addition of side groups has enhanced its solubility and processability, the electrical conductivity is reduced because of steric hindrance, increase of interchain length and decrease of conjugation length.[10]

Instead of modification, if bulkier counterions are used as doping agents, the solubility and the electrical conductivity increased. Moreover, the solubility in weakly polar solvents is achieved when the counterion protonates the polymer and also acts as a surfactant for the solvent, both simultaneously.[8]

Cao et al.[11] have shown that PANI can be solubilized in a number of common organic solvents in the metallic emeraldine salt form by the addition of protonic surfactants such as camphor sulfonic acid (CSA) and dodecyl-benzenesulfonic acid (DBSA). The charged (SO_3^-) headgroup of the surfactant associates with the positively charged backbone through Coulomb attraction, providing a solubilizing side chain compatible with organic solvents.

On the other hand, the demand for diverse compound libraries for screening in materials science and drug discovery is the driving force behind the development of new technologies for rapid parallel and combinatorial synthesis.[12] Then, to find a better dopant to improve PANI solubility in common solvents and conductivity, combinatorial synthesis of the amphiphilic counterions could be an efficient technique. However, if counterions are easily synthesized, the bottleneck of the discovery process becomes the screening of the ability of the counterion to solubilize PANI. To do that, we used two properties of polyaniline. One is its strong optical absorption in the visible which is due to the extended conjugation and, therefore, common with other conducting polymers. The other is the ability to deposit thin (<1 μm) films on solid subtrates making easier to manipulate the conducting polymer, as it was shown before.[14]

We report a new method of high-throughput screening designed to find amphiphilic counterions to solubilize PANI in CHCl₃. It could be extrapolated to other polymers, like polypyrrole, other solvents or other targets. Also, it is possible to use it to find counterions/solvent pairs that dope the polymer without dissolution.

Materials. Polyaniline (emeraldine base form) was deposited on a film of LDPE, as described previously.[13] Octyl-2-sulfobenzoate (A3O6) (Scheme 1) was synthesized by Fischer esterification from 2-sulfobenzoic acid cyclic anhydride and octanol. The synthetic procedure was performed using a domestic microwave oven (700 W, 2.45 GHz) and solvent-free in standard glass reaction tubes.

Characterization. The samples were analyzed by FTIR and UV−vis. Fourier transform infrared spectra (FTIR) were taken by a FTIR Impact 400 (Nicolet) Spectrometer and UV−vis spectras were recorded using a HP 8452 UV−vis spectrophotometer.

The method consists of depositing polyaniline (emeraldine base form) on a film of LDPE, which acts as solid support. Then, portions of the films are immersed in a solution of the amphiphilic counterion in ClCH₃. In this case, A3O6 was used as amphiphilic counterion as proof of concept. If the experiment is positive, the LDPE film will be clean and PANI will be doped (green color) and solubilized in the solution.

Scheme 1. A3O6 Chemical Structure
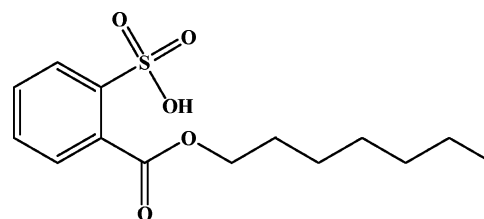
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Scheme 2. HTS Procedure
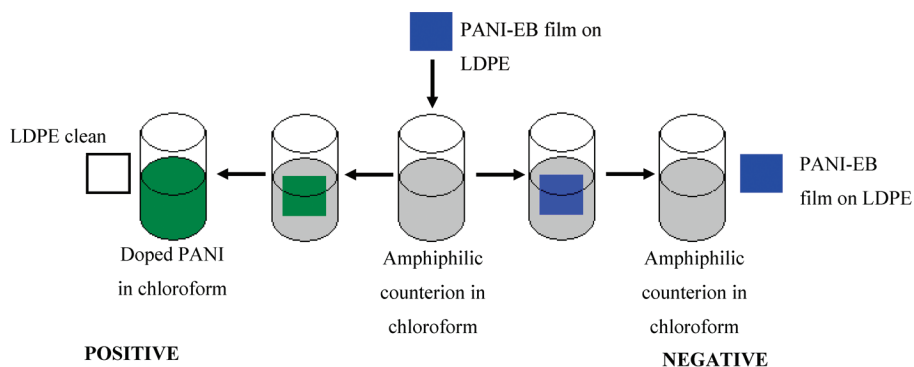
If the experiment is negative, PANI will remain supported onto LDPE film (Scheme 2).

In Figure 1 a photographic record of the use of the procedure can be seen.

In the left box, the tubes containing solutions of the counterion (A3O6), together with the PANI (EB) films on PE are shown before testing. Specifically, the solution of A3O6 in $CHCl_3$, CH_3OH, and H_2O are shown, revealing the absence of color in the counterion solutions.

In the right box, the tubes containing solutions of the counterion (A3O6), together with the PANI (EB) films on PE are shown after testing. As it can be seen the counterion solution in $CHCl_3$ (Figure 1d) has changed color to a deep green, characteristic of the solution of doped PANI. Accordingly, the PE film that was immersed in the tube shows no traces of the EB film, indicating that the PANI has solubilized in the $CHCl_3$ solution. On the other hand, the solutions of A3O6 in water (Figure 1e) and A3O6 in CH_3OH (Figure 1f) remain unchanged, suggesting that polyaniline is not soluble in those counterion/solvents pairs. However, while the PANI/PE film remain unchanged (blue color) when immersed in A3O6/H_2O solution (Figure 1e), the PANI/PE film immersed in A3O6/CH_3OH solution has a green color because of the doping of the PANI film by the counterion. It seems that methanol is not able to solubilize PANI but wets the film enough to allow the protonation of the polymer backbone by the acid.

While the result in water is negative, it also reveals that water is unable to wet the polymer enough to effect the doping/dedoping. Accordingly, the doped film remains doped upon immersion in water. This is an important result toward the use of doped PANI films in wet environmental conditions.
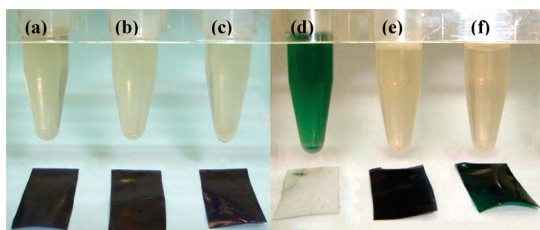

Figure 1. HTS proceeding: Before film dipping in each solution: (a) A3O6 solution in Cl3CH and PANI-EB film, (b) A3O6 solution in water and PANI-EB film, and (c) A3O6 solution in methanol and PANI-EB film. After film dipping in each solution: (d) PANI doped with A3O6 solution in Cl3CH and PE film clean (POSITIVE), (e) A3O6 solution in water and PANI-EB film (NEGATIVE), and (f) A3O6 solution in methanol and PANI doped with A3O6 film (POSITIVE for doping, NEGATIVE for solubilization).

To verify further this method, the FTIR and UV−vis spectra of the PANI/PE films and of the solution of PANI were measured.

LDPE has few bands in the mid-IR region (Figure 2d): at 2920 cm^{-1} (asymmetrical stretching mode C−H of the methyl group), at 2850 cm^{-1} (symmetrical stretching mode C−H of the methyl group), at 1463 cm^{-1} (C−H bending vibrations of the methyl group), and at 710 cm^{-1} (rocking vibration of the methylene group). Then it is possible to sense the bands of the polymer deposited on LDPE and the modifications on it, like the presence of dopants.

Figure 2a shows the FTIR spectrum of a PANI (emeraldine base) film deposited on LDPE. The spectrum of PANI shows all characteristic bands of LDPE and those corresponding to itself: 1588 (C=C stretching of the quinoid rings), 1496 (C=C stretching of benzenoid rings), 1306 (C−N stretching mode), and 1164 cm^{-1} (N=Q=N, where Q represents the
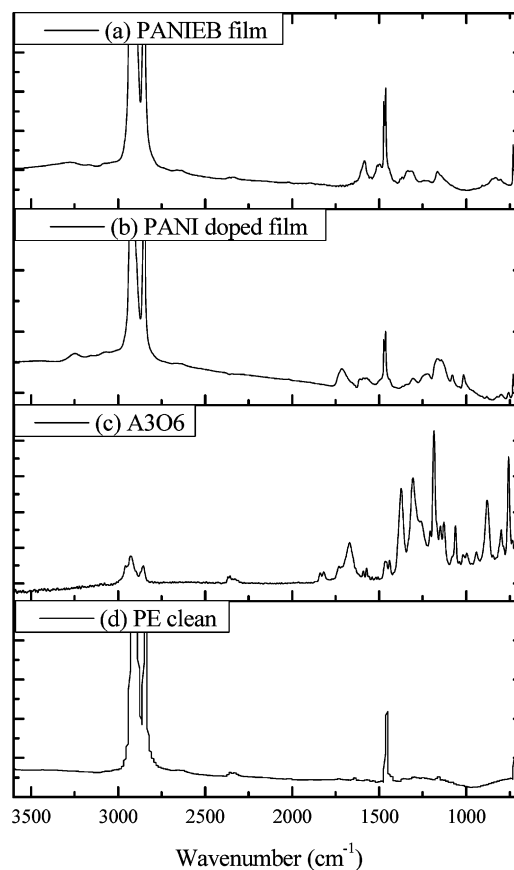

Figure 2. FTIR spectra of the materials produced during the HTS procedure.
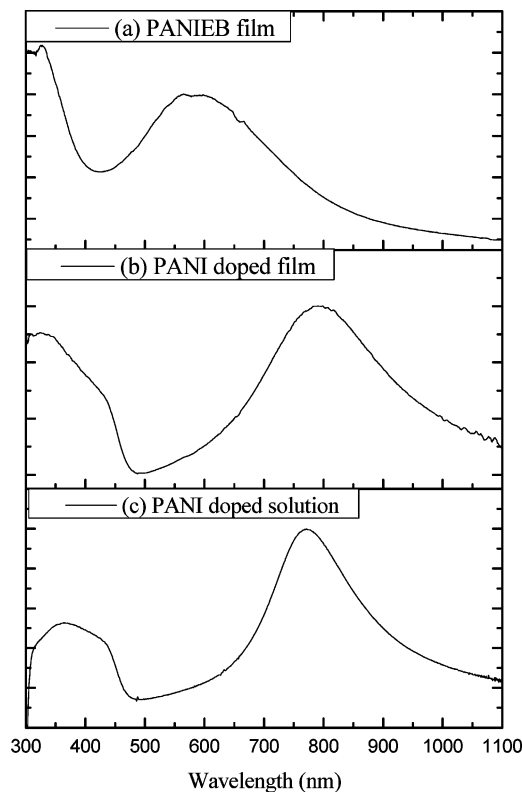
Figure 3. UV−vis spectra of the different parts of the proceeding.

quinoid ring).[14] Figure 2c shows the FTIR spectrum of A3O6, which presents the following main bands: 1670 (C=O stretching), 2924 (asymmetrical stretching mode C−H of the methyl group), 2855 (symmetrical stretching mode C−H of the methyl group), 1185 (symmetric stretching of the $S(=O)_2$), and 1375 cm^{-1} (asymmetric stretching of the $S(=O)_2$).[15]

Figure 2b shows the FTIR spectrum of PANI doped with A3O6, deposited on LDPE. The presence of the doping agent is detected by the occurrence of the characteristic vibrational bands of the counterion. It is observed that the absorption band of carbonyl group rise in the stretching frequency from 1670 (C=O of A3O6) to 1723 cm^{-1} (C=O of PANI/A3O6 complex), which indicates the interaction between PANI and the amphiphilic counterion.

LDPE does not exhibit absorption in the UV−vis region; then, it is possible to verify the HTS method using UV−vis spectroscopy. Figure 3a shows the UV−vis spectra of PANI-EB film deposited on LDPE. It presents two absorption peaks at 330 and 630 nm. The absorption at 330 nm is due to a $\pi \rightarrow \pi^*$ transition and has been suggested to arise from excitation of the benzene segment including amine structures in polyaniline, and the peak at 630 nm has been assigned to an intermolecular and/or intramolecular charge-transfer process from the benzenoid to the quinoid ring, leading to the formation of a molecular exciton.[16]

The UV−vis spectrum of doped PANI film, obtained by doping in A3O6 solution in methanol, (Figure 3 (b)) presents three characteristic bands: at 349 nm, attributed to the $\pi \rightarrow \pi^*$ transition of the aniline ring, 413 nm, assigned to the $n \rightarrow \pi^*$ transition of the localized radical cation, and the band assigned to polarons/bipolarons in protonated PANI at 745 nm for PANI/A3O6 film (Figure 3b).

The UV−vis spectrum of doped PANI solution (Figure 3c) presents three characteristic bands: at 349 nm, attributed to the $\pi \rightarrow \pi^*$ transition of the aniline ring, 413 nm, assigned to the $n \rightarrow \pi^*$ transition of the localized radical cation, and the band assigned to polarons/bipolarons in protonated PANI at 725 nm for PANI/A3O6 solution.[17]

In summary, the UV−vis and FTIR bands due to PANI-EB/PE can be seen in the original films. When the films are immersed in the methanol solution of amphiphilic counterion, PANI becomes doped. It can be seen visually, by the change of color of the film from blue to green (Figure 1f), by FTIR (Figure 2b), where the bands corresponding to the amphiphilic counterion (A3O6 in this case (Figure 2c) appears in the spectra of PANI EB on LDPE, and by UV−vis (Figure 3b), where a typical UV−vis spectra of PANI doped is presented.

When the dissolution of PANI is performed, the color of the solution changes from transparent to green and the color of the film changes from green to transparent (Figure 1d). Accordingly, the UV−vis spectra of doped PANI solution is observed, while the FTIR and UV−vis spectra of the film correspond to clean PE.

A new method of high-throughput screening has been developed to find an amphiphilic counterion to solubilize PANI in chloroform. It is simple and flexible, so it can be used with other polymers, other solvents and other targets. Using this procedure, it was found that octyl-2-sulfobenzoate (A3O6) solubilizes PANI in CHCl$_3$, while a solution of the same counterion in methanol is able to dope PANI. On the other hand, a solution of the counterion in water does not solubilize nor doped polyaniline.

References and Notes

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