Protonation of Polyaniline in Hexafluoro-2-propanol. Spectroscopic Investigation

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ABSTRACT: Three principal forms of polyaniline, leucoemeraldine (LEB), emeraldine (EB), and pernigraniline (PNB), have been prepared, and their spectral properties have been studied in a newly discovered polyaniline solvent, hexafluoro-2-propanol (HFIP). In HFIP a significant hypsochromic shift of the absorption due to main electronic transitions is observed with respect to the analogous transitions in the spectra recorded for *N*-methylpyrrolidinone (NMP). In particular, the π to π^* transition is shifted to 308 nm in LEB and to 305 nm in EB and PNB and the benzoid to quinoid ring excitonic transition is shifted to 502 nm in EB and PNB. In EB and PNB spectra, an additional peak at 800 nm is observed, which can be ascribed to the protonation of these forms of polyaniline by the highly acidic solvent. EB has been protonated in HFIP solution with three types of protonating agents: camphorsulfonic acid (CSA), phenylphosphonic acid (PPA), and poly(hexamethylene phosphate) (PHMeP). Protonation in HFIP facilitates the formation of the extended coil conformation of emeraldine similarly to the protonation in *m*-cresol. The extended coil conformation favors in turn the delocalization of polarons. The degree of polaron delocalization, as judged from UV−vis−NIR spectra, depends strongly on the protonation agent, the highest delocalization being observed for EB(PPA)$_y$.

Introduction

Research works on processible polyaniline (abbreviated here as PANI) have been intensified after the discovery in 1992 that polyaniline protonated with selected functionalized sulfonic acids may be processed from solutions prepared from solvents commonly used in industry.[1] More recently, other types of protonating agents that improve the processibility of polyaniline have been discovered, namely phosphoric acid diesters and phosphonic acids.[2,3] However, several important rheological properties vital for processing depend not only on the protonating agent but also on the solvent. Moreover, polyaniline chain conformation can be altered by appropriate selection of the couple: protonating agent−processing solvent.[4,5] Thus, both spectroscopic properties of protonated polyaniline and its transport properties after casting strongly depend on the processing conditions.

Spectacular results have been obtained for polyaniline protonated with camphorsulfonic acid processed from *m*-cresol and some other phenols.[6,7] Films cast from such solutions exhibit very high conductivities (*ca.* 300 S/cm) of metallic type. In addition, blends of polyaniline with classical bulk polymers like, for example, PMMA show an extremely low percolation threshold, typically below 0.3% wt of PANI.[1,8]

Polyaniline processed from phenol type solvents has spectral features significantly different from those characteristic of other types of processed PANI. In particular, both in *m*-cresol solution and in the solid state an absorption tail extending toward the NIR region can be observed in PANI UV−vis−NIR spectra.[4,5,9] It is believed that this featureless broad absorption is associated with charge carrier delocalization in highly conductive PANI.

Two main properties that distinguish phenols from other types of solvents used for PANI processing are their high acidity and H-bonding formation capability. Exploiting this research pathway, Hopkins *et al.*[10] have discovered that fluorinated alcohols, which are even more acidic than phenols, also dissolve PANI in the basic (unprotonated) and salt (protonated) form. For example, hexafluoro-2-propanol (HFIP) can be used for the preparation of protonated PANI solutions and films in which the extended coil conformation of the polymer chain is observed. However, in many cases, the spectral features of PANI dissolved in HFIP are different from those observed in *m*-cresol and in “inert” solvents like chloroform.

In this communication we present spectroscopic studies of PANI in HFIP solution. Polyemeraldine has been protonated with three types of protonating agents: phenylphosphonic acid (PPA), camphorsulfonic acid (CSA), and the polymeric ester of phosphoric acid, poly(hexamethylene phosphate) (PHMeP). In addition, spectra of polyaniline in the oxidation state of polyleucoemeraldine and polypernigraniline were measured.

Experimental Section

(a) Synthesis of Polymers. Polyaniline (PANI) in the oxidation state of emeraldine was synthesized chemically by the oxidation of aniline (POCh Poland) with $(NH_4)_2S_2O_8$ (POCh Poland) using the procedure described in ref 11. The obtained emeraldine hydrochloride was then treated with a 0.1 M aqueous solution of NH_3 in order to convert emeraldine into its basic form. Emeraldine base (abbreviated here as EB) powder was then washed with distilled water and then methanol and dried in dynamic vacuum for 72 h.

Polyaniline in the oxidation state of pernigraniline (PNB) was prepared by the oxidation of EB dissolved in *N*-methylpyrrolidinone (NMP) with *m*-chloroperbenzoic acid, as recommended in ref 12. PNB powder was washed consecutively with acetone and diethyl ether. Finally, it was dried in a dynamic vacuum for 48 h.

Polyaniline in the oxidation state of leucoemeraldine (LEB) was obtained by the reduction of EB with liquid phenylhydrazine.[13] The refluxing temperature was 120 °C. Then the

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resulting LEB powder was washed with methanol and dried in dynamic vacuum for 72 h. Since LEB is very reactive, all operations have been carried out in the atmosphere of dry nitrogen.

(b) UV−Vis−NIR Spectra. For the spectroscopic studies, EB (4.4 mg) was mixed in 6 mL of hexafluoro-2-propanol (HFIP) (Aldrich) and the mixture stirred for 5 days at room temperature (RT). The solution was then filtered through a 0.2 μm Millipore filter. The concentration of EB in the filtrate was determined as 0.7 mg of EB/mL of HFIP.

The spectra of protonated emeraldine were also measured. For the protonation of EB, three protonating agents were used: camphorsulfonic acid (CSA) (Aldrich), phenylphosphonic acid (PPA) (Aldrich), and a polymeric acidic ester, namely poly(hexamethylene phosphate) (PHMeP). This last compound was prepared by following the procedure described in ref 14. All protonating agents were vacuum dried prior to use.

Two methods of protonation were used. In method A, filtered EB solution in HFIP was mixed with an appropriate amount of the solution of the protonating agent in the same solvent. For example, 0.1 mL of 8×10^{-3} M EB solution (calculated per EB mer, $C_6H_{4.5}N-$) in HFIP was mixed with 0.6 mL of 6.3×10^{-4} M camphorsulfonic acid solution in HFIP. The mixture was diluted with 1.9 mL of HFIP and vigorously stirred. The final concentration of PANI in the solution (again calculated per EB mer) was equal to 3.1×10^{-4} M. This solution was used directly for UV−vis−NIR spectroscopic measurements.

In method B, EB powder was first mixed with the solid acid. HFIP solvent was subsequently added, and the protonating mixture was then stirred for 48 h. A green solution of protonated PANI was then filtered through a 0.2 μm Millipore filter and diluted with HFIP prior to spectroscopic measurements. For example: 3.3 mg of EB powder was mixed with 4.1 mg of dried CSA. Then 0.5 mL of HFIP was added, and the mixture was stirred and finally filtered.

Solid films of protonated emeraldine were cast from the solutions (prepared with the use of method B) on quartz slides by evaporating HFIP at RT.

Leucoemeraldine is not soluble in HFIP; however, one can record the spectra from mixed NMP and HFIP solvents. Mixed solvents of the following compositions were used: 20% vol NMP−80% vol HFIP, 40% vol NMP−60% vol HFIP, 50% vol NMP−50% vol HFIP.

Pernigraniline is soluble in HFIP. For the spectroscopic studies, 1.3 mg of PNB was dissolved in 1 mL of HFIP, and the solution was stirred for 48 h and then filtered through a 0.2 μm Millipore filter. Prior to spectroscopic measurements, it was diluted with the appropriate amount of HFIP.

Two spectrometers were used in this study: Cary 2315 (Varian) working in the spectral range 200−2000 nm and Lambda 2 (Perkin-Elmer) covering the spectral range 200−1100 nm.

Results and Discussion

In Figure 1 the spectra of three principal polyaniline forms differing in their oxidation states, *i.e.*, LEB, EB, and PNB, recorded in HFIP solutions are shown. Since LEB is not soluble in pure HFIP, only spectra in mixed NMP/HFIP solvents can be recorded. If LEB is first dissolved in NMP, it can be consecutively diluted up to 80% vol with HFIP without the precipitation of the polymer. The spectra recorded in HFIP differ significantly from those registered for NMP solutions. In the case of LEB one distinct peak can be distinguished whose maximum is being continuously blue shifted with the increasing HFIP content in HFIP/NMP mixed solvent. In pure NMP this peak is located at 340 nm, whereas in the 80% vol HFIP−20% vol NMP mixed solvent it is at 314 nm. The extrapolation of the relationship between the content of NMP in the solvent and the position of the peak gives the value of 308 nm for a hypothetical LEB solution in pure HFIP, close to the value of 305 nm observed in the cases of EB and PNB. For EB and PNB two additional peaks are observed at 502 nm and *ca.* 800 nm. The spectrum of EB is very similar to that reported by Hopkins *et al.*[10] In the simplest interpretation the band at 305 nm (308 nm for LEB) can be ascribed to the π to π^* transition in the benzoid ring. As has already been mentioned, this band shows a hypsochromic shift with respect to the analogous peak observed for NMP solutions (320 nm for EB and PNB and 340 nm for LEB in NMP solution). The band at 502 nm appears only in the oxidized forms of polyaniline; therefore it must be associated with the appearance of imine nitrogens and quinoid rings. It is usually ascribed to a benzoid to quinoid ring excitonic transition. Again this peak is blue shifted as compared to the corresponding peaks of EB and PNB in NMP solution (620 nm for EB/NMP and 540 nm for PNB/NMP).

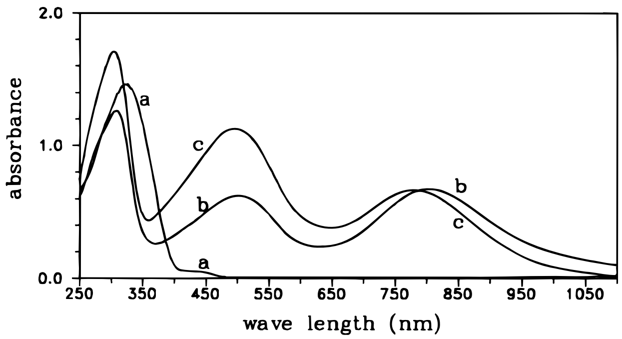

Figure 1. Absorption spectra of the solutions of polyaniline in different oxidation states: (a) leucoemeraldine in 20% vol NMP−80% vol HFIP solution; (b) emeraldine in HFIP conditioned for 5 days; (c) pernigraniline in HFIP conditioned for 5 days.

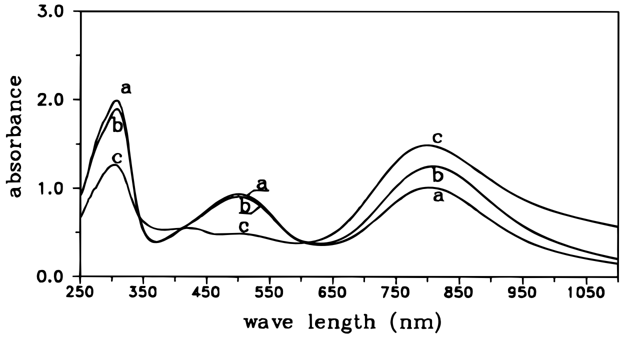

Figure 2. Absorption spectra of EB conditioned in HFIP for 5 days: (a) recorded immediately after the separation of the nondissolved fraction; (b) recorded after an additional 6 days; (c) recorded after 6 days but with addition of a deficit of a strong protonation agent PPA/EB = 0.3.

The third peak at 800 nm seems to be associated with the protonation of the oxidized forms of polyaniline by HFIP solvent. The protonation of EB by acidic solvents such as *m*-cresol has been reported.[1] HFIP is even more acidic than *m*-cresol.[10]

The spectra of EB in HFIP are strongly time dependent (Figure 2). With increasing storing time, a decrease of the 502 nm peak intensity with a simultaneous increase of the 800 nm peak intensity can be observed, indicating that the solvent continues to protonate the dissolved polymer. If a more efficient than HFIP protonating agent is added to the solution, as for example, phenylphosphonic acid (PPA), the protonation process is strongly accelerated (compare Figure 2a−c). Extended storage of EB in pure HFIP (4 months) results

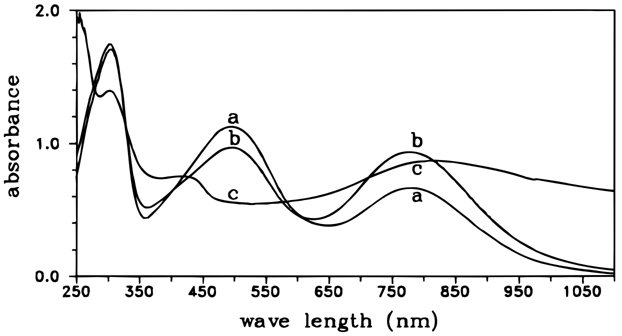

Figure 3. Absorption spectra of PNB conditioned in HFIP for 5 days: (a) recorded immediately after the separation of the nondissolved fraction; (b) recorded after an additional 10 days; (c) recorded after 5 days but with addition of a strong protonation agent PPA/PNB = 1.

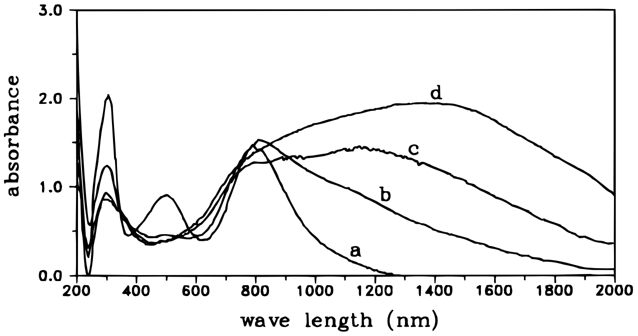

Figure 4. Absorption spectra of EB doped with CSA in HFIP solution, recorded after 12 days: (a) CSA/EB = 0.1; (b) CSA/EB = 0.3; (c) CSA/EB = 0.5; (d) CSA/EB = 0.7.

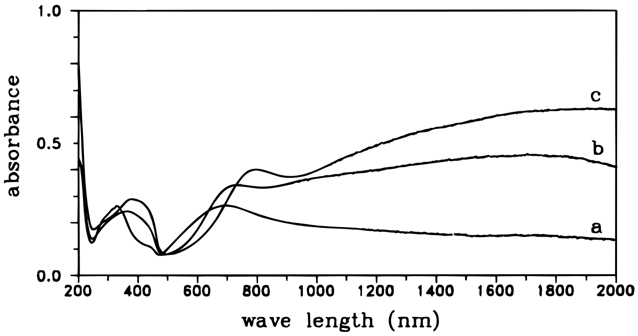

Figure 5. Absorption spectra of EB(CSA)$_y$ films prepared from HFIP solutions: (a) $y = 0.2$; (b) $y = 0.5$; (c) $y = 0.7$.

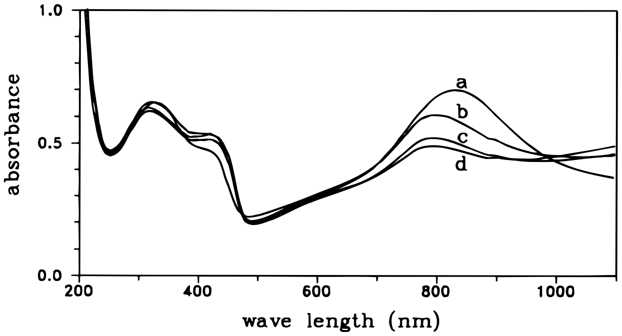

Figure 6. Changes of UV–vis spectra of the EB(CSA)$_{0.5}$ film spun from NMP and then exposed to the vapor of HFIP at room temperature for (a) 0 min, (b) 6 min, (c)12 min, (d)22 min.

in a total disappearance of the 502 nm peak similarly to the addition of PPA. Thus the above presented results unequivocally indicate that HFIP is not an inert solvent, but it protonates polyemeraldine.

The spectra of PNB in HFIP solution also undergo a significant evolution with time (Figure 3). As in the case of EB, increasing protonation by the solvent is manifested by an increase of the 800 nm peak intensity and gradual disappearance of the 502 nm peak. Again, the addition of a more efficient than HFIP protonating agent, for example, PPA, results in a significant acceleration of the protonation process. It should be, however, stressed here that protonation of PNB is much slower than in the case of EB and higher contents of PPA are required in order to achieve total disappearance of the 502 nm peak.

In general, the spectra of protonated EB depend on the type of protonating agent and the method of protonation (method A or B). In the case of CSA-protonated PANI for both protonating protocols, essentially the same results are obtained. The spectra of EB(CSA)$_y$ depend strongly on the ratio of CSA/EB (Figure 4). The addition of increasing amounts of CSA to EB/HFIP solution results in a gradual disappearance of the 502 nm peak with a concomitant increase of the 800 nm peak intensity. The latter significantly broadens on its lower energy side. This broadening can be considered as a spectroscopic manifestation of polaron delocalization. However, even for the excess of the protonating agent (CSA/EB = 0.7) the delocalization is less pronounced than in the case of EB(CSA)$_y$ in *m*-cresol since a broad maximum is still seen in the vicinity of 1500 nm.

The free carrier tail extending toward the NIR is better seen in solid EB(CSA)$_y$ obtained after the evaporation of HFIP. Again, the extent of delocalization depends on the protonation level, y, but even for $y = 0.7$ a residual peak ascribed to localized polarons is still present (Figure 5). This monotonically increasing NIR absorption is frequently ascribed to the existence of the extended coil conformation of the polyaniline chain, which leads to better transport properties.

The use of inert solvents like chloroform or benzyl alcohol gives rise to three localized absorptions in EB(CSA)$_y$ solutions, characteristic of the less conductive coil conformation of the polymer chain. In more acidic, H-bonding solvents like phenols the extended coil conformation is obtained, which favors the delocalization of charge carriers. In this case only one peak at 440 nm is observed in addition to the already mentioned free carrier tail.[4,9] The exposure of EB(CSA)$_{0.5}$ cast from chloroform to *m*-cresol vapors results in a transformation of the spectrum characteristic of coil conformation to the one characteristic of extended coil conformation.

Similar behavior is observed during the treatment of EB(CSA)$_y$ with HFIP vapors. If EB(CSA)$_{0.5}$ film cast from NMP is exposed to the vapors of HFIP, a gradual change of the polymer conformation is observed by UV–vis–NIR spectroscopy. The transformation toward the extended coil conformation is manifested by the decrease of the peaks at 360 and 800 nm with a simultaneous increase of the peak at 440 nm and a significant increase of the absorption above 1000 nm (Figure 6).

Protonation of EB with phenylphosphonic acid (PPA) leads to different, than the case of EB(CSA)$_y$, absorption spectra. In addition, for this protonating agent the spectra depend on the protonation method. Figure 7 shows the spectra of EB(PPA)$_y$ solutions obtained according to method A (protonation of EB dissolved in HFIP with the solution of PPA in HFIP). For a strong deficit of PPA (PPA/EB = 0.2), the spectrum is similar to those obtained in inert solvents with a characteristic

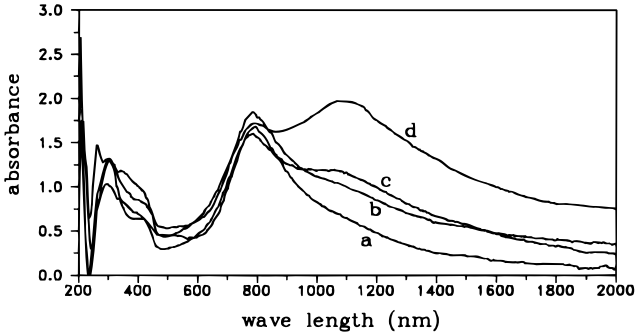

Figure 7. Absorption spectra of EB doped with PPA in HFIP solution (method A), recorded after 12 days: (a) PPA/EB = 0.2; (b) PPA/EB = 0.35; (c) PPA/EB = 0.5; (d) PPA/EB = 0.8.

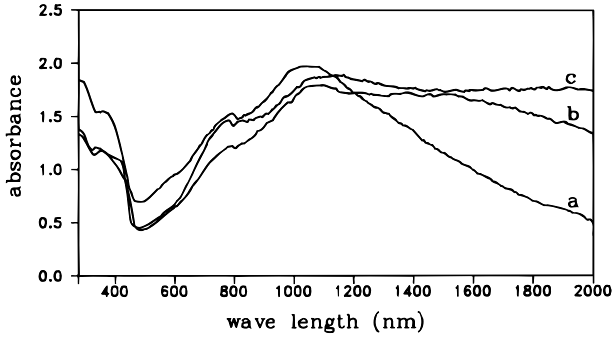

Figure 8. Absorption spectra of EB doped with PPA in HFIP solution (method B), recorded after 2 days: (a) PPA/EB = 0.3; (b) PPA/EB = 0.45; (c) PPA/EB = 0.7.

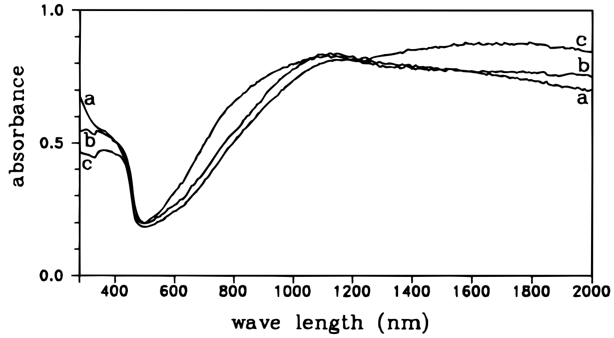

Figure 9. Absorption spectra of EB(PPA)$_y$ films prepared from HFIP solutions (method B): (a) $y = 0.3$; (b) $y = 0.45$; (c) $y = 0.7$.

absorption showing the maximum at *ca.* 800 nm. With increasing PPA/EB ratio a new broad absorption appears ($\lambda_{max} = 1065$ nm), which is superimposed on the 800 nm absorption. This new absorption can be taken as evidence of the increasing carrier delocalization with increasing protonation level. For PPA/EB = 0.8 this new absorption dominates the spectrum.

Protonation in a concentrated solution (method B) facilitates the formation of the extended coil conformation. This is manifested by the much more pronounced free carrier tail in the UV–vis–NIR spectra of the B series samples as compared to the analogous spectra of the samples prepared with the use of method A (compare Figures 7c and 8b).

In Figure 9 the spectra of EB(PPA)$_y$ solid films prepared by casting from the solutions of the B series are collected. In the solid state the free carrier tail can be observed even for the samples with a strong deficit of the protonating agent ($y = 0.3$), which in the solution show a broad but localized absorption. For higher PPA contents ($y = 0.45$ and 0.7), the peak due to localized polarons at *ca.* 800 nm is essentially nonexistent.

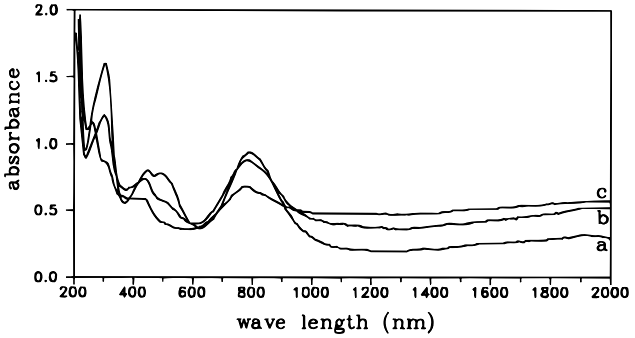

Figure 10. Absorption spectra of EB doped with PHMeP in HFIP solution (method A), recorded after 12 days: (a) PHMeP/EB = 0.3; (b) PHMeP/EB = 0.5; (c) PHMeP/EB = 0.7.

Frequently, it is advantageous to protonate EB with the acids of polymeric nature because in this case the deprotonation of conductive polyaniline films is severely impeded due to kinetic reasons. We have tested poly(alkylene phosphates) (PAPs) as EB protonating agents.[15] The solutions of EB(PAP)$_y$ in *m*-cresol show the desired extended coil conformation.[16] However, if the protonation with poly(hexamethylene phosphate) is carried out in HFIP the transformation of the chain conformation toward the extended coil is more difficult (Figure 10). Although a significant increase in the absorption is observed above 1000 nm, the peak in the vicinity of 800 nm is still present even for PHMeP/EB values exceeding 0.5. It should be mentioned here that the protonation of EB with poly(alkylene phosphates) is much slower than in the case of low molecular weight protonating agents. This is obviously associated with the polymeric nature of the protonating agent.

Conclusions

To summarize, we have studied spectroscopic properties of principal forms of polyaniline in newly discovered polyaniline solvent, namely hexafluoro-2-propanol (HFIP). The spectra of leucoemeraldine (LEB), emeraldine (EB), and pernigraniline (PNB) differ significantly from the corresponding spectra recorded in NMP solutions. In particular, in HFIP solutions two principal absorptions (the π to π^* transition and the benzoid to quinoid ring excitonic transition) undergo a significant hypsochromic shift as compared to the absorption in NMP solutions of the same compounds. HFIP strongly interacts with EB, causing its partial protonation, as manifested by the appearance of an additional peak at 800 nm. To a lesser extent this interaction is also observed in PNB.

HFIP is a very convenient protonation medium. Due to its high acidity, similarly as *m*-cresol, HFIP favors the extended coil conformation of the protonated emeraldine, which in turn facilitates the delocalization of charge carriers (polarons). The extent of polaron delocalization strongly depends on the protonating agent and the method of protonation. The highest degree of delocalization has been obtained in the protonation with phenylphosphonic acid (PPA).

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