Doping of Polyaniline in the Solid State with Photogenerated Triflic Acid

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The objective of this study was to adjust work function of polyaniline (PANI) in the solid state by precisely dosed UV irradiation. For this purpose triphenylsulfonium triflate salt was used as a photo acid generator. The structure of PANI before and after irradiation was characterized by UV−vis and FTIR spectroscopy. It has been observed that the appearance of the 1143-cm^{-1} band, corresponding to the polaron stretching mode, correlates with the changes of the Fermi level. This observation indicates that electrons in the proton-doped PANI are delocalized, leading to a change in the electronic structure of PANI. The changes result in lowering of the work function of PANI as measured by the field-effect transistor. Nondecomposed triflate salt can be removed by dipping the irradiated film into methanol to prevent further UV light sensitivity and further postexposure acid doping.

Introduction

It is known that a nonconducting emeraldine base form of polyaniline (PANI) can be converted to the highly conducting emeraldine salt form (the half-oxidized PANI, $x = 0.5$, Figure 1) by doping with Brönsted acids.[1,2] In this step the number of electrons is not changing; therefore, it is not a redox process. As shown in Figure 1, the protonation of emeraldine base (I) to emeraldine salt is followed by an internal redox rearrangement which transforms (II) into (III), obeying the polaron formalism. In the semiquinone radical units (III) the C−N bond order is intermediate between those of amine and imine groups. In Figure 1 the PANI is shown as a conductor in the "conductor/dielectric/silicon" structure. Such an arrangement can be found in, for example, a field-effect transistor with a PANI gate conductor, a conductor/insulator/semiconductor capacitor, or a Kelvin probe measurement. In all such cases the distribution of electrons between the conductor and silicon is enabled by an external connection and is governed by the difference of the electron affinities of the two electronic materials. In this study such a structure allows us to track the changes of electron affinity of PANI after the UV irradiation step.

Previous studies have shown that triarylsulfonium salts $Ph_3S^+ X^-$ are effective precursors for in situ doping agents of polyaniline. These salts with, for example, $X^- = BF_4^-$, AsF_6^-, $CF_3SO_3^-$, undergo irreversible photolysis when irradiated with UV light to form protic acids HX.[3-7] Among them triphenylsulfonium triflate salts
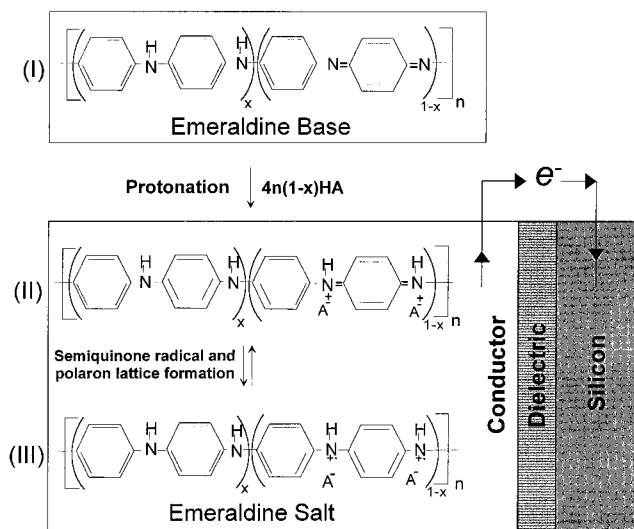

Figure 1. Schematic diagram of photoacid doping of PANI and its effect on the conductor/dielectric/semiconductor structure.

(PhT) are currently the only known source from which the organic acid, triflic acid (CF_3SO_3H), may be generated.[8] Mechanistic studies have shown that when these compounds are irradiated at wavelengths of 190−365 nm, the carbon sulfur bond is cleaved to form radical fragments ($Ph_2S^{+\bullet}$, $Ph^\bullet$) $CF_3SO_3^-$. In the absence of a proton-containing solvent, the subsequent "dark" interaction of the radicals produces diarylsulfide and (arylthio)biaryls, which serve as the proton source for the formation of triflic acid (Scheme 1). The photolysis of

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(1) Bredas, J. L. *Conjugated Polymers and Related Materials*; Salaneck, W. R., Lundström, I., Ranby, B., Eds.; Oxford University Press: New York, 1993; p 86.
(2) Chiang, J. C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193.
(3) Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307.
(4) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977.
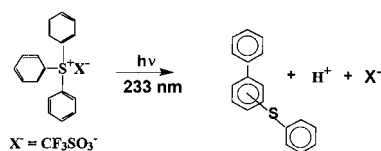
(5) Angelopoulos, M.; Shaw, J. M.; Huang, W. S.; Kaplan, R. D. *Mol. Cryst., Liq. Cryst.* **1990**, *189*, 221.
(6) Angelopoulos, M.; Shaw, J. M.; Kaplan, R. D.; Perreault, S. *J. Vac. Sci. Technol.* **1989**, *B7*, 1519.
(7) Dektar, J. L.; Hacker, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 6004.
(8) Nakano, K.; Maeda, K.; Iwasa, S.; Hasegawa, E. *IEICE Trans. Electron.* **1998**, *E81-C*, 1045.

Scheme 1

triarylsulfonium salts is rapid and relatively efficient with high quantum yields for the salts on the order of 0.2.[4,9,10]

The objective of the present study is to investigate changes in the doping level of solid-state PANI with photogenerated triflic acid. This effect can then be used to predictably control the work function of PANI and hence to tune the threshold voltage, V_T, of a polyaniline-gate field-effect transistor. The majority of previous doping studies have focused on changes of conductivity upon photochemical doping. FT-IR and UV−vis spectroscopy have been used for evaluation of photogenerated acid doping. The interpretation of changes in the polyaniline absorption spectra in the UV−vis range is consistent with the polaron structure model used for conjugated conducting polymers.[11] Subsequent removal of residual amounts of PhT using methanol enhances the stability of the (triflic acid)-doped polyaniline.

Experimental Section

Chemicals. Aniline (Aldrich, 99.5+%), tetrafluoroboric acid (Aldrich, 44% weight percent solution in water), triphenylsulfonium trifluoromethanesulfonate (PhT) (Aldrich), acetonitrile (ACN) (Aldrich, 99.9%, HPLC grade), tetrahydrofuran (THF) (Aldrich, 99.9% HPLC grade), methylene chloride (CH_2Cl_2) (Fisher, 99.9% ACS reagent), *N,N*-dimethylformamide (DMF) (Fisher, 99.9% ACS reagent), methanol (MeOH) (Fisher, 99.9% ACS reagent), and ammonium hydroxide (Fisher, ACS reagent) were used as received.

Preparation. The emeraldine base (EB) form of electrochemically synthesized polyaniline (PANI) was obtained as previously described.[12] Solutions of polyaniline were made by dissolving EB in DMF (8 mg/ml) and passing the solution through a 0.2-μm microfilter. PhT was added to the solutions at a EB-to-PhT mass ratio of 1:10. The high concentration of PhT was chosen because of the low quantum efficiency (≈30%) of the acid photogeneration. This concentration of PAG is necessary to reach an adequate protonation level. The ratio 1:10 (PANI:PhT) describes the weight ratio and corresponds to a molecular ratio of 1:2 (!) (polymer unit: PAG). Taking into account the effective efficiency of photoacid liberation[3] (mol of acid/mol of PAG) of 0.2−0.4 mol of acid is liberated per 1 mol of polymer (or aniline) unit, which yields a maximum protonation level of 40%. It can be assumed that this level has not been reached because of the strong absorption of PANI at 245 nm. This can be seen in the much less pronounced increase of the polaron bands (400 and 800 nm) in Figure 1 compared to, for example, chemical doping with strong acids. The presence of PAG did not adversely affect the film-forming properties of PANI/PAG.

Thin blue films of EB, thickness ranging from 0.2 to 0.6 μm, were formed by drop-casting onto quartz slides from DMF solutions. Films were dried in ambient laboratory air in the dark for at least 24 h before any measurements were conducted. Films of EB/PhT were doped by exposure to UV

radiation from a 5-W deuterium lamp (Hamamatsu Photonics K. K., Japan).

Residual nonphotolyzed acid precursor was removed by dipping the irradiated EB/PhT film into a solvent such as MeOH, CH_2Cl_2, THF, ACN, and DMF for 2−10 s. A longer time was used for thicker films.

The insulated-gate field-effect transistors without the usual polysilicon gate conductor were fabricated by a standard silicon process. Details on the fabrication can be found in ref 13. The polyaniline was deposited on the silicon oxide/nitride gate insulator by solution-casting with a microliter syringe and dried in air before exposure to UV light. Voltage was applied to the PANI with gold leads on either side of the transistor gate.

Measurements. UV−vis spectroscopy was performed on a Shimadzu UV-3101PC spectrophotometer (Shimadzu Scientific Instruments, Inc.). The absorption spectra of doped and undoped PANI were recorded between 300 and 900 nm and with a resolution setting of 2 nm.

The absorbance of the sample is dependent on the layer thickness. A blank quartz substrate was used as reference. Background and baseline correction were carried out to compare the spectra and the absorption changes upon UV irradiation either of different samples or of one sample measured in different experimental sets. The spectra were baseline-corrected with respect to layer thickness by setting the absorption band intensity of the isosbestic point at 464 nm to the value of a PANI layer of 0.5-μm thickness. Thereafter, difference spectra, ΔA, were obtained by subtracting a reference spectrum of the sample taken before irradiation, A_{ref}, from all consecutive spectra of one sample, A_{samp} ($\Delta A = A_{samp} - A_{ref}$). When this procedure is used, only the electronic transitions which change their intensity due to the change of the polymer electronic band structure are determined. Absorption changes affected by the background or by the layer thickness disappear from the difference spectra.

FT-IR measurements were performed in the frequency range of 400−4000 cm^{-1} using a BIO-RAD FTS-6000 with a BIO-RAD UMA-500 IR microscope attachment. IR reflectance spectra were obtained using the rapid scan mode at a mirror modulation frequency of 10 kHz with a resolution setting of 2 cm^{-1}. An average of 200 scans was used to produce each spectrum. Background spectra were obtained using a quartz glass slide. The background was subtracted from the sample spectra using BIO-RAD WIN-IR PRO software.

Film thickness was measured using a Dektak[3]ST Surface Profiler (Sloan/Veeco Instruments, Inc.). Drain current−gate voltage (I_D vs V_G) characteristics of the FET utilizing a PANI gate before and after irradiation were measured on a Solartron SI 1287 Electrochemical Interface controlled by CorrWare for Windows, 32-bit, Version 2.3d (Scribner Associates, Inc.). In the FET "source-follower" configuration, the source contact was grounded while a positive potential scan was applied to the drain/gate lead.[14] Threshold voltage, V_T, was determined from the recorded I_D vs V_G curves.

Results and Discussion

It was observed that PANI EB cast from DMF with no dopant remained stable after exposure to UV irradiation within the experimental conditions. No changes were observed in UV−vis, FT-IR, or FET characteristics after irradiation.

UV−Vis Spectra. The "as-cast" EB/PhT film is blue but with exposure to UV light the film color changes to green. Optical absorption spectra of a single film cast from DMF before and after UV exposure are shown in Figure 2A. The recorded UV−vis spectrum of poly-

(9) Angelopoulos, M.; Shaw, J. M.; Huang, K. L. *Polym. Eng. Sci.* **1992**, *32*, 1535.

(10) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1988**, *53*, 1833.

(11) Huang W. S.; MacDiarmid, A. G. *Polymer* **1993**, *34*, 1833.

(12) Hatchett, W.; Josowicz, M.; Janata, J. *J. Electrochem. Soc.* **1999**, *146*, 4535.

(13) Polk, B. J.; Smith, J. A.; DeWeerth, S. P.; Zhou, Z.; Janata, J.; Domansky, K. *Electroanalysis* **1999**, *11*, 70.

(14) Potje-Kamloth, K.; Polk, B. J.; Josowicz, M.; Janata, J. *Adv. Mater.* **2001**, *13*, 1797.
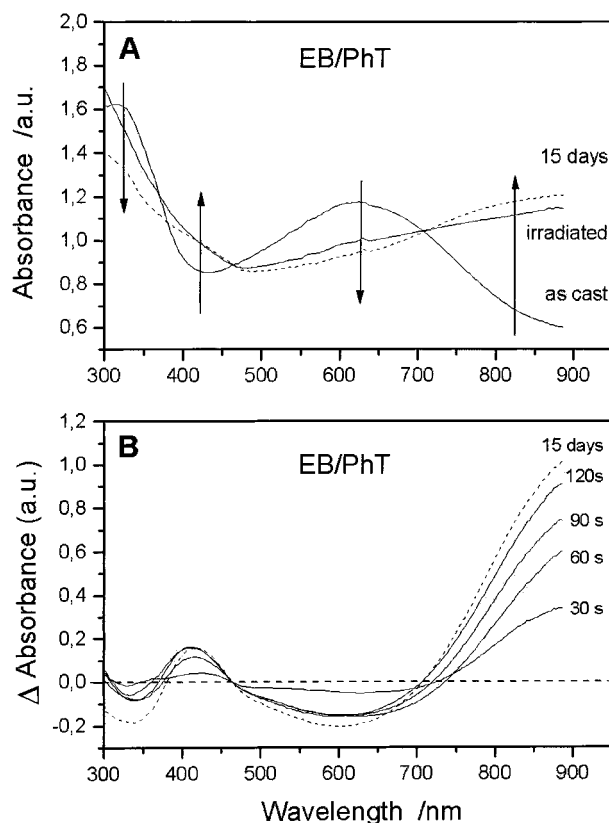
Figure 2. (A) UV—vis absorption spectra of a film of EB/PhT before and after irradiation by UV light from a deuterium lamp (solid line) and after 15 days of exposure to air stored in the dark (dotted line). (B) Difference absorption spectra of a EB/PhT film after different exposure times to UV light (solid line) and storage in air as indicated. The spectrum of the as-cast polymer film was used as reference.

aniline depends strongly on its protonation state. The strong absorption at 320 nm (4.1 eV) is associated with the $\pi-\pi^*$ transition in the benzoid/quinoid ring structure and is considered a good estimate of the material band gap. Nonirradiated emeraldine base shows a band at 620—650 nm ($\approx$2.0 eV) attributed to the molecular "exciton" in the quinoid segments.[15] With exposure to UV light the band at 320 nm shows significant reduction in intensity and the band centered around 600 nm disappears. This indicates the absence of the exciton in the polaron lattice formed upon protonation.[16] Protonated emeraldine gives two bands, one at 430 nm (2.8 eV) and another around 800 nm (1.5 eV) that can be ascribed to the polaron—π^* and π—polaron transition, respectively.[17] The latter is superimposed on a steadily increasing absorption tail extended toward the NIR region. Such an extended "free-carrier tail" is characteristic of charge carrier delocalization in conducting polymers.[18] Similar results were obtained by Angelopoulos et al. using polyaniline films of an EB/triphenylsulfonium hexafluoroantimonate salt composition.[5]

(15) Bredas, J. L. *Conjugated Polymers and Related Materials*; Salaneck, W. R., Lundström, I., Ranby, B., Eds.; Oxford University Press: New York, 1993; p 195.
(16) Stafstrom, S.; Bredas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1987**, *59*, 1464.
(17) Quillard, S.; Berrarda, K.; Lefrant, S.; Lapkowski, M.; Pron, A. *New J. Chem.* **1995**, *19*, 365.
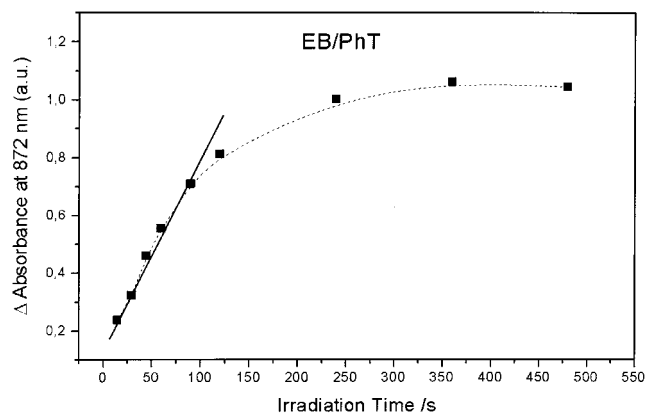(18) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci.* **1998**, *23*, 277.

Figure 3. Dependence of the normalized absorption band intensities at 872 nm (ΔA_{872}) on the irradiation time of a EB/PhT film.
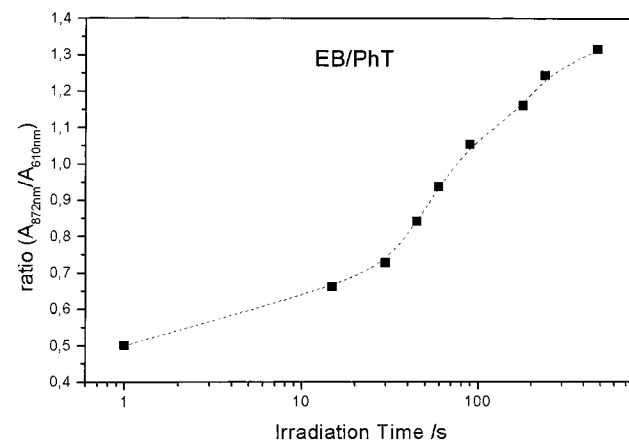

Figure 4. Ratio of absorption band intensity at 872 nm to that at 610 nm (A_{872}/A_{610}) with different irradiation times for a EB/PhT film.

In Figure 2B difference spectra, ΔA (solid line), show the relative changes in absorbance that take place in a single polyaniline film mixed with PhT after an increasing UV irradiation dose. With an increasing UV dose the spectrum shows changes analogous to those already discussed in Figure 2A. The increase of the intensity of the bands at 430 and 800 nm suggests the formation of mid band gap states of the material upon protonation. The decrease of the band intensity at 610 nm is due to the destabilization of the EB structure, analogous to that of a bipolaron lattice (Figure 1, form II). The extra charges carried by protons, coupled to the quinoid segments, lead to reorganization of the EB structure and result in a formation of polarons (Figure 1, form III). Consequently, the polarons separate to minimize the electrostatic repulsion between two positive charges, thus forming a polaron lattice.[19] Figure 3 depicts the absorption band intensity at 872 nm from Figure 2B as a function of the irradiation time. Initially, the absorbance increases linearly with the irradiation time and levels off when either the available PANI is fully doped or most of the photoacid generator in the film is photodecomposed to triflic acid. Figure 4 depicts the ratio of the absorbance at 872 nm to that at 610 nm with different irradiation time. This dependence re-

(19) Bredas, J. L. *Conjugated Polymers and Related Materials*; Salaneck, W. R., Lundström, I., Ranby, B., Eds.; Oxford University Press: New York, 1993; p 215.
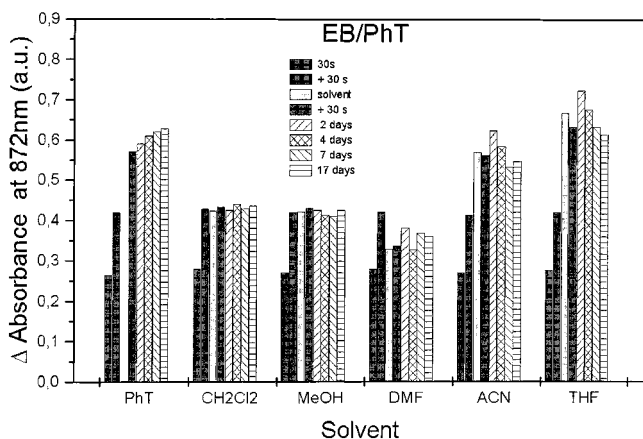
Figure 5. Absorption band intensities at 872 nm (ΔA_{872}). Solid columns after different exposure times to UV light and solvent treatment as indicated. Shaded columns: (ΔA_{872}) after storage in air for different periods of times as indicated. The sequence of the patterns for different solvents follows the sequence given in the insert.

sembles the shape of a titration curve and increases with the irradiation time, correlating to an increase in the PANI protonation state. This feature is comparable to the relationship between the conductivity at room temperature and the protonation state of the emeraldine salt as previously published.[2,20]

The change in absorbance of polyaniline after UV irradiation of a mixture of EB with PhT shows clearly the protonation of imine sites and the formation of the polaronic structure of emeraldine salt due to the photochemical formation of triflic acid. This dependence on the irradiation time allows precise control of the doping level of emeraldine salt by the exposure dose.

Solvent Treatment. After the last irradiation step, the absorbance of the polaron band at 872 nm increases slightly over a long period of time when stored in the dark in ambient air (see Figure 2A,B (dashed line)), suggesting that the protonation process is continuing even without irradiation. Incompletely decomposed PhT is present after the irradiation step as seen in noticeable absorption by the polyaniline film in the 254-nm region of the UV spectrum. Because of the moisture sensitivity of PhT, a slow release of triflic acid takes place. An obvious remedy of the postexposure protonation is to remove the nondecomposed photoacid generator PhT by an appropriate solvent. The following solvents have been evaluated for this puprose: methylene chloride (CH_2Cl_2), methanol (MeOH), *N,N*-dimethylformamide (DMF), acetonitrile (ACN), and tetrahydrofuran (THF). In principle, the removal of unreacted precursor salt should be a matter of its solubility in a given solvent. The condition of charge neutrality dictates the equivalent amount of triflate anion that remains in the film while the protonated ES is insoluble, by definition. Nevertheless, various solvents proved to be more or less optimal for this task. To optimize the washing step, the procedure depicted in Figure 5 was adopted. The PANI/PhT film was irradiated two times for 30 s and the absorbance spectrum was measured after each irradiation step. The film was then dipped in one of the above solvents for 5 s and the absorbance at 872 nm was again
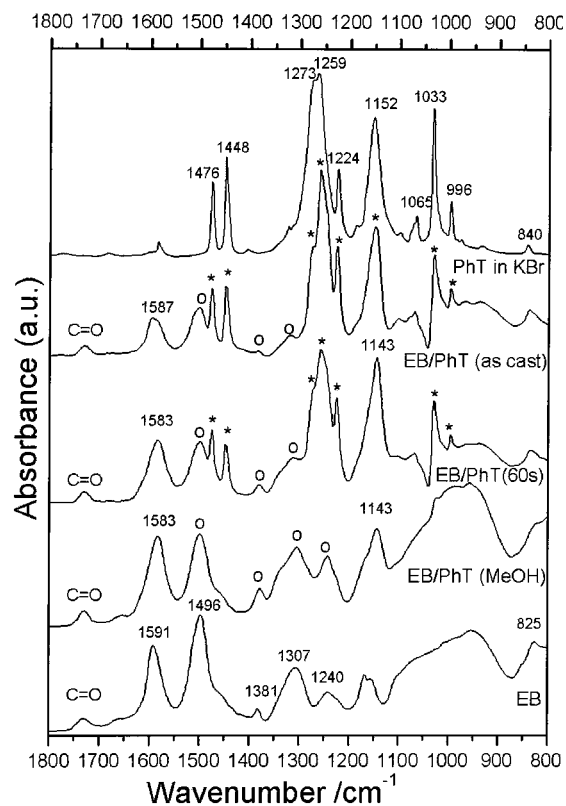
(20) Wan, M.; Zhou, W.; Li, Y.; Liu, J. *Solid State Commun.* **1992**, *81*, 313.

Figure 6. FT-IR reflectance spectra for PhT, as-synthesized EB, and a EB/PhT film: (as cast) before, (60 s) after irradiation by UV light, and (MeOH) methanol treatment.

measured. The film was then irradiated one more time for 30 s and absorbance was recorded. Finally, the film was stored in air in the dark. Absorbance spectra were recorded after 2, 4, 7, and 17 days.

Figure 5 shows the absorption band intensities at 872 nm (ΔA_{872}) for each procedure step and solvent used. The absorbance at each step was normalized to the absorbance after 60 s of exposure for the same film. For comparison, ΔA_{872} for a PANI/PhT film without solvent treatment is included. Not surprisingly, all layers show the same increase in ΔA_{872} after the first two irradiation steps of 30 s. After the irradiated film was dipped in CH_2Cl_2 or MeOH, no further change in ΔA_{872} could be observed due to further exposure to UV light and storage in the dark, as compared with that in DMF, THF, and ACN. It can be assumed that both solvents effectively remove the nondecomposed PhT from the layer.

IR Spectra. Additional insight into the photochemical doping process and the solvent treatment can be obtained from FTIR spectroscopy. Figures 6 and 7 show the spectra of EB/PhT 1:10 before and after UV radiation for 60 s and after dipping of the irradiated film in MeOH to remove the nondecomposed photoacid generator. For comparison, spectra of as-synthesized EB and PhT are included. The relevant spectral assignments and the vibrational energies associated with the IR spectra of Figures 6 and 7 are summarized in Table 1.

The spectrum of PhT shows the C−H stretching vibrational bands in the range of 3092−3027 cm^{-1} and at 1224 cm^{-1}, which are attributed to the triphenylsulfonium cation. The 1476 and 1448 cm^{-1} modes are assigned to benzene ring deformation. The strong bands

Table 1. Spectral Assignments and Vibrational Energies of PANI Associated with the IR Spectra of EB and of EB/PhT Film Shown in Figures 6 and 7[a]

assignment				EB/PhT (weight ratio 1:10)			EB
vibrational mode	group (citations)	PAG	polymer	(as cast)	(60 s)	(MeOH)	as-synthesized
ν_s(N–H)	amine free[18,26]		PANI				3377 s
ν_s(N–H)	amine H-bonded[12,18,21]		PANI	3321 m	3262 s	3275 s	3305 s
ν_s(C–H)	benzene[12,25,26]	PhT	PANI	3071 s	3071 s	3065 m	3059 s
		PhT	PANI	3049 m	3049 m	3039 m	3043
			PANI			2957 w	2951 m
			PANI		2862 w	2862 w	2855 m
ν_s(C=C)	quinoid[12,18,27]		PANI	1595/1587 s	1583 s	1583 s	1591 s
	benzene[12,18,21,27]			1510/1496 s	1496 s	1496 s	1496 s
ν_s(C–N)	benzene[18]		PANI	1381 w	1379 w	1378 m	1381 m
			PANI		1342 w	1335 sh	
ν_s(C–N)	sec. amine[12,18]		PANI			1305 s	1307 s
ν_s(C–N).	sec. amine[18]		PANI	1246 sh	1246 sh	1243 s	1240 m
δ(C–H)	quinoid[18,26]		PANI	1166 sh	1168 sh	1165 sh	1166 s
ν_{as}(C=N)	semiquinone radical[12,18]		PANI		1143 s	1143 s	
	ref 18		PANI			959 s	954 s
	ref 18		PANI				850 sh
γ(C–H)	1,4-benzene[12,18]		PANI			820 sh	825 s

a Vibrational assignments are taken from the literature.[12,18,21,25–27] Intensity descriptions: s, strong; m, medium; w, weak; sh, shoulder. Vibration descriptions: ν, stretching; γ, out-of-plane bending; δ, in-plane-bending. For abbreviations see text.
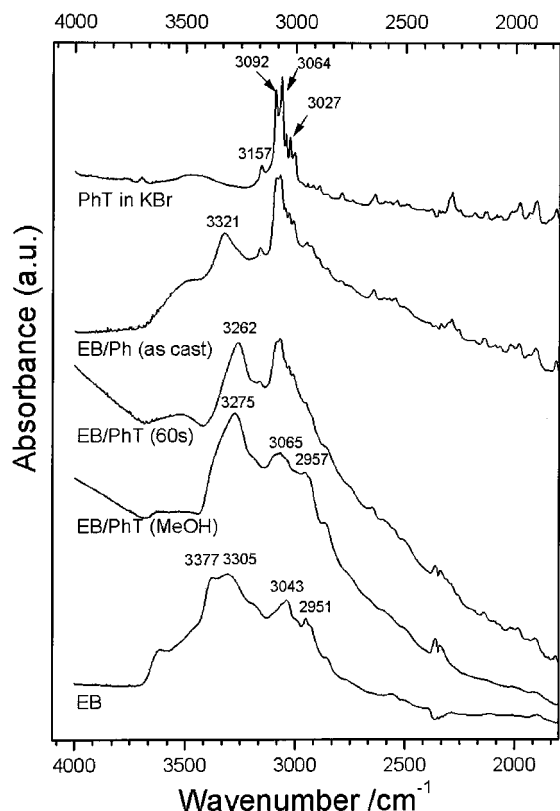

Figure 7. FT-IR reflectance spectra for PhT, as-synthesized EB, and a EB/PhT film: (as cast) before, (60 s) after irradiation by UV light, and (MeOH) methanol treatment.

characteristic for the S–O stretching vibration of sulfonic acid salt are observed at 1273, 1065, and 996 cm^{-1} and those characteristic for C–F vibration of the anion at 1262 and 1152 cm^{-1}.

All IR absorption spectra of PANI show a weak absorption band at 1730 cm^{-1}, which can be assigned to the C=O vibration. It indicates residual amounts of DMF from which all layers were cast. The IR absorption spectrum of EB obtained after polymerization is in good agreement with previously reported results.[21,18] The bands in the range of 1240–1381 cm^{-1} are assigned to the C–N stretch of secondary aromatic amine and those

in the range of 825–1166 cm^{-1} to the aromatic C–H bending vibration. The bands at 3377 and 3305 cm^{-1} in Figure 7 are attributable to the non-hydrogen and hydrogen-bonded N–H stretching mode of EB containing amine (reduced) and imine (oxidized) sites.[21] The C–H bands in the range of 3060–2850 cm^{-1} are attributed to the stretch vibration of the benzenoic/ quinoid units. The bands at 1591 and 1496 cm^{-1} are consistent with quinone and benzene ring deformation. The intensity ratio of these bands is usually related to the oxidation level of the polymer.[22] In the spectra of EB/PhT films measured before (indicated as "as cast") and after UV irradiation (indicated as "60 s"), the vibrational bands characteristic for triflate salt and EB are superimposed. They are indicated with (*) and (o), respectively.

Upon photochemical protonation of EB/PhT, the quinoid units are believed to be converted to semiquinone radical units by a proton-induced spin-unpairing mechanism (Figure 1, form III) and the absorption band at 1143 cm^{-1} (Figure 6), attributed to C–N stretching of the semiquinone radical units, becomes more prominent.[22] Furthermore, an increase in absorption at 1240 cm^1 is observed, which corresponds to the bipolaron structure characteristic of the protonated form of polyaniline.[23] The long absorption tail above 2000 cm^{-2} in Figure 7 observed for the irradiated films is associated with the electronic absorption of protonated PANI by free carriers (unpaired electrons and positive charges), indicating high electrical conductivity and a high degree of electron delocalization in PANI.[22,24] The N–H stretching frequency is shifted lower by nearly 110 cm^{-1} and is superimposed on the electronic absorption

(21) Zheng, W.; Angelopoulos, M.; Epstein, A. J.; MacDiarmid, A. G. *Macromolecules* **1997**, *30*, 2953.
(22) Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.* **1988**, *24*, 231.
(23) Stejskal, J.; Sapurina, I.; Trchova, M.; Prokes, J.; Krivka, I.; Tobolkova, E. *Macromolecules* **1998**, *31*, 2218.
(24) Cao, Y.; Li, S.; Xue, Z.; Guo, D. *Synth. Met.* **1986**, *16*, 305.
(25) Miyatake, K.; Yamamoto, K.; Kazuhisa, E.; Tsuchida, E. *J. Org. Chem.* **1998**, *63*, 7522.
(26) Socrates, G. *Infrared Characteristic Group Frequencies*; Wiley: New York, 1980.
(27) Hediger, H. J. *Infrarotspektroskopie*; Akademische Verlagsgesellschaft: Frankfurt/Main, 1971.

of protonated PANI. The spectrum of EB/PhT after irradiation exhibits all characteristic features of the protonated PANI, thus confirming the ability of photo-generated triflic acid to protonate the emeraldine base in the solid state upon irradiation of PhT.

The interaction of the dopant anion in PANI after irradiation can be observed by examining the N−H and C−H bands of the benzene ring, which are sensitive to hydrogen bonding and electron density changes based on the interaction with electron-accepting or -donating species in the polymer. Photochemical acid doping of EB with triflic acid results in hydrogen-bonded N−H bands at 3262 cm^{-1}, which can be compared to ES doped with, for example, H_2SO_4, showing low hydrogen bond between the amine group and the anion.[12] This is consistent with the positions of the C−H bands in the region between 3071 and 2862 cm^{-1} of ES.

It is often stated that the oxidation state of PANI refers to the relative ratio of quinoid and benzoid units.[22] It can be obtained by taking the relative ratio of the areas of the IR bands at 1590 cm^{-1} ("quinoid" band) and 1496 cm^{-1} ("benzenoid" band). In our experiments, this ratio is not changing upon irradiation of PANI/PhT with UV light. The most prominent change of the spectrum of the EB after the solid-state protonation is the appearance of the 1143-cm^{-1} band due to the semi-quinone structure, which increases with irradiation.[22] It was observed that the intensity changes of this band correlate with the changes of the position of the Fermi level. The observed correlation can be explained by the reorganization of the lattice and associated reorganization of the energy levels in the PANI film. This is consistent with the changes in the UV spectra (Figure 2B). It has been previously shown that the work function of the PANI/PhT layer decreases upon photochemical doping.[14]

The results show that photodecomposition of PhT to triflic acid in the solid state leads to the protonation of PANI. After treatment of the irradiated EB/PhT film with MeOH, the same characteristic vibration bands of polyaniline as those for the EB/PhT (60 s) film are observed. The absorption bands, which indicate the presence of nondecomposed PAG, disappear when the protonated PANI layer is treated with MeOH, which is supporting evidence for the removal of nondecomposed PhT by treatment with the solvent.

Solvent Treatment of (Triflic Acid)-Doped Polyaniline Used as the Polymer Gate of FET. EB/PhT was used as the gate conductor in a field-effect transistor (FET) structure as depicted in Figure 1. The field-effect transistor serves as a convenient tool for investigation of changes of work function of PANI used as the gate conductor. It has been previously shown that the photoacid doping of the polyaniline gate shifts the V_T to lower values, indicating the decrease in work
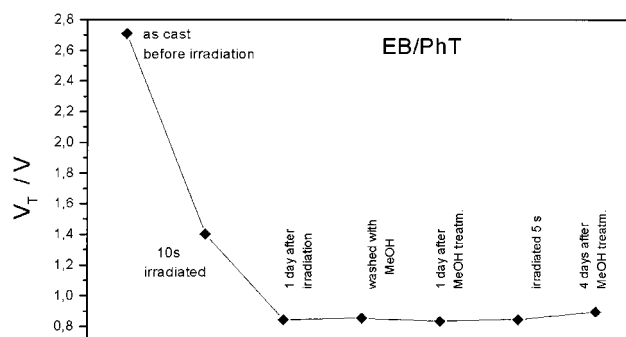

Figure 8. Threshold voltages, V_T, of a field-effect transistor with a EB/PhT polymer obtained after light exposure, methanol treatment, and different storage times as indicated.

function of PANI upon photochemical doping with triflic acid.[14] This observation is consistent with the flow of electrons depicted in Figure 1.

The change of the V_T values for the PANI gate FET upon irradiation and after MeOH treatment are shown in Figure 8. The shift of the threshold voltage during the storage of the irradiated FET in the dark is consistent with the change in the polaron absorbance band intensity observed in the UV−vis spectrum of the polyaniline film upon exposure to UV radiation (Figure 2A,B and Figure 5). No further shift is obtained during storage of the protonated polyaniline-gate FET in ambient air and after further exposure to UV light when dipped in MeOH. The treatment with MeOH prevents postexposure protonation reaction due to UV light and moisture sensitivity of residual amounts of photoacid generator.

Summary

Polyaniline base can be protonated by triflic acid, which is generated by UV photolysis of the photoacid generator, triphenylsulfonium triflate salt. A change in the protonation degree of PANI after irradiation was observed by UV−vis and FT-IR. Washing with methanol removes the residual nondecomposed photoacid generator and prevents further UV light sensitivity and postexposure drift. Measurements using a FET reveal that the photochemical acid generation process can be used to lower the work function of PANI. The extent of protonation can be adjusted by the irradiation dose, thus allowing control of both the work function and the threshold voltage of the polyaniline-gate FET.