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PVC as photodonor of HCl for protonation of polyaniline

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Abstract

A novel photoinduced protonation of PANI(EB) from PVC as donor of HCl is proposed. The polymer-composite is a polyvinylchloride (PVC) blended with the base form of polyaniline called emeraldine base (EB). The UV-induced protonation of the polymer chain is studied through its optical absorption. The protonation of EB occurs through HCl diffusion within the polymer chains in the PANI(EB)/PVC composite. After UV-exposure, the PANI(EB)/PVC-composite turns to green-color, which is typical of the emeraldine salt (ES). Contrary to film prepared from THF, a negative coloration is obtained with blends prepared from *N*-methylpyrrolidinone (NMP). Origin could be a proton-trapping effect from solvent traces behaving as usual PVC additives.

Keywords: Polyvinylchloride (PVC); Protonation; Polyaniline

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1. Introduction

Conducting polymers have attracted considerable attention in the last 15 years. Electrically conducting polymers are new materials that combine the physical and chemical attributes of plastics with electronic properties of metals. Since organic polymers are normally insulators, it can be presumed that a polymer that is an electronic conductor must have an unusual structure. The relationship between the structure and the ability to convey electric charges is the key to progress on this area. Among them, polyaniline occupies an important place due to its specific doping and conductivity characteristics and its applications in electronic devices [1,2] and sensors [3,4]. Polyaniline is primarily of interest because it can be used as an electrode material. Among all conducting polymers, it is the preferred choice. Its discharge capacity is greater than that of polypyrrole(+)perchlorate(−), its self-discharge is better than that of, e.g., polythiophene or Ni/Cd battery systems. Among them, polyaniline (PANI) plays a noticeable role due to its remarkable environmental stability. Additionally, it benefits from a relatively good understanding of the chemical structure and electronic property relationships [5,6].

EB form of polyaniline is moderately soluble in polar organic solvents such as *N*-methylpyrrolidinone (NMP), *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) [7]. Conducting polymer composites and blends in different host-polymers such as polypyrrole–poly(vinylmethyl ketone) [8], polypyrrole–teflon [9], polypyrrole–poly(vinyl alcohol) [10], polyaniline-nitile rubber [11] have been obtained. Indeed, spectral and electrical properties of polyaniline can be reversibly controlled through electron-transfer doping or through protonation by acids [1] or even through the used of low molecular acid photo-generators such as Crivello-salts [12].

In this paper, we report some of the first results concerning UV radiation induced effect on PANI(EB)/PVC polymer films on the basis of the spectroscopic analyses. We demonstrate that the host-polymer can be use as a photo-acid generator for the protonation of EB.

2. Experimental

The emeraldine-base form of PANI (purchased from AC&T, France) was dissolved in THF and the solution was filtered through a 0.2-mm filter. The dissolved solution of additive-free PVC in THF was added to the EB solution and stirred at room temperature in a glass-soppered Erlenmeyer flask. The polymer films were cast from the solution on glass plates. After drying, polymer films were exposed to ultraviolet radiation at 254 nm under 0.1-mW/cm^2 power. Experimentally, the optical spectrum of the PVC/EB composite was monitored before and after UV-exposure using different doses in the same film.

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As another film preparation technique, we used a solution of PANI(EB) dissolved in NMP with concentration 0.5% free PVC in NMP added to this solution and stirred at room temperature in a glass-soppered Erlenmeyer flask.

Absorption spectra were recorded on a Perkin–Elmer 19 UV/VIS spectrophotometer.

3. Protonation of PANI

In our previous works, we found that photoinduced protonation of dyes, incorporated into PVC films is very efficient [13,14]. As a result, the use of PVC as a donor of HCl in a PANI(EB)/PVC blend may have several important merits.

(1) Photoregulation of the conductivity of the polyaniline during the different stages of protonation.

$$\mathrm{PANI(EB)} \xrightarrow[\mathrm{PVC}]{h\nu,\mathrm{HCl}} \mathrm{PANI(EB)H^{+}} \xrightarrow[\mathrm{PVC}]{h\nu,\mathrm{HCl}} \cdots$$

(2) Possibilities for very high values of the conductivity (PVC can be donor of many moles of HCl).

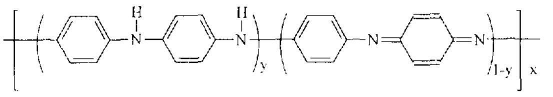
(3) The system can be made reversible on the basis of the deprotonation of the protonated EB using NH_3 for example.

$$\mathrm{PANI(EB)H^{+}Cl^{-}} \xrightarrow{\mathrm{base}} \mathrm{PANI(EB)+HC}$$

or through addition of HCl to the ethylenic double bonds of the irradiated PVC.

$$\mathrm{HCl} + \left(\mathrm{CH{=}CH}\right)_n \longrightarrow \left(\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}\mathrm{-CH_2}\right)_n$$

The emeraldine oxidation state of polyaniline ($y=0.50$)



in its non-conducting or base form emeraldine base (EB) has been the most widely studied of the polyaniline materials. The doping process has generally involved reacting the emeraldine base in either a powder or a film form heterogeneously with a dopant solution [15–17]. Alternatively, the doping process has been accomplished homogeneously be reacting a solution of the emeraldine base in an appropriate solvent, e.g., *N*-methylpyrrolidinone (NMP), with a solution of the dopant.

4. Results and discussion

Using the films compositions PANI(EB)/PVC prepared from THF-solution, the effect of the UV-exposure can be seen visually. Prior to exposure, the PVC/EB film is dark blue, which is characteristic of the non-conducting form of PANI. After UV-exposure, it becomes green, corresponding to the protonated form of PANI, the so-called emeraldine salt (ES). Optical absorption spectra of a 20-μm thick PANI(EB)/PVC-film in THF before and after UV-exposure are given in Fig. 1.

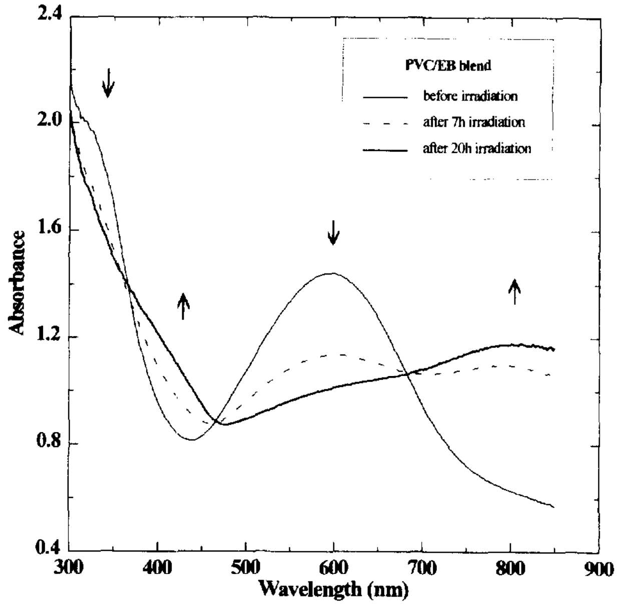


Fig. 1. Optical absorption spectra of a free-standing PANI(EB)/PVC-film from THF before and after different UV-exposure times.

Upon UV-exposure of PANI(EB)/PVC, the absorption maxima around 320 nm and at 595 nm decrease and two absorption bands appear at 800 nm and 415 nm. The 320-nm band is generally attributed to the π–π^*-transition of the EB-benzene-rings. The 800 nm and 415-nm bands are generally attributed to the polaron states [18,19]. Similar results were obtained by Angelopoulos et al. [12] using PANI/onium-salt films or by Neoh et al. [20] in PANI solutions. When THF is used as a solvent for PANI(EB)/PVC preparation, PVC produces HCl and a protonation reaction occurs (Scheme 1).

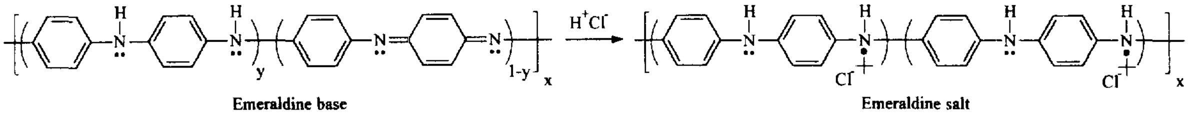
When we use NMP solvent, we can not see effect of protonation, i.e., we cannot find a new absorption bands at 420 nm and 830 nm which are typical for reaction of protonation. We observed that the absorption peaks at 330 nm and at 650 nm decreased. In this case, reaction of protonation is not valid (Fig. 2).

Two effects are observed during irradiation of PANI(EB)/PVC films: (a) production of HCl (Scheme 2); and (b) protonation of PANI(EB) in the composition (Scheme 1).

UV–light exposure of PANI(EB)/PVC-blends may give rise to changes in the absorption, as a result of dehydrochlorination of PVC (Scheme 2) and EB protonation with HCl (Scheme 1).

5. Conclusion

In this paper, we have shown that PVC, which upon UV-exposure undergoes dehydrochlorination, can be used as a solid solvent for PANI(EB)-composite films. The protona-



Scheme 1.

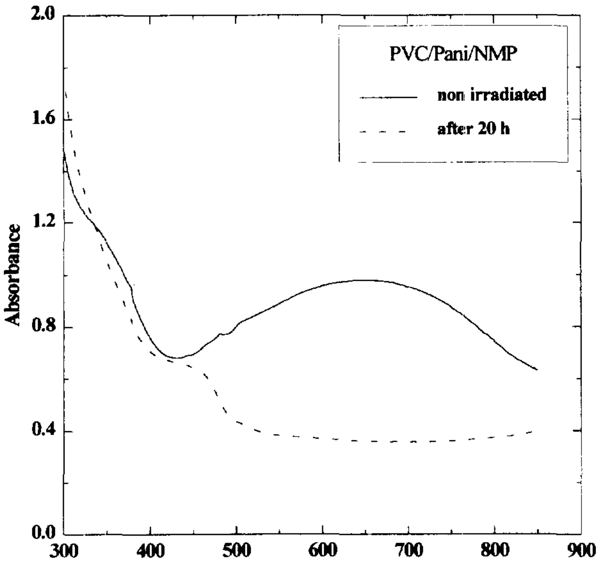
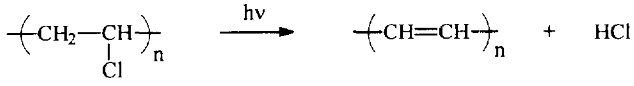


Fig. 2. Optical absorption spectra of a free standing PANI(EB)/PVC-film from NMP before and after UV-exposure.



$$\left(CH_2-\underset{Cl}{CH}\right)_n \xrightarrow{h\nu} \left(CH=CH\right)_n + HCl$$

Scheme 2.

tion of EB occurs through HCl diffusion within the polymer chains in the PANI(EB)/PVC composite. After UV-exposure, the PANI(EB)/PVC-composite turns to green-color, which is typical of the emeraldine salt. Until now, the electrical conductivity of the blend is undetectable, even after a long exposure time. The reason could be that the EB-concentration in the blend is well below the percolation threshold for conductivity (low doping degree) [10,11,21]. On the hand, the reason for the negative coloration obtained with blends prepared from NMP-solvent could be a proton trapping effect of solvent traces, having an analogous effect to usual PVC-additives. We find that NMP is not a good solvent for the preparation of solid state such compositions in which include PVC. NMP is a good solvent for PANI(EB) but not for PVC because in this case PVC can not play the role of HCl photogenerator.

Further experiments are in progress to increase the amount of conducting polyaniline in the PANI(EB)/PVC-composite in order to get significant conductivity. The reported protonation method may find advantageous applications in the preparation of conducting composites.

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References

[1] A.G. MacDiarmid, A.J. Epstein, Faraday Discuss. Chem. Soc. 88 (1989) 317.
[2] M. Kaneko, H. Nakamura, J. Chem. Soc., Chem. Commun., 1441 (1985).
[3] T. Hanawa, S. Kuwabata, H. Yoneyama, J. Chem. Soc., Faraday Trans. 84 (1) (1988) 1587.
[4] N.E. Agbor, M.C. Petty, A.P. Monkman, Sensors and Actuators B28 (1995) 173.
[5] A.J. Epstein, A.G. MacDiarmid, Makromol. Chem., Macromol. Symp. 51 (1991) 217.
[6] A.G. MacDiarmid, A.J. Epstein, Synth. Met. 69–71 (1995) 85.
[7] M. Wolszczak, J. Kroh, Radiat. Phys. Chem 48 (1996) 114.
[8] H. Wang, J.E. Fernandez, Macromolecules 25 (1992) 6179.
[9] X. Lafosse, Synth. Met. 68 (1995) 227.
[10] T. Ojio, S. Miyata, Poly. J. 48 (1986) 95.
[11] E.L. Tassi, M.A. De Paoli, Polymer 33 (1992) 2427.
[12] M. Angelopoulos, J.M. Shaw, W.S. Huang, R.D. Kaplan, Mol. Cryst. Liq. Cryst. 189 (1990) 221.
[13] I. Petkov, T. Deligeorgiev, N. Sertova, Mol. Cryst. Liq. Cryst. 246 (1994) 359.
[14] I. Petkov, T. Deligeorgiev, P. Markov, M. Evstatiev, S. Fakirov, Polym. Degradation and Stability 33 (N1) (1991) 53.
[15] J.C. Chiang, A.G. MacDiarmid, Synth. Met. 13 (1986) 193.
[16] M. Angelopoulos, A. Ray, A.G. MacDiarmid, A.J. Epstein, Synth. Met. 21 (1987) 21.
[17] M. Angelopoulos, G.E. Asturias, S.P. Ermer, A. Ray, E.M. Scherr, A.G. MacDiarmid, Mol. Cryst. Liq. Cryst. 160 (1988) 151.
[18] A.J. Epstein, J.M. Ginder, F. Zuo, R.W. Begelow, H.S. Woo, D.B. Tanner, A.F. Richter, W.S. Huang, A.G. MacDiarmid, Synth. Met. 18 (1987) 303.
[19] S. Stafstrom, J.L. Bredas, A.J. Epstein, H.S. Woo, D.B. Tanner, W.S. Huang, A.G. MacDiarmid, Phys. Rev. Lett. 59 (1987) 1464.
[20] K.G. Neoh, E.T. Kang, K.L. Tan, Polymer 33 (1992) 2292.
[21] I.A. Tchmutin, A.T. Ponomarenko, V.G. Shevchenko, D.Y. Godovski, Synth. Met. 66 (1994) 19.