

PHOTO-INDUCED DOPED POLYANILINE BY THE VINYLIDENE CHLORIDE AND METHYL ACRYLATE COPOLYMER AS PHOTO ACID GENERATOR*

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ABSTRACT

The emeraldine base form of polyaniline (PANI) can be doped by a photo-induced doping method. In this method a copolymer of vinylidene chloride and methyl acrylate (VCMAC) was used as photo acid generator which can release proton when it is exposed to ultraviolet light ($\lambda = 254 \text{ nm}$). The structure of PANI-VCMAC system before and after irradiation was characterized by elemental analysis, IR, XPS, and SEM images. Results obtained indicate that the photo-induced doping characteristics, such as doping position and type of charge carriers, are similar to that of PANI doped with HCl. The poor room-temperature conductivity ($\sim 10^{-5} \text{ S/cm}$) of PANI-VCMAC system after irradiation may be due to low doping degree ($\sim \text{pH} = 3$) and the difference in morphology as compared with PANI-HCl film.

INTRODUCTION

The emeraldine base form of polyaniline (PANI) can be doped chemically or electrochemically by proton to form its emeraldine salt form, which is a conducting state with conductivity of 10 S/cm at room-temperature. It is known that the number of electrons on the polymer chain of PANI does not change after protonation, which is different from the oxidation or reduction doping used in polyacetylene and polypyrrole. Angelopoulos et al.^[1] have reported for the first time that triphenylsulfonium hexafluoroarsenate salt was used as an ionic photo acid generator to dope PANI films, which is cast from N-methyl-2-pyrrolidinone (NMP) solvent and exposed the system to 240 nm wavelength ultraviolet of electro-beam radiation. Moreover, they

* The work was supported by the National Natural Science Foundation of China

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Received November 20, 1995

reported^[2] that water-soluble PANI can be used in the photoetching processes to fabricate integrated circuits. Recently, Venugopal et al.^[3] reported that the base form of methyl-substituted PANI, poly(o-toluidine) (POT), can be converted to the electrically conductive salt by using nonionic photo acid generator, which produces sulfonic acid when irradiated with ultraviolet (UV) light. All of these results suggest that the photo-induced doping of PANI is possible if the photo acid generator can release proton when it is exposed to ultraviolet light.

In this article, photo-induced doping of PANI was performed by a copolymer of vinylidene chloride and methyl acrylate (VCMAC) as photo acid generator. The resulting PANI-VCMAC system was characterized by elemental analysis, IR, ESR, XPS, SEM and room-temperature conductivity. The mechanism of photo-induced doping by using VCMAC copolymer is discussed.

EXPERIMENTAL

The emeraldine base powder was synthesized by a chemical method reported by MacDiarmid et al.^[4]. A thin film of the emeraldine base form of PANI was coated on the surface of a quartz substrate by evaporating the solution of the emeraldine base dissolved in NMP at 70–80°C as described in a previous article^[5]. The copolymer of vinylidene chloride and methyl acrylate (VCMAC) was used as photo acid generator^[6]. A thin layer of VCMAC copolymer was coated on the surface of the PANI films by evaporating the THF solution of copolymer dissolved at room temperature. Before irradiation, the color of PANI-VCMAC layer is blue, which is the characteristic color of the emeraldine base form of PANI. It turns into green after irradiation with ultraviolet light ($\lambda = 254 \text{ nm}$, $3400 \mu\text{W}/\text{cm}^2$). The sample structure of PANI-VCMAC system for photo induced doping is shown in Fig.1. The process of photo-induced doping for PANI-VCMAC system was monitored by a UV-3100 Spectrophotometer.

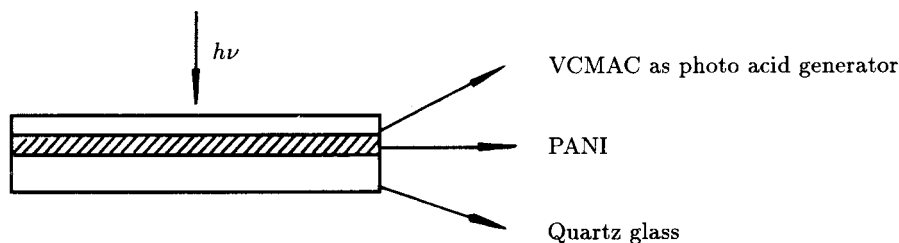


Fig.1 The structure of PANI-VCMAC system sample for photo-induced doping

RESULTS AND DISCUSSION

The variation of UV-Vis absorption of PANI-VCMAC system with the irradiation time is shown in Fig.2. Two peaks at 320 nm and 630 nm are observed before irradiation, which are the characteristic peaks of the emeraldine base form and they correspond to the $\pi-\pi^*$ transition and excitation of the segments of the quinoid rings on the polyemeraldine chain, respectively^[7]. It is noted that the intensity of the peak at 630 nm decreases with the increase of the irradiation time and then disappeared after irradiation. This suggests that the photo-induced doping for PANI-VCMAC system takes place on the segments of the quinoid rings of the polyemeraldine chain. This is consistent with the observations from PANI protonated by HCl^[8]. Moreover, a new peak at 950 nm is observed after irradiation, and its intensity increases with the increase of the irradiation time. This new peak results from polaron formed after protonation^[7]. This is proved by a strong ESR signal ($g = 2.0031$, $\Delta H = 10.48$ G). Therefore, the variation of absorption of PANI-VCMAC system with the irradiation time is similar to that of PANI with the protonation state^[7]. This suggests that PANI can be doped by VCMAC copolymer as photo acid generator under irradiation of ultraviolet light.

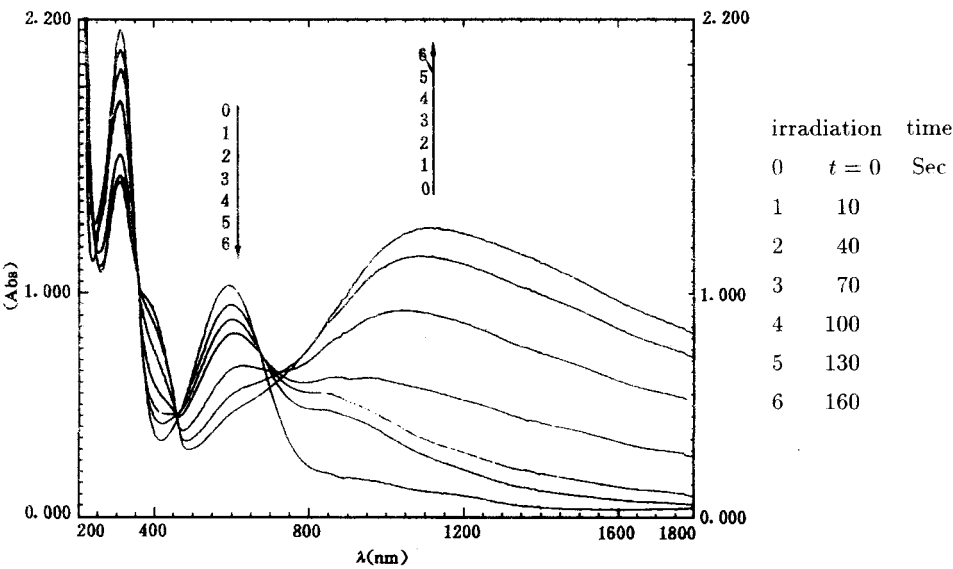


Fig.2 Dependence of the UV-Vis. absorption of PANI-VCMAC system on the irradiation time

In order to understand its photo-induced doping mechanism of VCMAC copolymer as photo acid generator, it is necessary to characterize the structure of PANI-

VCMAC system before and after irradiation. Firstly, it was found that the IR spectra of VCMAC copolymer after irradiation with 254 nm UV light are similar to that of the original VCMAC copolymer except for the appearance of a new peak at 609 cm^{-1} as shown in Fig.3. This peak is assigned to vibration mode of halogenated compounds, and it was noted that the intensity of this peak decreased significantly after irradiation at 254 nm. This indicates that VCMAC copolymer can release hydrochloride after irradiation. The resulting hydrochloride after irradiation can be considered as a resource of proton for doping PANI. Secondly, the content of Cl element in PANI-solution of the used VCMAC copolymer is 8.0%. It notes that the content of Cl element in PANI-VCMAC system after irradiation was estimated to be 8.0%. This indicates that the released hydrochloride from VCMAC copolymer after irradiation is completely used to dope PANI. According to the dependence of conductivity of PANI at room-temperature on the protonation state^[5], this content of Cl element corresponds to doping level at $\text{pH} = 3$ ($\text{Cl} \sim 7.8\%$). Thirdly, the binding energies of N_{1s} were measured to be 399.8 and 400.2 eV, and the latter is related to protonation, i.e. a polaron formed after irradiation. The binding energies of Cl_{2p} were measured to be 197.0 eV, which is assigned as Cl^- counter-ions after irradiation.

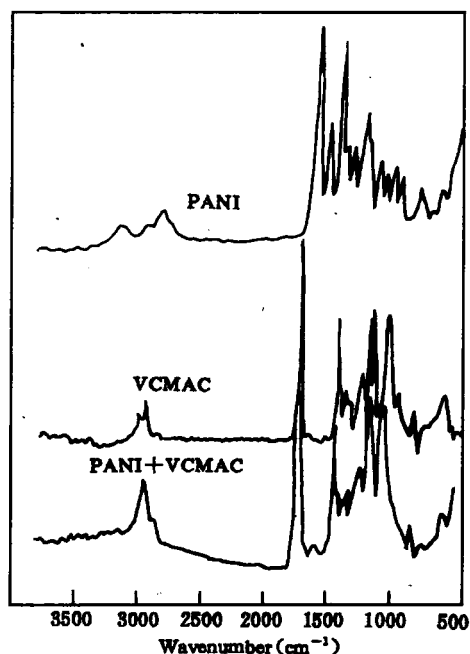


Fig.3 IR spectra of PANI-VCMAC system before and after irradiation at 254 nm

As discussed above, therefore, the photo-induced doping mechanism of the method

CONCLUSIONS

1. The emeraldine base form of PANI can be doped by a photo-induced doping method to the emeraldine salt form. In this method, the VCMAC copolymer was used as photo acid generator as it can release hydrochloride when irradiated with ultraviolet light ($\lambda = 254 \text{ nm}$).

2. The photo-induced doping characteristics, such as doping position and type of charge carriers are similar to the of PANI doped with HCl.

3. The poor room-temperature conductivity observed from PANI-VCMAC system after irradiation may be due to lower doping degree ($\sim \text{pH} = 3$) and difference in morphology from PANI doped with HCl.

Acknowledgements Authors thank Prof. Qiu Jiabai for valuable discussions.

Keywords:

Polyaniline; Photo-induced doping; Vinylidene chloride and methyl acrylate copolymer (VCMAC); Photo acid generator

REFERENCES

- [1] Angelopoulos, M.; Shaw, J.M.; Lee, K.L., et al. *Polym. Eng. Sci.*, **1992**, *32*: 1535.
- [2] Angelopoulos, M.; Patel, N. and Shaw, J.M., *NATO ASI ser*, **1993**, ser E246: 147.
- [3] Venugopal, G.; Quan, X.; Johnson, G.E., et al., *J. Am. Chem. Soc.*, **1995**, *7*: 271.
- [4] McDiarmid, A.G.; Chang, J.C.; Halpern, M., et al., *Mol. Cryst. Liq. Cryst.*, **1985**, *121*: 187..
- [5] Wan, M.X.; Cao, Y.; Li, J.C., et al., *Chinese J. Polym. Sci.*, **1991**, *9*: 308.
- [6] Qiu J.B.; Zhou, X.M.; Wang, Z.P., et al., *Mol. Cryst. Liq. Cryst.*, **1992**, *218*: 129.
- [7] Wan, M.X., *J. Polym. Sci. Part A*, **1992**, *30*: 543.
- [8] Wan, M.X. and Yang, J.P., *J. Appl. Polym. Sci.*, **1995**, *55*: 399.
- [9] Wan, M.X.; Zhao, W.X. and Li, Y.F., *Chinese J. Polym. Sci.*, **1991**, *9*: 308.