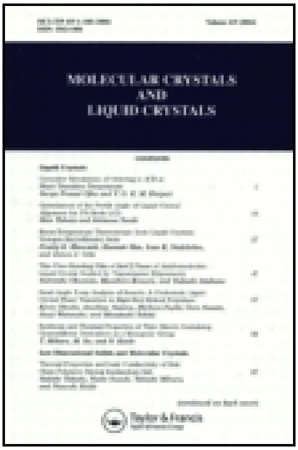
This article was downloaded by: [University of Haifa Library]
On: 16 August 2012, At: 12:30
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Near Infrared Studies of Polymer Blends

Jadwiga Laska [a] & Jacek Nizioł [b]

[a] University of Mining and Metallurgy, Dept. of Materials Science and Ceramics, ul. Mickiewicza 30, 30-059, Kraków, Poland

[b] University of Mining and Metallurgy, Dept. of Physics and Nuclear Techniques, ul. Mickiewicza 30, 30-059, Kraków, Poland

Version of record first published: 24 Sep 2006

To cite this article: Jadwiga Laska & Jacek Nizioł (2000): Near Infrared Studies of Polymer Blends, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 353:1, 561-566

To link to this article: http://dx.doi.org/10.1080/10587250008025689

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of Haifa Library] at 12:30 16 August 2012

Mol. Cryst. and Liq. Cryst., 2000, Vol. 353, pp. 561-566
Reprints available directly from the publisher
Photocopying permitted by license only

© 2000 OPA (Overseas Publishers Association) N.V.
Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Downloaded by [University of Haifa Library] at 12:30 16 August 2012

Near Infrared Studies of Polymer Blends

JADWIGA LASKA[a] and JACEK NIZIOŁ[b]

[a]*University of Mining and Metallurgy, Dept. of Materials Science and Ceramics, ul. Mickiewicza 30, 30–059 Kraków, Poland and* [b]*University of Mining and Metallurgy, Dept. of Physics and Nuclear Techniques, ul. Mickiewicza 30, 30–059 Kraków, Poland*

The dependence of absorption in the near-infrared region of cellulose acetate-polyaniline/camphorsulfonic acid blends on their conductivity and homogeneity has been studied. Thin films (10 to 100 μm) of the blends containing various amounts of protonated polyaniline show very high absorption in the NIR region. The absorption increases with increasing of conductivity and homogeneity of the sample.

Keywords: polyaniline; blends; conductivity; near-infrared spectroscopy

INTRODUCTION

Blends of polyaniline (PANI) with conventional polymers, like for example, polystyrene or poly(methyl methacrylate) have attracted attention of many research groups for several years[1-6]. They are interesting mainly because of their electrical properties, i.e. possibility of manufacturing homogenous fully organic material showing reasonably high conductivity. Therefore, they already have been applied as antistatic and anticorrosion coatings. In addition, they are very interesting for their potential optical applications, e.g., transparent electrodes[7,8], and infrared polarizers fabricated from uniaxially oriented blends[9].

It is known from UV-vis-NIR spectra[10-13] that acid doped polyaniline shows high absorbance in the near-infrared region. This phenomenon is considered to

Downloaded by [University of Haifa Library] at 12:30 16 August 2012

be characteristic of the presence of free charge carriers in the polymer, i.e., in the case of polyaniline – polarons. On the other hand, existence of polarons is crucial for conductivity of PANI. In this work we studied the correlation between absorbance and conductivity of polyaniline protonated with different organic acids and its blends. In case of the blends, the region around the percolation threshold was investigated where macroscopic homogeneity plays very important role for the existence of macroscopic conductivity.

In this article NIR absorption in blends of cellulose acetate (CA) and camphor sulfonic acid (CSA) doped polyaniline, and the dependence on their conductivity and homogeneity is described.

EXPERIMENTAL

Blends of PANI-CSA-cellulose acetate were prepared in the following way: Appropriate amounts of PANI and CSA with the molar ratio of 0.5 (0.5 mole of CSA per one phenylene-N repeat unit of PANI) were stirred together in m-cresol for several hrs. The obtained solution was mixed then with a solution of cellulose acetate in m-cresol. Freestanding films were cast onto the glass substrate and dried in air at 60°C for 48 hrs to remove the solvent.

Electrical conductivity was measured using standard four-probe method.

Near-infrared spectra were recorded on the Biorad FTS-6000 spectrometer. Samples of similar thickness (40±2 μm) were used to eliminate errors resulting from the dependence of the absorbance on the thickness. NIR spectra were recorded for two or three separate pieces of every film.

Microscopic studies were performed using an optical microscope (light transmission method). Samples of thickness of 500 nm were obtained by cutting parallel to the surface with microtome.

Downloaded by [University of Haifa Library] at 12:30 16 August 2012

RESULTS AND DISCUSSION

In the conducting (protonated) form, polyaniline shows two absorption peaks in UV-vis-NIR spectra, at 440 and 800 nm. Both of them were interpreted earlier as excitations to the polaron band[14]. The band at 800 nm in some cases continues to the far infrared and is known as a "free-carrier tail"[15]. This phenomenon is observed when polyaniline molecules have expanded-coil conformation. Protonated polyaniline is dark green, and the thickness of conducting films of either pristine polyaniline or its blends prepared by spin coating or solution casting is usually 10 – 100 μm. However, only very thin and optically transparent films can be studied by UV-vis-NIR spectroscopy. That is why the UV-vis-NIR method cannot be used to study, for instance, changes in PANI conformations during blending process. On the contrary, NIR spectroscopy allows for using of thicker samples, the same as for conductivity or microscopic investigations. Thus we correlated the conductivity, NIR absorption, and microscopic images of exactly the same films of cellulose acetate/PANI/CSA blends. Absorption in the near-infrared region reflects only the electronic structure of polyaniline. Pure cellulose acetate films are completely transparent in this region.

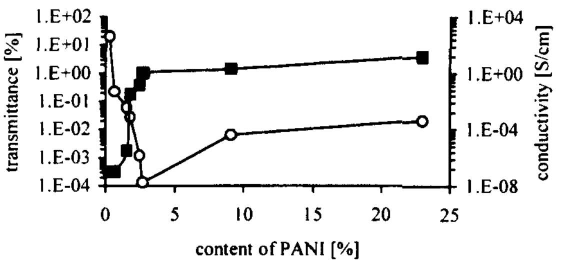


FIGURE 1 Transmittance at 1700 nm(○) and conductivity (■) of blends of polyaniline/CSA/cellulose acetate vs. content of polyaniline in the blend.

Downloaded by [University of Haifa Library] at 12:30 16 August 2012

Figure 1 shows the transmittance in the near-infrared region of samples of cellulose acetate blends containing polyaniline doped with CSA vs. content of PANI. In the same figure dependence of the conductivity of the samples on the content of PANI is plotted. The percolation threshold of the blends was determined as 1.5 wt% of polyaniline in the blend. As can be seen in the Figure 1 the transmission drops abruptly to several percent when the percolation threshold is reached. Then it stabilizes analogically to conductivity. From the diagram it is clear that the higher conductivity corresponds to lower transmittance. Both, conductivity and absorption of polyaniline, are the effects of the delocalization of the π-p electrons along the polymer chain, and creation of the polaron form. The longer delocalization length the bigger density of polaron states in the polaron band. The existence of the broad polaron band results in extending of NIR absorption band to low IR frequences.

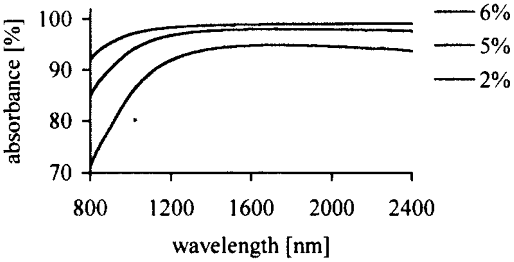


FIGURE 2 NIR spectra of PANI/CSA/CA blends with different PANI contents (spectra from the top: 6, 5 and 2 wt% of PANI, respectively).

In case of the PANI/ CSA/ CA blends high absorption in the whole NIR region is observed (see Figure 2) which suggests long distance delocalization and the expanded-coil conformation of polyaniline chains in the cellulose matrix[15].

Downloaded by [University of Haifa Library] at 12:30 16 August 2012

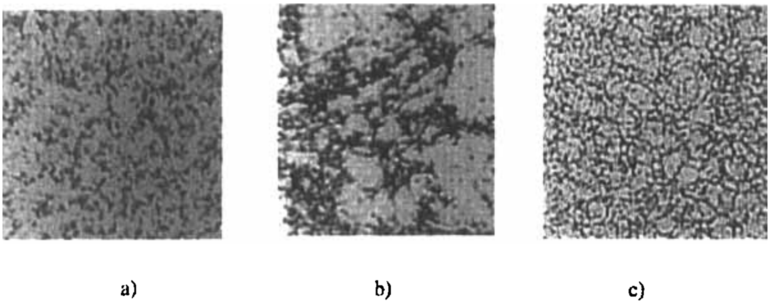


FIGURE 3 Microscopic images of cellulose acetate blends containing a) 1.5, b) 5 and c) 10 wt% of PANI

The homogeneity of samples also plays an important role in inducing high NIR absorption, especially in the region of the percolation threshold. Figure 3 shows microscopic images of three samples containing different amounts of polyaniline. The picture *a* shows structure of the blend very close to the percolation threshold. No conducting network of polyaniline is created (the black spots), although the distribution of the conducting phase is very even and the NIR absorption achieves value almost 100%. On the contrary, picture *b* shows the structure of the blend above the percolation threshold (5% of PANI) but with poor homogeneity. This sample shows conductivity of about 10^{-6} S/cm and very high transmittance of 80% in the NIR region. Only in blends containing more than 7% of polyaniline the continuos interpenetrating conducting network is created (see Figure 3c) and both conductivity and NIR absorption are high and similar for all samples.

Conclusions

Thin films (several micrometers) of cellulose acetate blends containing protonated polyaniline highly absorb near-infrared radiation. No transmission through the film above the percolation threshold is observed. In the samples below the percolation threshold it decreases with increasing of the content of conducting polyaniline. Additionally, near the percolation threshold, the homogeneity of the sample plays important role for both absorbance and conductivity.

Acknowledgements

This work was financially supported by the Polish Committee for Scientific Research (Grant No. 3 T09B 063 15).

References

[1] C. Y. Yang, M. Reghu, A. J. Heeger, Y. Cao, *Synth. Metals* **1996,** 79, 27.
[2] N. J. Pinto, C. M. Torres, P. K. Kahol, B. J. McCormick *J. Appl. Phys.* **1996,** 79(11), 8512.
[3] A. Wolter, E. Bańka, F. Genoud, A. Proń, M. Nechtschein, *Synth. Metals* **1997,** 84, 753.
[4] J. Laska, K. Żak. A. Proń, *Synth. Metals* **1997,** 84, 117.
[5] V. Jousseaume, M. Morsli, A. Bonnet, S. Lefrant, *Opt. Mat.* **1998,** 9, 484.
[6] V. Jousseaume, M. Morsli, A. Bonnet, O. Tesson, S. Lefrant, *J. Appl. Pol. Sci.* **1998,** 67, 1205.
[7] Y. Cao, G. M. Treacy, P. Smith, A. J. Heeger, *Appl. Phys. Lett.* **1992,** 60, 2711.
[8] Y. Yang, A. J. Heeger, *Nature* **1994,** 372, 344.
[9] Y. Cao, N. Colaneri, A. J. Heeger, P. Smith, *Appl. Phys. Lett.* **1994**, 65, 2001.
[10] A. P. Monkman, P. Adams, *Synth. Metals,* **1991,** 40, 87.
[11] M. Ohira, T. Sakai, M. Takeuchi, Y. Kobayashi, M. Tsuji, *Synth. Metals,* **1987,** 18, 347.
[12] M. Cochet, B. Corraze, S. Quillard, J. P. Buisson, S. Lefrant, G. Louarn, *Synth. Metals,* **1997,** 84, 757.
[13] M. Bartonek, N. S. Saricifci, H. Kuzmany, *Synth. Metals,* **1990,** 36, 83.
[14] S. Stafström, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang, A. G. MacDiarmid, *Phys. Rev. Lett.,* **1987,** 59(13), 1464.
[15] Y. Xia, J. M. Wiesinger, A. G. MacDiarmid, *Chem. Mater.* **1995,** 7, 443.

Downloaded by [University of Haifa Library] at 12:30 16 August 2012