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Formation of the Porous Polyaniline Structures

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The conductivity of polyaniline can be controlled depending on the doping mechanism. Porosity of polyaniline seems to be one of the important factors of solid state doping, and depends on several synthesis process parameters as well as subsequent refining steps. Results of studies on polyaniline refinement with common solvents: methanol, chloroform, DMF and THF are presented. The effect of solvent type used for extraction on the polyaniline porosity is discussed.

Keywords: doping; polyaniline; porosity; UV-Vis; WAXS

INTRODUCTION

Conducting polymers seems to be one of the very interesting groups of polymers during last two decades. Their interesting electric characteristics encourage scientist to further studies on other properties and applications [1]. Polyaniline seems to be the most attractive of conducting polymers so far, as it is widely analyzed and due to potential technological applications in several fields.

The chemical structure and conjugated bond system of polyaniline are necessary but insufficient to obtain conductive structures. So-called doping with acid is necessary in order to make polyaniline conductive.

Doping with molecules of complex organic acids like sulfonic acids and phosphoric acid esters, is leading to interesting properties of polyaniline, including solubility and thermal processing [2–4].

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The conductivity of polymer can be controlled depending on the doping mechanism. There are three principal types of polyaniline doping, among them "*in-situ*" doping during polymerization, post-doping in organic solvent and the third one, post-doping in the solid state. The two first methods have been widely analyzed, and the third one is still explored.

Post doping in the solid state can be carried on at room or elevated temperatures. The limited diffusion of doping agent into polyaniline' structure is one of the main difficulties in case of solid state doping, which is not enhanced even at elevated temperatures. So that effectiveness of solid state doping is also limited. The diffusion ability of doping agent in the solid state doping is not only dependent on the doping agent type and structure, but also on the accessibility of the polyaniline structure.

The effect of doping in solid state can be improved by mechanical mixing; however the mechano-chemical degradation occurs. The time of mixing should be shortened especially when the process is carried on at elevated temperatures. It seems that that effect of doping can be improved by increasing of polyaniline porosity, increasing surface area and control of pore sizes, leading to improvement of accessibility of the polyaniline structure for doping agents.

The article presents results of studies on application of several solvents for purification of as-synthesized polyaniline. There are observed changes in porosity, supermolecular structure, and spectroscopic properties of purified polyaniline.

MATERIALS

Polyaniline was synthesized at -40°C according to [5], ASP was used as the oxidant. Ammonia was used for deprotonation of polyaniline, and methanol, dimethylformamide, tetrahydrofuran, and chloroform (all pure p.a. grade from POCH Gliwice) as solvents in the process of polyaniline purification.

PURIFICATION OF POLYANILINE

As-synthesized polyaniline was at first rinsed with distilled water in order to remove post-synthesis contamination, and then deprotonated by rinsing with ammonia. The emergent ammonium chloride was then removed by subsequent rinsing with distilled water. The obtained polyaniline was then divided into samples subjected individually to extraction with organic solvents. Pure grade methanol, chloroform, dimethylformamide (DMF) and tetrahydrofuran (THF) were used as

solvents for extraction. The process was carried on in the modified Soxhlet extractor. The modification was done in order to avoid of the contact of warm solvent with the purified polyaniline sample. The process was carried on until the solvent remained colorless.

METHODS

Porosity was analyzed using multifunctional ASAP 2010 System by Micrometrics. The surface area was calculated from Brunauer-Emmet-Teller equation. The crystalline structure was analysed by Wide Angle X-Ray Scattering method, using Seifert URD-6 diffractometer, equipped with a scintillation counter. Ni-filtered CuK_α radiation was used. UV-Vis measurements were carried on Perkin-Elmer Lambda 35 system equipped with integrating sphere in the range of 190–1100 nm.

RESULTS AND DISCUSSION

Porosity measurements indicates that sizes of pores in polyaniline range from dozen to approx. 300 nm. In dependence on the solvent used for extraction process, the variation of pores sizes and surface area occurs (Figs. 1 and 2).

The group of pores of sizes up to 100 nm represents almost 80% of total pores' area and volume. They are formed mainly during the ammonia treatment. It may be the effect of polyaniline hydrolysis by ammonia, as the number of such pores in raw polyaniline before ammonia treatment is much lower.

The comparison of total area of pores and volume of pores indicates similar correlation (Figs. 3 and 4). The pore surface area and volume of untreated, raw polyaniline is relatively low. Rinsing with ammonia is leading to increasing of both pores' surface area and pores' volume. Simultaneously it can be stated that extraction with methanol and chloroform does not influence pores surface area and volume while extraction with THF is leading to insignificant decrease of those values. However the most pronounced decrease of both pores surface area and volume is observed in case of extraction with DMF.

There are also observed variations between UV-Vis reflectance spectra of differently extracted polyaniline samples (Fig. 5). The bathochromic shift of the polyaniline characteristic exciton peak at $\lambda_{\text{max}} = 500 \text{ nm}$ is observed, as the effect of polymer chain elongation [6]. So that one can conclude that as the effect of extraction with

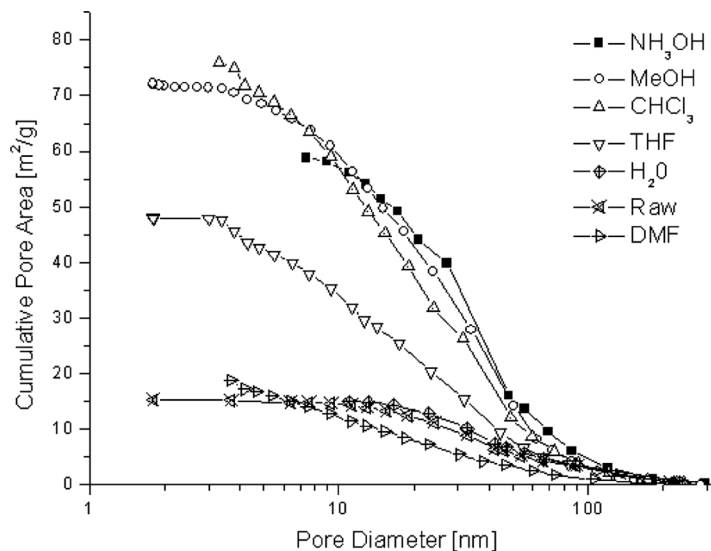


FIGURE 1 Pores diameters versus total pore surface area of polyaniline purified with various solvents.

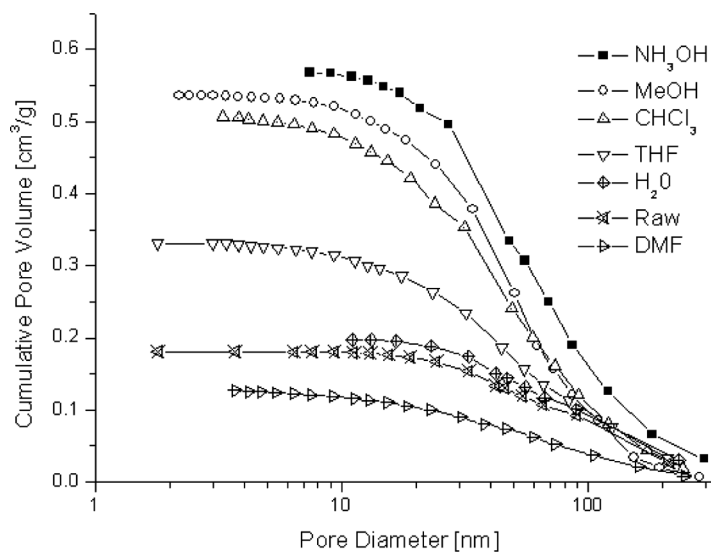


FIGURE 2 Pores diameters versus cumulative pores volume of polyaniline purified with various solvents.

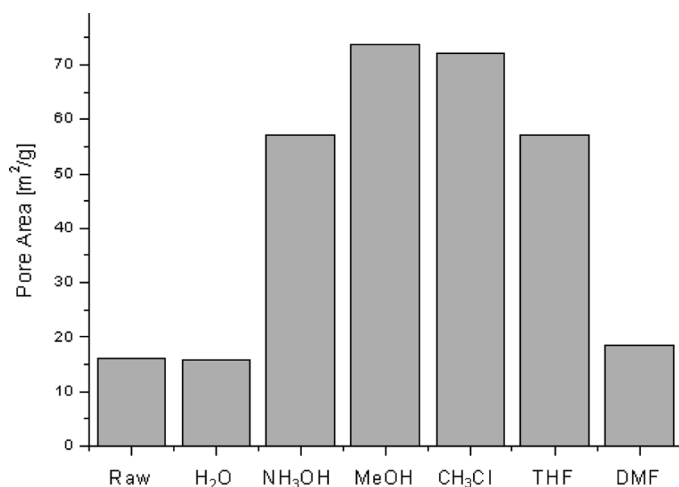


FIGURE 3 Pores surface area of polyaniline purified with different solvents.

above-mentioned solvents, the low molecular fraction of polymer is removed and as the consequence there are observed effects typical for higher average molecular weight polymer.

X-ray diffraction patterns of extracted polyanilines are presented in Figure 6, indicating the different structures obtained as the result of extraction with above-mentioned solvents. The ammonia treatment

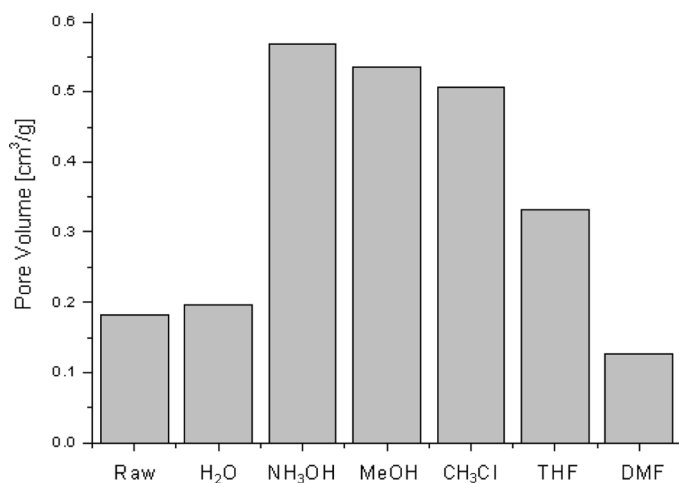


FIGURE 4 Pores volume of polyaniline purified with different solvents.

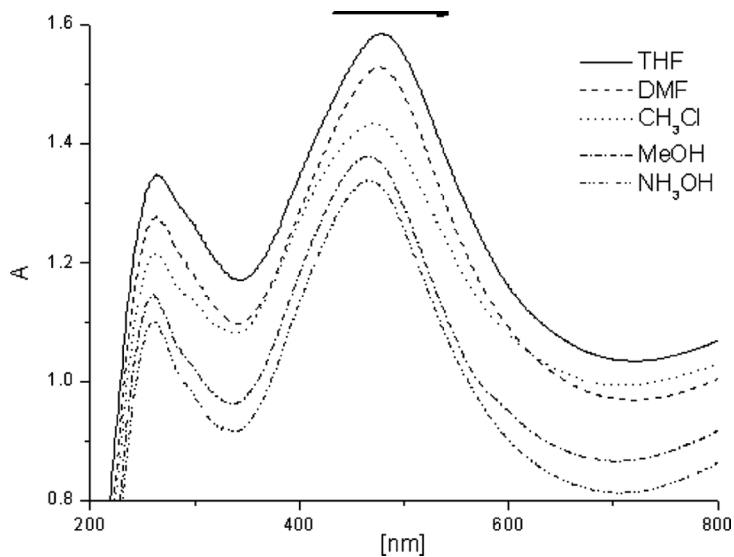


FIGURE 5 UV-Vis spectra of polyaniline purified with different solvents.

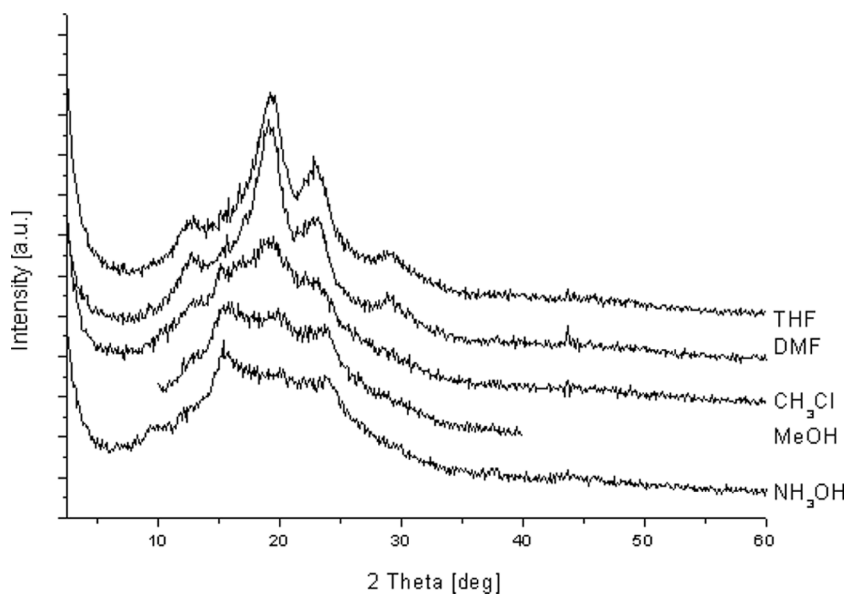


FIGURE 6 WAXS diffraction patterns of polyaniline purified with different solvents.

is leading to reported EB-1 form [7]. Both methanol and chloroform does not change the crystalline structure of polyaniline, while extraction with DMF and THF is leading to EB-2 form.

SUMMARY

Presented results indicate the importance of solvent used for extraction, which influence porosity of polyaniline. Extraction of polyaniline with both methanol and chloroform does not increase the pores' surface area, while after extraction with DMF the porosity changes dramatically. It may be explained by structural alignment observed from WAXS but also by increasing of average molecular mass, observed indirectly from UV-VIS. Presented results indicate the importance of solvent selection for post-reaction purification of polyaniline, which may be decisive in further processing, especially doping in solid-state.

REFERENCES

- [1] Pud, A., Ogurtsov, N., Korzenko, A., & Shapoval, G. (2003). *Prog. Polym. Sci.*, 28, 1701.
- [2] MacDiarmid, A. G. & Epstein, A. J. (1995). *Synth. Met.*, 69, 85.
- [3] Xia, Y., Wiesinger, J. M., & MacDiarmid, A. G. (1995). *Chem. Mater.*, 7, 443.
- [4] Laska, J., Trzandel, M., & Proń, A. (1993). *Materials Science Forum*, 122, 177.
- [5] Beadle, P. M., Nicolau, Y. F., Banka, E., & Djurado, D. (1998). *Synth. Met.*, 95, 29.
- [6] Zheng, W., Min, Y., MacDiarmid, A. G., Angelopoulos, M., Liao, Y-H., & Epstein, A.J. (1997). *Synth. Met.*, 84, 63.
- [7] Pouget, J. P., Józefowicz, M. E., Epstein, A. J., Tang, X., & MacDiarmid, A. G. (1991). *Macromolecules*, 24, 779.