A study of the antibacterial efficiency and coloration of dyed polyamide and polyester fabrics modified with colloidal Ag nanoparticles

VESNA ILIĆ[1], ZORAN ŠAPONJIĆ[2], VESNA VODNIK[2], DARKA MIHAILOVIĆ[1], PETAR JOVANČIĆ[1], JOVAN NEDELJKOVIĆ[2#] and MAJA RADETIĆ[1]*

[1]Textile Engineering Department, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade and [2]Vinča Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade, Serbia

Abstract: In this study, the influence of dyeing on the antibacterial efficiency of polyamide and polyester fabrics loaded with colloidal Ag nanoparticles and the influence of the presence of Ag nanoparticles on the color change of dyed fabrics were investigated. Dyes C.I. acid green 25 and C.I. disperse blue 3 were used for dyeing of polyamide fabrics, while dye C.I. disperse violet 8 was used for dyeing of polyester fabrics. The influence of Ag nanoparticles on the color change of polyamide fabrics depends on the dye type, but generally it was lower compared to polyester fabrics. Polyester fabrics exhibited excellent antibacterial efficiency against Gram-positive bacterium *Staphylococcus aureus* and Gram-negative bacterium *Escherichia coli*, independent of the order of dyeing and Ag loading. Polyamide fabrics provided a desirable level of antibacterial activity only if the Ag loading was performed after dyeing.

Keywords: Ag nanoparticles; polyester; polyamide; antibacterial efficiency; color change.

INTRODUCTION

The traditional approach to textile materials from only an aesthetic and comfort point of view must be considered as the past. Currently, in addition to conventional end-use properties, textile products must exhibit some advanced properties, such as UV protection, self-cleaning, antimicrobial and/or anti-electrostatic properties.[1–3] These effects can be achieved using new technologies that can provide targeted functionalization and long-term durability, as well as environmental and economical feasibility. Developments in the synthesis of dif-

---

ferent metal and metal oxide nanoparticles (NPs) and the wide range of their successful applications opened up new perspectives for the engineering of desired properties of textile materials. The greatest interests are oriented towards the imparting of antimicrobial effects.[4–15] Ag NPs seem to be particularly convenient for the improvement of antimicrobial properties of textile materials since bacteria do not become resistant to Ag as in the case of antibiotics.[4] The high stability and large surface to bulk ratio of Ag NPs provide an excellent antibacterial efficiency.

Although much work has been done on the antimicrobial activity of Ag NPs on different textile materials,[4–15] there are only few data on the synergism between loading of Ag NPs and dyeing or printing.[6,16] This aspect is of great importance from the technological point of view since textile products should preserve all the usual aesthetic and comfort standards. Therefore, the influence of dyeing on the antibacterial efficiency of polyamide (PA) and polyester (PES) fabrics loaded with Ag NPs, as well as the influence of Ag NPs on the color change of dyed fabrics were the focus of this study. Dyes C.I. acid green 25 and C.I. disperse blue 3 were used for dyeing of PA fabrics, while dye C.I. disperse violet 8 was used for dyeing of PES fabrics. The antibacterial efficiency was tested against Gram-positive bacterium *Staphylococcus aureus* and Gram-negative bacterium *Escherichia coli*.

EXPERIMENTAL

Desized and bleached PA (150 g/m^2) and PES (165 g/m^2) fabrics were cleaned in a bath containing 0.50 % nonionic washing agent Felosan RG-N (Bezema) at a liquor-to-fabric ratio of 50:1.[17] After 15 min of washing at 50 °C, the fabrics were rinsed once with warm water (50 °C) for 3 min and three times (3 min) with cold water. The samples were dried at room temperature.

The PA fabrics were dyed with acid dye C.I. acid green 25 (Ortolgreen B, BASF) and disperse dye C.I. disperse blue 3 (Colliton Blue FFR, BASF), whereas the disperse dye C.I. disperse violet 8 (Palanil Violet 3B, BASF) was used for dyeing of PES fabrics.

AgNO$_3$ (Kemika) and NaBH$_4$ (Fluka) of *p.a.* grade were used without any further purifycation for the synthesis of the colloidal Ag NPs.[18,19] Briefly, 8.5 mg of AgNO$_3$ was dissolved in 250 mL of water and purged with argon for 30 min. Under vigorous stirring, the reducing agent NaBH$_4$ (125 mg) was added to the solution and left for 1 h under an argon atmosphere. The concentration of the Ag colloid was 50 ppm.

One gram of fabric was immersed in 65 mL of Ag colloid for 5 min and dried at room temperature. After 5 min of curing at 100 °C, the procedure was repeated. Subsequently, the samples were rinsed twice (5 min) with deionized water and dried at room temperature.

A schematic presentation of the dyeing procedures for PA and PES fabrics is presented in Fig. 1. The PA fabrics were dyed in a bath containing 2.0 % (o.w.f.) acid dye and 4.0 % (o.w.f.) Na$_2$SO$_4$ at a liquor-to-fabric ratio of 60:1 and at pH 4.0. The dyeing of the PA fabrics with disperse dye was performed in a bath containing 2.0 % (o.w.f.) dye at a liquor-to-fabric ratio of 60:1 and at pH 5.0. The pH values were adjusted with CH$_3$COOH (30 %). The PES fabrics were dyed in a bath containing 1.0 % (o.w.f.) disperse dye, 1 g/L CHT dispergator (Bezema) and 0.50 mL/L CH$_3$COOH (30 %) at a liquor-to-fabric ratio of 25:1 and at pH 5.0. The fabrics were then washed in a bath containing 0.50 % Felosan RG-N (Bezema) at a liquor-to-

-fabric ratio of 40:1. After 30 min of washing at 40 °C, the fabrics were rinsed once with warm water (40 °C) for 3 min and four times (3 min) with cold water. Afterwards, the fabrics were dried at room temperature.
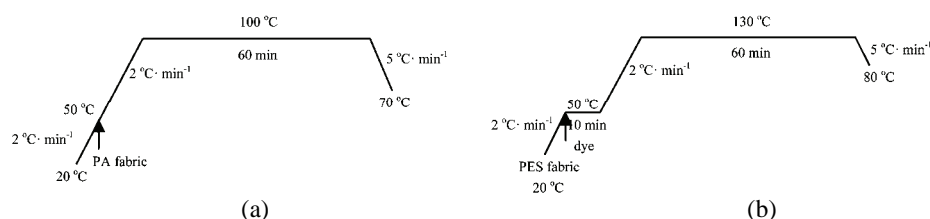

Fig. 1. Dyeing procedures for PA (a) and PES (b) fabrics.

The shape and size of silver NPs were determined using a Philips EM-440 transmission electron microscope (TEM) operating at 100 kV. Samples for the TEM measurements were prepared by placing a drop of Ag colloid onto a holey carbon-coated standard copper grid (400 mesh) and evaporating the solvent.

The UV/Vis absorption spectra of the silver colloid were recorded using a Thermo Evolution 600 spectrophotometer.

The fiber morphology was observed using a JEOL JSM 6460 LV scanning electron microscope (SEM). Prior to analysis, the samples were coated with a thin layer of gold.

The elemental analysis of the PES and PA fabrics loaded with silver NPs was realized using a Perkin Elmer 403 atomic absorption spectrometer (AAS).

The color coordinates of the dyed fabrics (CIE $L*$, $a*$, $b*$) were determined with Datacolor SF300 spectrophotometer under illuminant D_{65} using the 10° standard observer. On the basis of the measured CIE color coordinates, the color difference ($\Delta E*$) was determined as:

$$\Delta E* = \sqrt{(\Delta a*)^2 + (\Delta b*)^2 + (\Delta L*)^2} \qquad (1)$$

where: $\Delta L*$ is the color lightness difference between the treated (dyed fabric loaded with Ag NPs) and the control (dyed untreated fabric without Ag) samples; $\Delta a*$ is the red/green difference between the treated and control samples and $\Delta b*$ is the yellow/blue difference between the treated and control samples.

The influence of dyeing on the antibacterial efficiency of fabrics was quantitatively assessed using a Gram-positive bacterium *Staphylococcus aureus* ATCC 25923 and a Gram--negative bacterium *Escherichia coli* ATCC 25922. Sterile potassium hydrogen phosphate buffer solution of pH 7.2 (70 mL) was inoculated with 0.7 mL of a bacterial inoculum. One gram of sterile fabric cut into small pieces was put into the flask and shaken for 1 h. 1.0 mL aliquots from the flask were diluted with phosphate buffer and 0.10 mL of the solution was placed onto a tryptone soy agar (Torlak, Serbia). After 24 h of incubation at 37 °C, zero time and one hour counts of viable bacteria were made. The percentage bacteria reduction (R / %) was calculated using Eq. (2):

$$R = 100 \frac{C_0 - C}{C_0} \qquad (2)$$

where: C_0 (CFU – colony forming units) is the number of bacteria colonies on the control fabric (fabric without Ag, dyed in the described manner), and C (CFU) is the number of bacteria colonies on the dyed fabric loaded with Ag NPs.

RESULTS AND DISCUSSION

The absorption spectrum of the colloidal Ag NPs showed the presence of a strong surface plasmon resonance band with a maximum at 380 nm (Fig. 2). The position of the symmetric plasmon resonance band and its half-width (46 nm) indicated a narrow size distribution of Ag NPs without undesired aggregation. Based on the TEM analysis of the colloidal Ag NPs, the average diameter of the nearly spherical Ag NPs was found to be 10 nm (inset in Fig. 2).
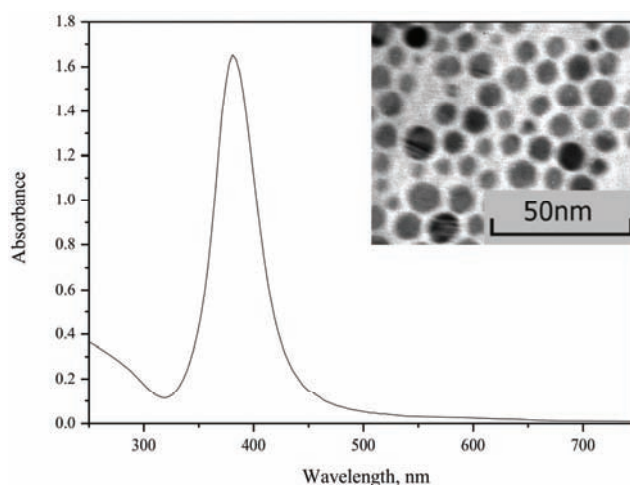

Fig. 2. Absorption spectrum of Ag NPs in aqueous solution; inset: TEM image of the Ag NPs.

The surface morphology of the PA and PES fibers loaded with Ag NPs was examined by SEM. The SEM images of the Ag loaded PA and PES fibers are shown in Fig. 3. It can be noticed that almost spherical aggregates of Ag NPs with diameters less than 100 nm are unevenly distributed over the surface of both fibers.
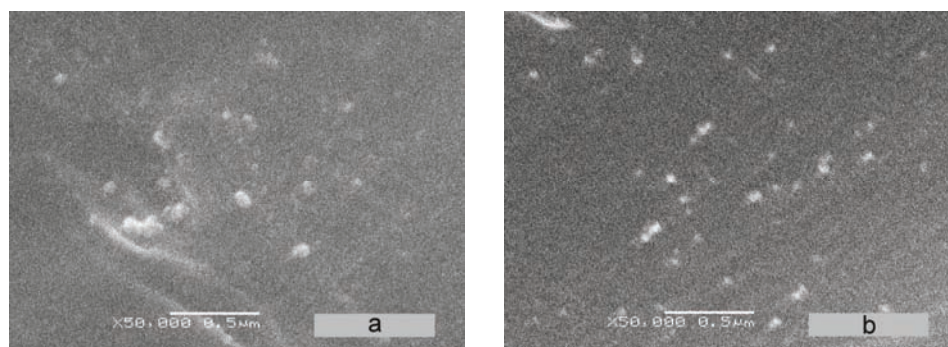

Fig. 3. SEM images of Ag-loaded PA (a) and PES (b) fibers.

To quantify the Ag on the fabrics after loading the colloidal NPs, elemental analysis using atomic absorption spectrometry was performed. It was found that

one gram of PA and PES fabrics contained 1.79 and 21.12 μg of Ag, respectively. Evidently, the amount of Ag on PES fabrics was more than ten times higher. The higher content of Ag NPs on the PES fibers indicates their stronger binding, most likely due to the existence of benzene rings in polymer structure. It is well known from surface-enhanced Raman spectroscopy (SERS) studies of benzoic acid and its derivates on Ag NPs that there are strong interactions between the Ag surface and benzene rings.[20,21]

These results are in good correlation with the color changes of the fabrics, which were evaluated by measuring the UV/Vis reflectance spectra (Fig. 4). Loading of Ag NPs caused color changes of the PA and PES fabrics. Due to loading of Ag NPs, an overall decrease in the reflectance was observed for both samples, demonstrating a color change of the PA and PES fabrics from white to yellowish. The observed color changes are in accordance with literature data.[8] The more pronounced color change of the PES fabric could be anticipated because of the higher amount of Ag NPs detected by AAS. The color difference between fabrics loaded with Ag NPs and control fabrics (untreated fabrics) was expressed *via* the ΔE^*, ΔL^*, Δa^* and Δb^* values (also presented in Fig. 4).
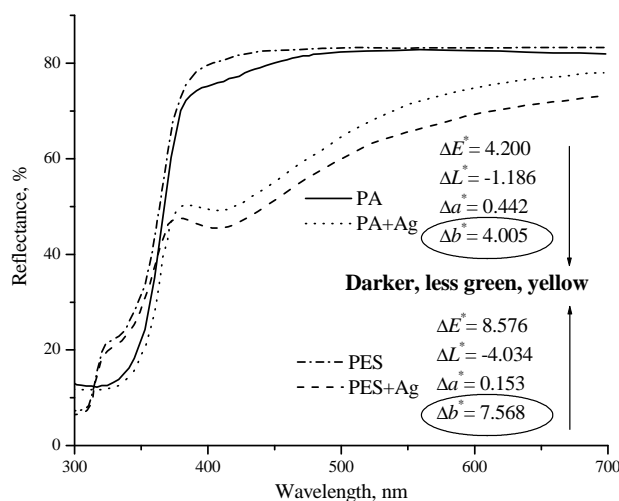

Fig. 4. Reflectance curves of the control (untreated fabrics)
and silver-loaded PA and PES fabrics.

Bearing in mind that the fiber surface is responsible for many important properties of textile materials (wettability, dyeability, printability, *etc.*), it can be expected that modification of PA and PES fibers with Ag NPs might affect their dyeability. In order to establish the influence of the Ag NPs presence on the color of dyed PA and PES fabrics, colorimetric determination based on the CIELAB color system was performed. The colorimetric data for the fabrics loaded with Ag NPs before and after dyeing are given in Table I.

The obtained results indicate that the color of PA fabrics dyed with AG25 was almost unaffected by Ag loading, regardless of the order of Ag loading and dyeing. The obtained color changes could not be visually detected since the values of the color difference (ΔE^*) were less than one. However, the influence of the Ag NPs was more pronounced after dyeing of PA fabrics with DB3. The loading of Ag NPs onto the PA fabrics before and particularly after dyeing brought about considerable color changes. The fabrics became darker (ΔL^*), less red (Δa^*) and less blue (Δb^*). A similar trend was observed in the case of PES fabrics dyed with DV8, although the color difference (ΔE^*) was several times greater, demonstrating a significant color change. The increased greenness and decreased blueness are attributed to the presence of the Ag NPs on the fabrics.

TABLE I. Colorimetric data for PA and PES fabrics loaded with Ag NPs before and after dyeing

Dye	Sample	L^*	a^*	b^*	ΔE^*	Description
AG25	Control PA[a]	30.16	–25.40	–4.72		
	Silver loading before dyeing					
	PA+Ag	29.92	–25.46	–4.75	0.251	Darker
	Silver loading after dyeing					
	PA+Ag	29.80	–24.82	–4.23	0.833	Darker, less green, less blue
DB3	Control PA[a]	34.80	6.15	–44.78		
	Silver loading before dyeing					
	PA+Ag	33.23	6.83	–43.87	1.934	Darker, less red, less blue
	Silver loading after dyeing					
	PA+Ag	34.47	4.28	–41.69	3.629	Darker, less red, less blue
DV8	Control PES[a]	43.38	14.55	–39.52		
	Silver loading before dyeing					
	PES+Ag	43.37	11.94	–35.31	4.962	Less red, less blue
	Silver loading after dyeing					
	PES+Ag	42.19	9.75	–30.95	9.901	Darker, less red, less blue

[a]Dyed fabric without Ag NPs

Despite the low content of Ag on the PES and, particularly, the PA fabrics, these amounts were sufficient to impart a desirable level of antibacterial activity. The influence of the order of dyeing and loading of Ag NPs on the antibacterial activity of the PA and PES fabrics was evaluated for the Gram-positive bacterium *Staphylococcus aureus* and the Gram-negative bacterium *Escherichia coli*. The values of bacterial reduction by the PA and PES fabrics which had been Ag-loaded before and after dyeing are given in Tables II and III.

The PES fabrics showed outstanding antibacterial efficiency for both bacteria regardless of the order of the operations. Similarly, the PA fabrics exhibited excellent antibacterial efficiency when the loading of the Ag NPs was performed after dyeing, regardless of the dye studied. However, the opposite order of operations led to a significant decrease in bacterial reduction of *E. coli* on the PA fab-

rics. These PA fabrics can be considered as inactive. Evidently, to obtain the maximum antibacterial efficiency, the order of the operations must be carefully planned. Hence, it is recommended that the loading of Ag NPs onto PA fabrics should be performed after dyeing, while Ag loading of PES fabrics after dyeing should be avoided due to the strong color change of the fabrics.

TABLE II. Antibacterial efficiency of PA and PES fabrics loaded with Ag NPs before dyeing

Dye	Sample	Initial number of bacterial colonies ($\times 10^{-5}$)	Number of bacterial colonies on the fabric after 24 h	R / %
		S. aureus		
AG25	Control PA[a]	2.4	2.4×10^5	
	PA+Ag		5.2×10^3	97.8
DB3	Control PA[a]	2.4	1.3×10^5	
	PA+Ag		<10	99.9
DV8	Control PES[a]	3.0	2.5×10^4	
	PES+Ag		<10	99.9
		E. coli		
AG25	Control PA[a]	5.2	2.7×10^5	
	PA+Ag		1.8×10^5	33.3
DB3	Control PA[a]	5.2	1.7×10^5	
	PA+Ag		1.2×10^5	29.4
DV8	Control PES[a]	3.0	8.5×10^4	
	PES+Ag		<10	99.9

[a]Dyed fabric without Ag NPs

TABLE III. Antibacterial efficiency of PA and PES fabrics loaded with Ag NPs after dyeing

Dye	Sample	Initial number of bacterial colonies ($\times 10^{-5}$)	Number of bacterial colonies on the fabric after 24 h	R / %
		S. aureus		
AG25	Control PA[a]	2.4	2.4×10^5	
	PA+Ag		<10	99.9
DB3	Control PA[a]	2.4	1.3×10^5	
	PA+Ag		<10	99.9
DV8	Control PES[a]	3.0	2.5×10^4	
	PES+Ag		<10	99.9
		E. coli		
AG25	Control PA[a]	3.9	2.2×10^5	
	PA+Ag		<10	99.9
DB3	Control PA[a]	3.9	1.3×10^5	
	PA+Ag		130	99.9
DV8	Control PES[a]	3.0	8.5×10^4	
	PES+Ag		<10	99.9

[a]Dyed fabric without Ag NPs

CONCLUSIONS

The order of loading of Ag NPs and dyeing has a strong influence on the color change of PA and PES fabrics. It was shown that the color of the PA fabrics dyed with C.I. acid green 25 was slightly affected by Ag loading, regardless of the order of the operations. On the contrary, the loading of Ag NPs onto fabrics before and particularly after dyeing with C.I. disperse blue 3 induced considerable color changes. Moreover, the color changes became even more prominent on the PES fabrics which were Ag loaded after dyeing with C.I. disperse violet 8. The obtained color changes are suggested to be due to the presence of Ag NPs on the fabrics.

The antibacterial efficiency of the PES fabrics for *S. aureus* and *E. coli* is independent of the order of dyeing and loading of Ag NPs. In order to achieve desired level of antibacterial efficiency of PA fabrics, the loading of the Ag NPs after dyeing is recommended.

И З В О Д

ПРОУЧАВАЊЕ АНТИБАКТЕРИЈСКЕ ЕФИКАСНОСТИ И ПРОМЕНЕ ОБОЈЕЊА ПОЛИАМИДНИХ И ПОЛИЕСТАРСКИХ ТКАНИНА МОДИФИКОВАНИХ КОЛОИДНИМ НАНОЧЕСТИЦАМА СРЕБРА

ВЕСНА ИЛИЋ[1], ЗОРАН ШАПОЊИЋ[2], ВЕСНА ВОДНИК[2], ДАРКА МИХАИЛОВИЋ[1], ПЕТАР ЈОВАНЧИЋ[1], ЈОВАН НЕДЕЉКОВИЋ[2] и МАЈА РАДЕТИЋ[1]

[1]*Катедра за текстилно инжењерство, Технолошко−металуршки факултет, Карнеѓијева 4, 11120 Беоѓрад и* [2]*Институт за нуклеарне науке "Винча", п.пр. 522, 11001 Беоѓрад*

Циљ овог рада је да се утврди утицај бојења на антибактеријску ефикасност полиамидних и полиестарских тканина модификованих колоидним наночестицама сребра као и утицај присуства сребра на промену обојења бојених тканина. Боје C.I. acid green 25 и C.I. disperse blue 3 су коришћене за бојење полиамидних тканина, а боја C.I. disperse violet 8 за полиестарске тканине. Промена обојења полиамидних тканина зависи од типа боје, али је генерално мања у поређењу са полиестарским тканинама. Антибактеријска ефикасност тканина модификованих сребром је тестирана на Грам-позитивне бактерије *Staphylococcus aureus* и Грам-негативне бактерије *Escherichia coli*. Полиестарске тканине показују одличну антибактеријску ефикасност независно од редоследа бојења и наношења сребра. Да би полиамидна тканина обезбедила жељени ниво антибактеријске активности, неопходно је нанети сребро после бојења. Морфологија влакана модификованих нанчестицама сребра утврђена је СЕМ анализом, док је за елементарну анализу коришћена атомска апсорпциона спектрометрија.

(Примљено3. септембра, ревидирано 11. новембра 2008)

REFERENCES

1. T. Wakida, S. Tokino, *Indian J. Fibre Text. Res.* **21** (1996) 69

2. M. Ueda, S. Tokino, *Rev. Prog. Coloration* **26** (1996) 9
3. Y. W. H. Wong, C. W. M. Yuen, M. Y. S. Leung, S. K. A. Ku, L. I. Lam, *AUTEX Res. J.* **6** (2006) 1
4. D. Pohle, C. Damm, J. Neuhof, A. Rösch, H. Münsted, *Polym. Polym. Compos.* **15** (2007) 357
5. N. Vigneshwaran, A. A. Kathe, P. V. Varadarajan, R. P. Nachane, R. H. Balasubramanya, *J. Nanosci. Nanotechnol.* **7** (2007) 1893
6. H. J. Lee, S. Y. Yeo, S. H. Jeong, *J. Mater. Sci.* **38** (2003) 2199
7. S. Y. Yeo, H. J. Lee, S. H. Jeong, *J. Mater. Sci.* **38** (2003) 2143
8. T. Yuranova, A. G. Rincon, A. Bozzi, S. Parra, C. Pulgarin, P. Albers, J. Kiwi, *J. Photochem. Photobiol. A* **161** (2003) 27
9. U. C. Hipler, P. Elsner, J. W. Fluhr, *J. Biomed. Mater. Res. B* **77B** (2005) 156
10. S. H. Jeong, Y. H. Hwang, S. C. Yi, *J. Mater. Sci.* **40** (2005) 5413
11. H. J. Lee, S. H. Jeong, *Text. Res. J.* **75** (2005) 551
12. S. H. Jeong, S. Y. Yeo, S. C. Yi, *J. Mater. Sci.* **40** (2005) 5407
13. L. Hadad, N. Perkas, Y. Gofer, J. Calderon-Moreno, A. Ghule, A. Gedanken, *J. Appl. Polym. Sci.* **104** (2007) 1732
14. H. Y. Ki, J. H. Kim, S. C. Kwon, S. H. Jeong, *J. Mater. Sci.* **42** (2007) 8020
15. N. Duran, P. D. Marcato, G. I. H. De Souza, O. L. Alves, E. Esposito, *J. Biomed. Nanotechnol.* **3** (2007) 203
16. M. Gorensek, P. Recelj, *Text. Res. J.* **77** (2007) 138
17. M. Radetić, V. Ilić, V. Vodnik, S. Dimitrijević, P. Jovančić, Z. Šaponjić, J. Nedeljković, *Polym. Adv. Technol.* **19** (2008) 1816
18. V. V. Vuković, J. M. Nedeljković, *Langmuir* **9** (1993) 980
19. Z. V. Šaponjić, R. Csencsits, T. Rajh, N. Dimitrijević, *Chem. Mater.* **15** (2003) 4521
20. D. Wu, Y. Fang, *J. Colloid Interface Sci.* **265** (2003) 234
21. Y. Badr, M. A. Mahmoud, *J. Mol. Struct.* **749** (2005) 187.