

The influence of some factors on the electrical conductivity and particle size of core/shell polystyrene/polyaniline composites

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Abstract: The electrically conductive, micron-sized, core/shell polystyrene (PS)/polyaniline (PANI) composite particles were synthesized by chemical oxidative polymerization of aniline in the presence of micron-sized PS particles in 1 M HCl. The conditions of the dispersion polymerization of styrene were optimized. The influence of the initiator type employed for the chemical oxidative polymerization of aniline and the aniline (ANI) concentration on the PS/PANI particle size and size distribution and their conductivity was investigated. The obtained results show that the conductivity of the samples increased with increasing ANI concentration. The conductivity of the PS/PANI composite particles obtained with the highest ANI concentration was of the same order of magnitude as that for PANI powder. The particle size did not depend on the concentration of ANI, while the particle size distribution was narrower at higher concentrations of ANI.

Keywords: core/shell polystyrene/polyaniline composite, dispersion polymerization of styrene, chemical oxidative polymerization of aniline.

INTRODUCTION

Electroconducting polymers (ECPs) are still the subject of numerous investigations in spite of the fact that many of them suffer from a lack of environmental stability and poor processability. The main reason for such an interest in ECPs is the wide variety of their potential applications. For example, thin polymer films having controlled electrical conductivity can be used for photovoltaic cells, solar cells, photoconductors, batteries, optical devices, gas sensors, conducting paints for electromagnetic shielding and antistatic coatings.¹ Of all the ECP, polyaniline (PANI) is among the most useful. It has good thermal and oxidative stability and its conductivity is readily tuned by varying the pH value at which it is prepared. However, like most ECPs prepared to date, it is also intractable and only its emeraldine base is soluble in a limited range of very polar solvents.

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In order to improve the processability of PANI, efforts have been made to obtain soluble conducting polymers or composites which contain both PANI and non-conducting polymers. The preparation of an ECP as a colloidal dispersion is one of the approaches toward processability. This method is based on the chemical oxidative polymerization of aniline in the presence of water soluble polymers or tailor made copolymers.² Stable PANI colloidal dispersions were obtained by chemical synthesis of aniline in a solution of poly(vinyl methyl ether)³ or using poly(vinyl alcohol) as an efficient stabilizer.⁴ There are also some reports on the polymerization of aniline in the presence of polystyrene (PS) latexes,⁵ a poly(butadiene-co-styrene-co-2-vinylpyridine latex)¹ and some chlorinated copolymer latexes.⁶ The other, recently applied, approach consists in producing monodisperse, micron-sized electrically conductive PS/PANI composite particles by the chemical oxidative seeded dispersion polymerization of aniline in the presence of monodisperse micron-sized PS seed particles in aqueous HCl solution, where the pH value was kept at 2.5. The composite particle consisted of a PS core and a PANI shell.⁷

In the present work, electrically conductive micron-sized core/shell PS/PANI composite particles were synthesized by the chemical oxidative polymerization of aniline in the presence of micron-sized PS particles in 1 M HCl. The conditions of the dispersion polymerization of styrene were investigated, as was the influence of the initiator type employed for the chemical oxidative polymerization of aniline and the aniline concentration on the particle size and size distribution and conductivity of the obtained PS/PANI.

EXPERIMENTAL

Materials

Styrene was obtained from A.D. "Duga", aniline and potassium persulphate (KPS) from Fluka, poly(methacrylic acid) (PMA) and poly(acrylic acid) (PAA) from Aldrich, Merquat 550 (an aqueous solution of the highly charged cationic copolymer of 30 mole % diallyldimethylammonium chloride and 70 mol % acrylamide) from Merck, ammonium persulphate (APS) from Merck and *n*-butanol from Lachema. All chemicals were used as received except aniline, which was vacuum distilled.

Radical dispersion polymerization of styrene

The PS was prepared by radical dispersion polymerization of styrene using poly(acrylic acid), poly(methacrylic acid) or Merquat 550 as stabilizer. The stabilizer (1.85 g) was first dissolved in a mixture of ethanol (105.4 g) and water (30.8 g) by stirring with a magnetic stirrer for five hours at 60 °C. Styrene (15.4 g) and azobisisobutyronitrile (AIBN) initiator (0.26 g) were added to this solution. The polymerization reaction was carried out in a four-necked round-bottom flask under a nitrogen atmosphere using an anchor-type stirrer (60 rpm) at 70 °C for 10 h. Subsequently, the polymerization mixture was cooled to room temperature and 15 g of the mixture was taken and mixed with 500 cm³ of *n*-butanol and 100 cm³ of distilled water in order to remove the surplus stabilizer and non-reacted styrene. The mixture was stirred with a magnetic stirrer for 5 h at 60 °C. Two layers formed, the aqueous layer containing the dispersed PS particles being the lower one. The supernatant was decanted and a solution of Al₂(SO₄)₃ (1 g in 50 cm³ water) was added to the aqueous layer in order to coagulate the PS. The coagulated PS was then washed with 2 dm³ of distilled water after which the obtained PS particles were dried in a vacuum oven at 50 °C.

Polyaniline coating protocol

Polystyrene particles (0.5 g) were dispersed in distilled water (90 g) and the pH was adjusted to 2.5 with concentrated HCl or they were dispersed in 1.0 M HCl. The dispersion was stirred with the magnetic stirrer at 50 °C for 6 h. Then, the desired amount of aniline and the initiator (ammonium or potassium persulphate) were added and the obtained mixture was stirred with a magnetic stirrer for three hours at 0 °C. The non-reacted aniline and PANI oligomers were then extracted with *n*-butanol, which was added in surplus, by stirring the mixture with a magnetic stirrer for five hours at room temperature. After the stirring was stopped, two layers formed and the upper one, containing PANI oligomers, was discarded. The PS/PANI particles, which precipitated in the lower, aqueous layer, were filtered and washed with at least 2 dm³ of distilled water and then dried in a vacuum oven for 24 h at 50 °C.

The PANI molecules in the obtained composite material were doped by dispersing the PS/PANI particles in 1 M HCl solution and stirring the solution for 16 h. Subsequently, the particles were separated by filtration and dried in a vacuum oven at 50 °C to constant mass.

PANI synthesis

PANI "bulk powder" was obtained by chemical polymerization of aniline under the same conditions as employed for the PS/PANI composite except that no PS particles were present.

Measurement of conductivity

The electrical conductivity of the dried particles was determined on pressed pellets at room temperature using the conventional four-point-probe technique. A Valhalla scientific 4100 ATC digital ohmmeter was employed for the measurements.

Scanning electron microscopy

The particles were observed with a Jeol JSM 6460LV scanning electron microscope (SEM). The samples were sputter-coated with a palladium/gold alloy to minimize sample charging. The number average diameter (d_n) and the coefficient of variation (C_v) were determined by image analysis of the SEM photographs using Image pro plus, version 5.0 program. More than 1000 particles were analyzed for each sample.

Chemical composition

Elemental analyses (C, H and N) of PS, PS/PANI and PANI particles were performed at the Microanalysis Laboratory, Faculty of Chemistry, University of Belgrade, Serbia and Montenegro.

RESULTS AND DISCUSSION

PS synthesis

In order to synthesize PS/PANI composite material it is necessary to obtain PS in the form of monodispersed spherical particles having diameter between 0.5 and 10 μm . The simplest way to achieve this is to synthesize the PS by dispersion radical polymerization of styrene. For this kind of polymerization it is characteristic that monomer and initiator are dissolved in a mixture of a solvent and a polyelectrolyte. When the reaction mixture is heated to the desired temperature, the initiator decomposes and initiates the polymerization. If the polyelectrolyte were not in the reaction mixture, the obtained polymer would precipitate as a shapeless mass. The surface active polyelectrolyte plays a double role in the reaction mixture. On the one hand, it is adsorbed on the produced polymer particles making it easier for them to become spherical. On the other hand, the polyelectrolyte stops the growth of the particles when they reach a certain size and stabilizes the ob-

tained dispersion. The shape and the size of the obtained polymer depend very much on the properties and concentration of the polyelectrolyte.

Since during attempts to synthesize PS by radical dispersion polymerization under the conditions described in Ref. 7 there were problems with the dispersion stability and particle size and uniformity, trial experiments of the radical dispersion polymerization of styrene in an ethanol/water mixture using two anionic (PAA and PMA) and one cationic (Merquat 550) polyelectrolyte were performed. The results of these experiments showed that only with PAA as the polyelectrolyte were uniform spherical PS particles obtained. It was also experimentally shown that the PAA was successful as the polyelectrolyte only if it was first dissolved in the ethanol/water mixture and then added to the reaction mixture. The obtained PS dispersion was very stable and attempts were made to precipitate the PS particles by adding ether, ethanol or water to the reaction mixture. It was only possible to precipitate the PS with ether, but the precipitate was a shapeless mass. It was found that the PS particles could be successfully separated from the reaction mixture only by extraction of the excess PAA with *n*-butanol. The optimal conditions for this extraction and later precipitation of PS particles are those given in the Experimental.

Synthesis of PS/PANI composite

In order to obtain PS/PANI core/shell particles, the synthesized PS particles were dispersed in distilled water, the pH of which was adjusted with HCl to the desired value. The required amount of ANI and the initiator of the chemically initiated oxidation polymerization of ANI were added to this dispersion. The polymerization of ANI commences immediately after the addition of the initiator and the obtained PANI separates as a new phase when its degree of polymerization reaches the critical value, and precipitation occurs at the PS/reaction mixture interphase, *i.e.*, on the PS particles. It was found that it was much easier to separate the obtained composite material from the reaction mixture if the reaction mixture was first mixed with *n*-butanol, as was the case of PS polymerization. After addition to the reaction mixture, the *n*-butanol changes its color immediately, meaning that the residual ANI and PANI oligomers are extracted from the reaction mixture into the *n*-butanol.

A number of factors influences the amount of PANI coated on the PS particles and the conductivity of the core/shell PS/PANI composite, the most important being the reaction temperature, type of initiator (IN), ratio of ANI/IN and the ANI concentration. In this work, the mole ratio of ANI and initiator, $n(\text{ANI})/n(\text{IN})$, and the temperature were kept constant (1.2 and 0 °C, respectively) and the influence of the type of initiator and the concentration of ANI was investigated.

Influence of the type of initiator

The most common initiator used for the chemical polymerization of aniline is APS. However, it was shown⁸ that under certain conditions it is possible to obtain PANI with better conductivity when KPS is employed as the initiator. Bearing this in

mind, two samples of PS/PANI composite, PS/PANI-1 and PS/PANI-2, were synthesized in aqueous solution at pH 2.5 under the same conditions except that APS and KPS were used as the initiator for the former and latter, respectively. The obtained yield and conductivity of the samples are presented in Table I. The yield of the sample obtained with KPS as the initiator, PS/PANI-2, was higher than that for the sample obtained with APS, but its conductivity was below the measuring limit of the instrument used (1×10^{-3} S/cm). The conductivity of the sample PS/PANI-1, which was obtained with APS as the oxidant, was very similar to the conductivity of the PS/PANI composite particles obtained under similar conditions as were employed in Ref. 7. However, if the chemical polymerization of ANI was performed in 1 M HCl with KPS as the initiator, all other reaction conditions being the same, the obtained sample, PS/PANI-3, had a conductivity two orders of magnitude higher than that of the PS/PANI-1 sample (Table I). Preliminary experiments showed that the PANI obtained by the chemical polymerization of aniline in 1 M HCl using APS as the oxidant had a lower conductivity than the one prepared with KPS, suggesting a difference in the compactness of the particles in the PANI overlayer. At this time, it can only be assumed that the PANI particles in the overlayers obtained with KPS as the oxidant in the reaction medium with pH lower than 2.5 ($\text{pH} \approx 1$) have a more compact morphology than the ones prepared with KPS at $\text{pH} = 2.5$, or with APS at $\text{pH} \approx 1$.

The influence of the initiator was not investigated further but subsequent syntheses of PS/PANI composites were conducted in 1 M HCl using KPS as the initiator.

TABLE I. Reaction conditions for the preparation of PS/PANI composite particles, their yield and electrical conductivity [$n(\text{ANI})/n(\text{Ox.}) = 1.20$, $t = 0^\circ\text{C}$, $\tau = 3\text{h}$]

Sample	Initiator	Monomer concentration/mol dm^{-3}	Reaction medium	Yield/mass %	Electrical conductivity/S cm^{-1}
PS/PANI-1	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	0.03	water (pH 2.5)	68.8	3.0×10^{-3}
PS/PANI-2	$\text{K}_2\text{S}_2\text{O}_8$	0.03	water (pH 2.5)	81.2	$< 10^{-3}$
PS/PANI-3	$\text{K}_2\text{S}_2\text{O}_8$	0.03	1 M HCl	87.5	0.59
PS/PANI-4	$\text{K}_2\text{S}_2\text{O}_8$	0.1	1 M HCl	90.9	0.53
PS/PANI-5	$\text{K}_2\text{S}_2\text{O}_8$	0.2	1 M HCl	81.4	2.5

Influence of the ANI concentration

In this set of experiments, the PS concentration (and hence the total surface area) was kept constant and the ANI concentration was varied from 0.03 to 0.2 mol/ dm^3 . The polymerization of ANI onto PS particles was performed at 0°C in 1 M HCl, using KPS as the initiator. Three PS/PANI samples (PS/PANI-3, PS/PANI-4 and PS/PANI-5) were synthesized and the yield and electrical conductivity of the samples are shown in Table I. It is obvious that the conductivity of the samples increases with increasing ANI concentration. The yield goes through a maximum which is in accordance with the results obtained for PANI/PVA composites⁴ when a similar behavior was noticed, albeit for higher concentrations of ANI. The au-

thors explained this by assuming that the increase in initial ANI concentration results in an increase of the viscosity of the reaction medium, which ultimately leads to a larger fraction of non-reacted monomer, thereby lowering the yield of PANI.

The conductivities of PANI "bulk powder", the mixture of PANI "bulk powder" and PS particles mixed in the same ratio as in the PS/PANI-3 sample (67.5 mass % of PS and 32.5 mass % of PANI) and PS/PANI-3 sample were measured and the obtained results are shown in Table II. The conductivity of PS particles was not measured since it was shown¹ that its value was around 10^{-8} S/cm, which is lower than the limit of measurable conductivity for the employed instrument. The conductivity of the mixture of PS particles and PANI "bulk powder" was lower than 10^{-3} S/cm. This indicates that the continuous phase consists of PS component and that the PANI component disperses separately in the mixture. The conductivity of the PS/PANI-3 composite particles having the same PS/PANI mass ratio as in the mixture of PS and PANI was 0.59 S/cm, which is of the same order of magnitude as that for PANI powder (1.0 S/cm). The high conductivity indicates that the continuous phase in the PS/PANI-3 particles consists of the green protonated emeraldine form of PANI, which is known to be electrically conductive.⁷

TABLE II. Conductivities of PANI bulk powder, a mixture of PS and PANI particles (mass ratio same as in the PS/PANI-3 sample) and PS/PANI-3 composite particles

Sample	Conductivity/S cm ⁻¹
PANI	1.0
Mixture of PS and PANI particles	< 10 ⁻³
PS/PANI-3 composite particles	0.59

Chemical analysis

Chemical analysis of the synthesized PS, PANI and some of the PS/PANI samples was performed. The results of CHN microanalysis of the PS/PANI composite samples are shown in Table III. The PANI loading of the coated PS particles, w_{PANI} , was determined by comparing their nitrogen content, $m(\text{N})_{\text{PS/PANI}}$, to that of the corresponding uncoated PS particles (average nitrogen content was 0.158 % probably due to AIBN), $m(\text{N})_{\text{PS}}$, and to that of PANI "bulk powder" synthesized in the absence of PS particles (average nitrogen content was 10.8 %), $m(\text{N})_{\text{PANI}}$:

$$w_{\text{PANI}} = \frac{m(\text{N})_{\text{PS/PANI}} - m(\text{N})_{\text{PS}}}{m(\text{N})_{\text{PANI}}} \quad (1)$$

The obtained results are shown in Table III. The thickness of the PANI overlayer in the PS/PANI composite particles, δ , was calculated using the following equation:⁵

$$\delta = d(\text{PS}) \left(\sqrt[3]{\left(\frac{w_{\text{PANI}} \rho_{\text{PS}}}{w_{\text{PS}} \rho_{\text{PANI}}} + 1 \right)} - 1 \right) \quad (2)$$

where $d(\text{PS})$ is the radius of the uncoated PS particles, w_{PS} and ρ_{PS} are respectively

the mass fraction and density of the PS component, and ρ_{PANI} is the density of PANI. The densities of PS and PANI were taken from Ref. 5 and their values were 1.05 g/cm^3 and 1.40 g/cm^3 , respectively. The mass fractions of PS were calculated from the mass fractions of PANI given in Table III ($w_{\text{PS}} + w_{\text{PANI}} = 1$). The calculated values of the thickness of the PANI overlayer are also given in Table III.

TABLE III. Results of the microanalysis, PANI loadings of the coated PS particles, w_{PANI} , PANI overlayer thickness, δ , the number average diameter, d_n , and the coefficient of variation of the particle size distribution, C_v

Sample	Microanalysis			$w_{\text{PANI}}/\text{mass \%}$	$\delta/\mu\text{m}$	$d_n/\mu\text{m}$	$C_v/\%$
	C/%	H/%	N/%				
PS/PANI-3	76.4	7.00	3.67	32.5	0.0714	1.4	43.6
PS/PANI-4	72.0	6.45	6.69	60.3	0.191	1.3	40.6
PS/PANI-5	64.3	6.01	8.63	78.2	0.361	1.6	34.5

The results given in Table III show that the PANI loading of the coated PS particles and the overlayer thickness both increase with increasing ANI concentration, which results in the higher conductivity (Table I).

Scanning electron microscopy

A scanning electron micrograph of micron-sized PS particles produced by dispersion polymerization is shown in Fig. 1. The PS particles were spherical with a number average diameter, $d_n = 1.3 \mu\text{m}$. The coefficient of the variation of the particle size distribution C_v , defined as:

$$C_v = \frac{\sigma}{d_{av}} \times 100 \quad (4)$$

σ being the standard deviation, equalled to 27.2 %.

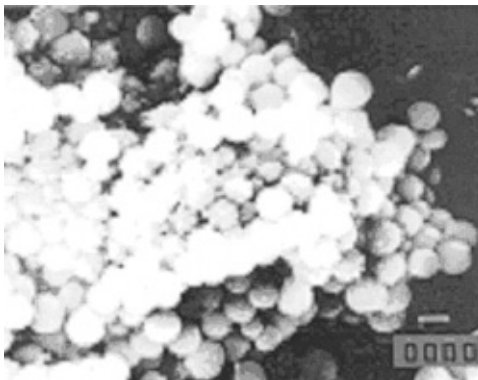


Fig. 1. Scanning electron micrograph of PS particles obtained by dispersion polymerization (scale bar = $1 \mu\text{m}$).

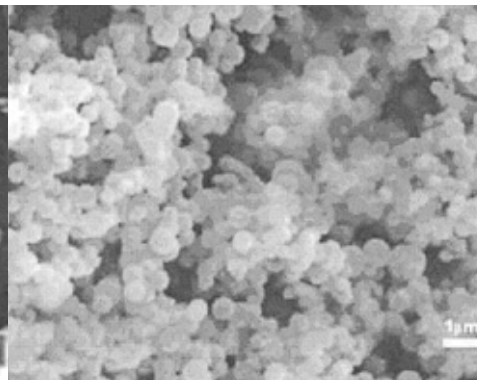


Fig. 2. Scanning electron micrograph of PS/PANI-5 composite particles (scale bar = $1 \mu\text{m}$).

A scanning electron micrograph of PS/PANI-5 particles is shown in Fig. 2. The number average diameters and the coefficients of variation of particle size distribution for all composite particles were calculated from the SEM photographs and are presented in Table III.

The results from Table III show that the particles size of all the samples was very similar and that they all had broad size distributions, which become narrower with increasing ANI concentration. The size distribution of these three samples was much broader than that of the PS particles, which might be a consequence of a non-uniform coating of the PS particles.

CONCLUSIONS

Electrically conductive micron-sized core/shell PS/PANI composite particles were synthesized in 1 M HCl by chemical oxidative polymerization of aniline in the presence of micron-sized PS particles. Firstly, the optimal conditions for the dispersion polymerization of styrene were determined. It was found that only with PAA as the polyelectrolyte were uniform spherical PS particles obtained. It was also shown that PS particles can be successfully separated from the dispersion only by extraction of the excess PAA with *n*-butanol. The influence of the initiator type for the chemical oxidative polymerization of aniline and of the aniline concentration on the particle size and size distribution and on their conductivity was also investigated. It was found that potassium persulphate was a better initiator than ammonium persulphate for ANI polymerization and that the optimal reaction medium was 1 M HCl. The obtained results showed that the conductivity of the samples increased with increasing ANI concentration and the yield went through a maximum. The conductivity of the PS/PANI composite particles obtained with the highest employed ANI concentration was of the same order of magnitude as that for PANI powder.

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ИЗВОД

УТИЦАЈ НЕКИХ ФАКТОРА НА ЕЛЕКТРИЧНУ ПРОВОДЉИВОСТ И ВЕЛИЧИНУ ЧЕСТИЦА КОМПОЗИТА СА ЈЕЗГРОМ ОД ПОЛИСТИРЕНА И ОМОТАЧЕМ ОД ПОЛИАНИЛИНА

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Синтетизоване су електропроводне честице композита величине око 1 микрона са језгром од полистирена (PS) и омотачем од полианилина (PANI) хемијском оксидативном полимеризацијом анилина у присуству честица PS у 1 M HCl. Оптимизовани су услови дисперзионе полимеризације стирена, и испитан је утицај типа иницијатора хемијске оксидативне полимеризације анилина и концентрације анилина на величину

честица добијеног композита PS/PANI, њихову расподелу и електричну проводљивост. Добијени резултати су показали да електрична проводљивост узорака расте са порастом ANI концентрације. Електрична проводљивост честица композита PS/PANI добијених са највећом почетном концентрацијом ANI је истог реда величине као и за прах полианилина. Величина честица није зависила од почетне концентрације анилина, док је расподела величине честица бивала ужа са повећањем ове концентрације.

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