Contents lists available at ScienceDirect

Polymer

Microwave-assisted synthesis of hybrid colloids for design of conducting films

Alexander Türke [a], Wolf-Joachim Fischer [a], Hans-Juergen Adler [b], Andrij Pich [c,*]

[a] Fraunhofer IPMS, Maria-Reiche-Str. 2, 01109 Dresden, Germany
[b] Technische Universität Dresden, Macromolecular Chemistry, Mommsenstr. 4, 01067 Dresden, Germany
[c] DWI RWTH Aachen University, Functional and Interactive Polymers, Pauwelsstr. 8, 52056 Aachen, Germany

ARTICLE INFO

ABSTRACT

We report synthesis of colloids with polymer core and inorganic shell consisting of silver nanoparticles (AgNPs) which can be used as building blocks for the preparation of conducting composite films. Polymer colloids based on copolymer of styrene and butyl acrylate with variable film formation temperature and functional surface have been prepared by surfactant-free emulsion polymerization. Polymer particles with average size between 140 nm and 220 nm and narrow size distribution were used as templates for deposition of AgNPs by microwave-assisted reduction of silver precursors in aqueous medium. The loading of the AgNPs on the polymer particle surface has been increased up to 60 wt.-%. Obtained hybrid colloids were used for preparation of composite films. The electrical conductivity of the composite films starts to increase if the AgNPs loading on the polymer particle surface is above 20 wt.-%.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

During the last decade, composite materials consisting of inorganic nanoparticles (NPs) and polymer matrices have been attracting much attention due to their application in many fields, such as catalysis, biochemistry, separation, sensing and biomaterials, which is attributed to their unique physicochemical properties [1–3]. Among those composites, silver(Ag)-based materials, in particular, silver-polymer hybrid colloids are of special interest. This is because silver has the properties of chemical stability, electrical conductivity and a broad spectrum of antimicrobial activities [4,5]. Recently, many research groups have focused their attention on the fabrication of polymer/Ag core/shell composites and several methods have been established. For example, Zhang et al. [6] prepared AgNPs in situ on the surface of poly(methyl methacrylate-co-methacrylic acid) (PMMA–PMAA) microspheres by employing ion exchange of counterions in the electrical double layer of latex particles. Wang et al. also developed a "One-pot" emulsification method of fabricating Ag/PMMA shell/core composites, in which method AgNO₃ are both silver source and initiator for polymerization of MMA [7]. Similarly, the in situ synthesis of AgNPs on PS-PAA hybrid particles was also achieved through a photoemulsion polymerization process [8]. Besides these in situ formation techniques, sonochemical method, a method

usually employed for the preparation of inorganic microspheres [9], was used for anchoring metallic nanocrystals into the surface of polystyrene (PS) spheres [10]. "Layer by layer" (LBL) [11] method and solvent- assisted route [12] were also conducted in the synthesis of a complete Ag shell with controlled thickness on PS latex. Radiation reaction was another commonly used technique for the preparation of Ag-polymer composite microspheres [13–15]. Unlike other techniques, the radiation reaction can be conducted at room temperature and at ambient pressure but not involving the addition of a reducing agent. Recently, poly(ethylenimine) (PEI), a cationic polymer with branched structure which can bond with both metal ions and negatively charged colloids was frequently used as both a linker and an "in situ" reducing agent to prepare Ag-polymer composites [16,17].

Besides these various techniques, microwave (MW) dielectric heating has been recently applied to the rapid synthesis of metallic nanostructures [18,19] and matrix deposition of NPs [20]. MW provides rapid and uniform heating of reagents, solvents intermediates and products. Fast heating accelerates the reduction of metal precursors and the nucleation of the metal cluster, resulting in nanostructures with smaller sizes, narrower size distributions and a higher degree of crystallization than those obtained in conventional oil-bath heating [18]. Recently, Hu et al. [21] developed a microwave-assisted rapid "green" synthesis of uniform silver nanoparticles in aqueous system.

Our aim was to design composite colloids containing a polymer component and a metal component to obtain conducting composite films by drying on solid substrates at moderate

* Corresponding author.
E-mail address: pich@dwi.rwth-aachen.de (A. Pich).

temperatures between 15 °C and 50 °C. In present study we used a two-step procedure to synthesize composite colloids in form of aqueous dispersions with a polymer core having low glass transition temperature and inorganic shell consisting of AgNPs. This approach ensures formation of conducting composite films by drying of aqueous dispersions of hybrid colloids at low temperatures on solid substrates. This strategy allows avoiding use of organic solvents and application of heat-sensitive substrates such as paper, polymer films etc.

2. Experimental part

2.1. Materials

Monomers styrene (ST) (≥99%), butyl acrylate (BA) (≥99%), 2-carboxyethyl acrylate (CA), (2-acetoacetoxy)ethyl methacrylate (95%) (AAEM), and initiator sodium per sulfate (≥99%) ($Na_2S_2O_8$) were purchased from Aldrich. Monomers were purified by passing through column filled with an inhibitor remover (activated alumina powder) (Polysciences, Inc.). Silver nitrate ($AgNO_3$) (≥99%) and sodium hypophosphite (NaH_2PO_2) were obtained from Aldrich and used as received.

2.2. Synthesis of polymer particles

The synthesis of polymer particles was carried out in 250 ml double-walled glass reactor. First 180 ml water were placed in the reactor and purged with argon gas for 20 min at room temperature. Then the monomers were added under constant stirring (400 rpm) and the reaction temperature was raised to 70 °C. The polymerization was initiated by addition of aqueous initiator solution. After 8 h the reaction was finished. Obtained polymer dispersions were dialyzed against deionized water (Spectra/Pore Dialysis Membrane; MWCO: 3.500).

2.3. Synthesis of hybrid colloids

Hybrid particles were synthesized in a two-step procedure. Typically 27 ml of a 0.2 wt.-% polymer colloid was mixed with 0.5 ml silver salt solution of different silver concentrations. After 30 min stirring at room temperature, the reducing agent sodium hypophosphite was added. 5 ml of the reaction solution was placed in a microwave tube and heated (microwave CEM 300 was used). In the first 30 s the samples were heated up to the reaction temperature. In the second stage this temperature was hold for 2 min. Then the microwave tube was cooled with pressurized air. The

Table 1
Ingredients used for the synthesis of polymer particles.

Sample	BA [g]	CA [g]	AAEM [g]	ST [g]	$Na_2S_2O_8$ [g]	H_2O [g]	SC^a [%]	pH
1	1.0	1.0	1.5	6.5	0.3	190	4.64	2.4
2	2.0	1.0	1.5	5.5	0.3	190	4.50	2.4
3	3.0	1.0	1.5	4.5	0.3	190	4.78	2.4
4	4.0	1.0	1.5	3.5	0.3	190	4.93	2.4
5	5.0	1.0	1.5	2.5	0.3	190	4.89	2.4

[a] Solids content.

reaction product was dialysed against water for 3 days to remove non-reacted ingredients and by-products.

2.4. Formation of films

Composite films were prepared on glass substrate by spin coating of aqueous particle dispersions at room temperature. Additionally, composite particles were deposited on glass substrates by using laboratory ink-jet printer (Dimatix DMP-2800) to form arrays of different dimensions.

2.5. Characterization techniques

Particle size (hydrodynamic radius, R_h) was determined by photon correlation spectroscopy (PCS) with Zetasizer Nano-ZS (Malvern Instruments). The samples were diluted with distilled water prior to characterisation with PCS (polymer concentration 0.005 g/l).

Measurements of particle size (radii of gyration, R_g) and particle size distribution were performed with asymmetric Flow-Field-Flow-Fractionation system (aF-FFF) (Wyatt, Eclipse with 350 μm spacer and DAWN-DSP-MALLS detector). Distilled water was used as a solvent.

Sedimentation analysis of composite particles was performed with separation analyser (LUMIFuge 114, L.U.M. GmbH, Germany). Samples were investigated in plastic cuvettes at 3000 rpm and room temperature. The slope of sedimentation curves was used to calculate the sedimentation velocity and to get information about stability of the samples.

Microscopy investigations were performed with scanning electron microscope (SEM Hitachi S-4700) equipped with back-scattered electron (BSE) detector. Samples were prepared on glass substrates and coated by ultra-thin layer of carbon to enhance the resolution. Images were taken at voltage 4 kV.
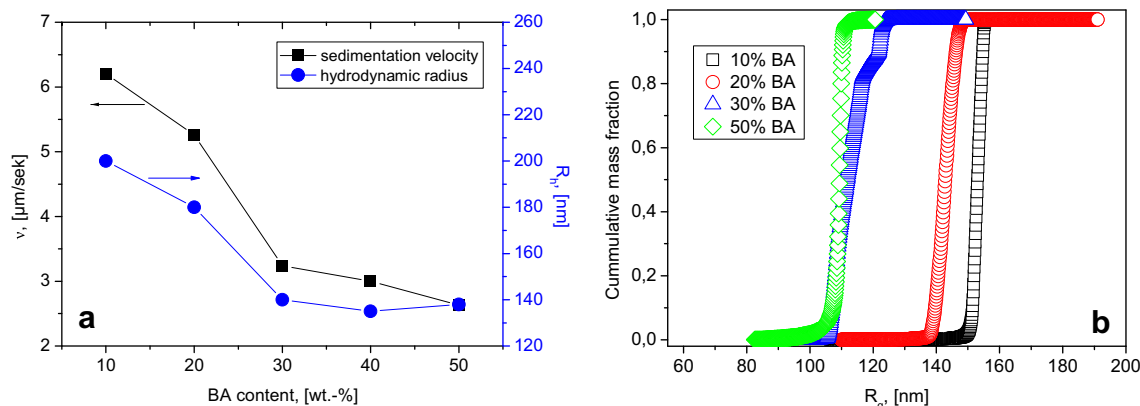

Fig. 1. a) Hydrodynamic radii and sedimentation velocity of polymer colloids as a function of BA content in polymer colloids; b) Size distribution curves for polymer colloids.
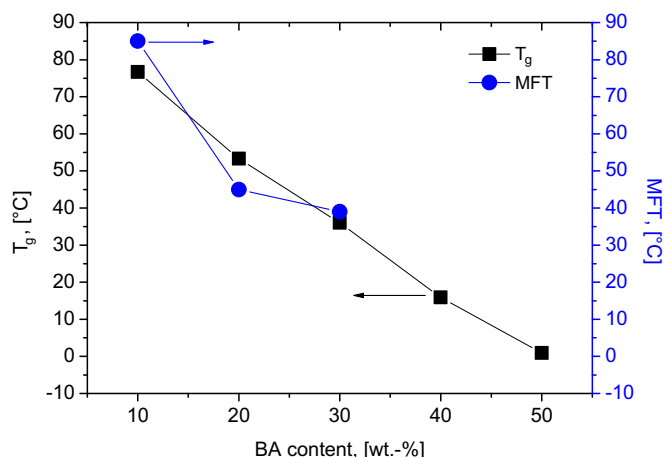
Fig. 2. Glass transition temperatures (T_g) and minimal film-formation temperatures (MFT) of polymer colloids a function of BA content in polymer colloids.

The surface analysis of particles was performed by XPS (Phi 5700 XPS/AES-Spectrometer, Physical Electronics). Al-K_α radiation source was used at take-off angle of 45° and penetration depth of 10 nm.

Determination of glass transition temperatures (T_g) of polymer particles was performed with differential scanning calorimetry (DSC) by using Mettler TA 4000 instrument. Before measurement samples were dried in vacuum for ca 48 h. Samples were analyzed in closed aluminum cups. Measurements were made at heating rate 5 K/min in nitrogen atmosphere. For each sample 3 heating/cooling runs have been made from −30 °C to 150 °C to determine average glass transition temperature. DSC spectra exhibited single glass transition indicating the formation of copolymer-based particles.

The minimal film-formation temperature (MFT) for polymer latexes was determined with gradient aluminium heating plate. As MFT the temperature was defined at which the formation of continuous crack-free polymer film was observed [22].

AgNPs content in composite particles was determined by thermogravimetrical analysis (TGA) with 7 Perkin Elmer instrument. Before measurement samples were dried in vacuum for ca 48 h. Samples were analyzed in closed aluminium cups in temperature range 25−600 °C (heating rate 5 K/min in nitrogen atmosphere).

Conductivity measurements were performed on spin coated films at room temperature. The film conductivity was measured with Automatic Four Point Analyser (Semiconductor Solutions).

3. Results and discussion

3.1. Synthesis of polymer colloids

The most important requirements for the polymer colloids used in present study are: a) reactive surface groups (to ensure controlled growth and attachment of AgNPs) and b) film-forming ability. Additionally, the small particle size and narrow size distribution are also important parameters since both influence the film-formation

process and quality of films. The polymer colloids were prepared by copolymerization of styrene (ST), butyl acrylate (BA), 2-carboxyethyl acrylate (CA) and acetoacetoxyethyl methacrylate (AAEM) (Table 1). The hydrophilic functional monomers CA and AAEM were used to introduce carboxylic and β-diketone groups into the surface layer of polymer colloids respectively. Both carboxylic and β-diketone groups are able to complex metals and therefore it was assumed that this will support growth of AgNPs on the polymer colloid surface. The hydrophobic monomers ST and BA were used to design the core of polymer particles in such a way that film formation can be realized at low temperatures. The ratio between ST and BA allows tuning the glass transition temperature (T_g) of the polymer in a broad range. As shown in Table 1 in the surfactant-free emulsion polymerization process the amount of CA and AAEM was constant (10 wt.-% and 15 wt.-% respectively) and amount of ST and BA was varied.

The sedimentation velocity was measured for obtained polymer particles to evaluate the colloidal stability of dispersions. As shown in Fig. 1a the sedimentation velocity decreases with increase of BA content and reduction of the particle size. The low sedimentation velocity values measured for investigated latex samples indicate that polymer particles exhibit superior colloidal stability. This is due to the hydrophilic particle surface consisting mostly of hydrophilic AAEM and negatively charged CA units.

Obtained latexes were characterized by photon correlation spectroscopy to determine the size of polymer colloids. The experimental results presented in Fig. 1a show that hydrodynamic radius (R_h) of polymer particles decreases with increase of BA amount in the monomer mixture. If BA content exceeds 30% particle size is not changing considerably. The reduction of the particle size in surfactant-free emulsion copolymerization upon addition of 17 mol% of BA to ST was observed by Guillot and coworkers [23]. Further increase of the BA content did not influence the size of polymer particles. Authors noticed the increase of the polymerization rate with increase of the BA content in the monomer mixture. This was explained by an increase of the average number of radicals per particle in the case of rich BA copolymerization (either due to a gel effect or to a flocculation of small particles resulting in the burial of oligoradicals). Similar observations were reported by Countino et al. [24]. for copolymerization of ST and BA in presence of anionic surfactant sodium lauryl sulphate. In our system the strong electrostatic repulsion induced by carboxylic groups of 2-carboxyethyl acrylate reduces the probability of the flocculation of the primary particles. This might lead to the increase of the particle number and reduction of the particle size upon increase of BA content in the monomer mixture.

To evaluate the particle size distribution of polymer colloids we used Flow-Field-Flow-Fractionation (F-FFF) instrument coupled with multi-angle laser light scattering (MALLS) detector. The size distribution curves (cumulative mass fraction vs. particle radius) for selected samples are presented in Fig. 1b. It should be noted that by using MALLS we detect radius of gyration (R_g) for polymer particles. Fig. 1b shows that the decrease of particle size with increase of BA content does not influence the size distribution of latex particles. Independently from the composition obtained polymer particles

Table 2
Ingredients used for the optimization of the microwave-assisted AgNPs deposition on the polymer particle surface.

Sample	Latex[a] [g]	AgNO$_3$ [g]	NaH$_2$PO$_2$ [g]	H$_2$O [g]	T [°C]	AgNO$_3$: NaH$_2$PO$_2$ [mol:mol]	AgNPs^{theor} [wt.-%]	AgNPs[b] [wt.-%]
1	4.5	0.007	0.011	0.5	80	3: 1	33	2.0
2	4.5	0.007	0.011	0.5	100	3: 1	33	10.6
3	4.5	0.007	0.011	0.5	120	3: 1	33	18.3

[a] Solids content 0.2%.
[b] TGA data; AgNPs amount related to the polymer.

Table 3
Ingredients used for the synthesis of hybrid colloids with variable AgNPs content.

N	Latex[a] [g]	AgNO$_3$ [g]	NaH$_2$PO$_2$ [g]	H$_2$O [g]	AgNO$_3$: NaH$_2$PO$_2$ [mol:mol]	AgNPs^{theor} [wt.-%]	AgNPs[b] [wt.-%]	ν [µm/sek]
1	4.5	0.0017	0.003	0.5	3:1	11	5.0	0.08
2	4.5	0.0035	0.005	0.5	3:1	20	11.2	0.2
3	4.5	0.007	0.011	0.5	3:1	33	18.3	0.75
4	4.5	0.009	0.014	0.5	3:1	40	22.5	0.83
5	4.5	0.014	0.022	0.5	3:1	50	45.2	1.1
6	4.5	0.021	0.033	0.5	3:1	60	60.9	1.25
7	4.5	0.028	0.044	0.5	3:1	66	64.2	3.25

[a] Solids content 0.2%.
[b] TGA data; reaction temperature 120 °C; ν − sedimentation velocity measured at 3000 rpm (sedimentation velocity for latex without AgNPs was 0.03 µm/sek); AgNPs amount related to the polymer.

exhibit narrow size distribution. The shoulder in the distribution curve for the particles prepared at 30% BA indicates the presence of small fraction (app. 10%) of particles with R_g around 120 nm. The distribution curves obtained from measurements of hydrodynamic radii by PCS for this sample do not confirm this result. Additionally, SEM investigations confirmed monodisperse nature of this sample (see Fig. 3). We assume that this effect can originate from attractive particle interactions with membrane during focusing step and delayed elution of small particle fraction from separation channel.

As it was mentioned before, the film-forming properties of obtained polymer colloids are of high importance for the preparation of composite films. The film-forming properties can be
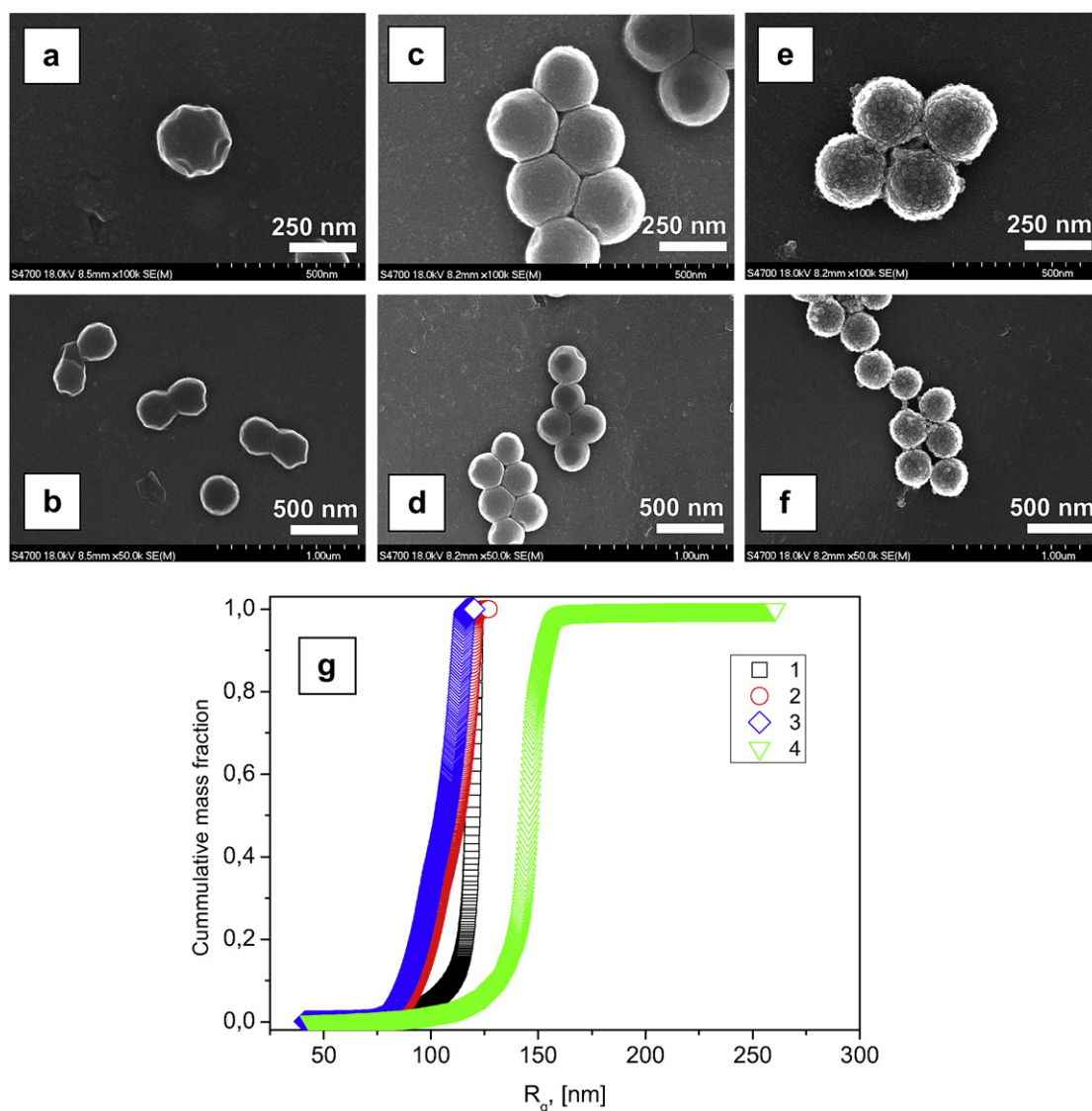

Fig. 3. SEM images of hybrid particles prepared at different reaction temperatures: a,b)80 °C; c,d) 100 °C; e,f) 120 °C. Distribution of radius of gyration (F-FFF-MALLS data) for hybrid colloids as a function of reaction temperature (1 − polymer template; 2−80 °C; 3−100 °C; 4−120 °C) (g).
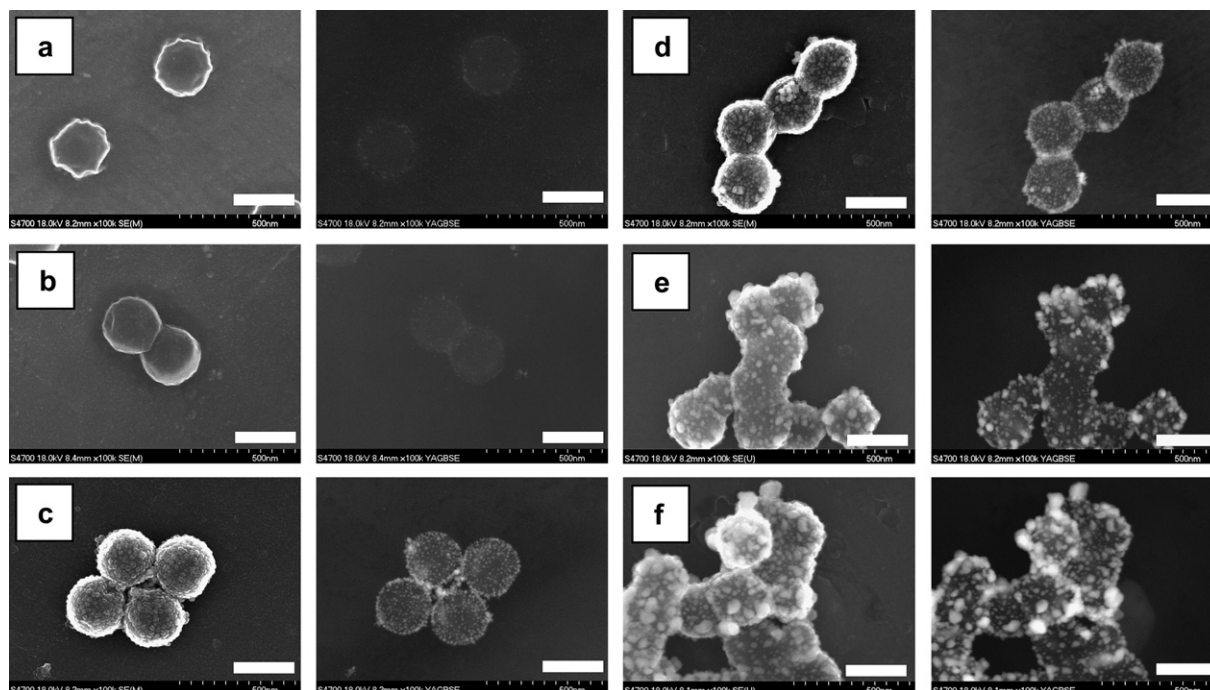
Fig. 4. SEM images of hybrid colloids with different AgNPs loading: a) 5.0 wt.-%; b) 11.2 wt.-%; c) 18.3 wt-%; d) 22.5 wt.-%; e) 45.2 wt.-%; f) 64.2 wt.-% (right side images were taken with back-scattered electron (BSE) detector, bar scale 250 nm).

described by determination of glass transition temperature (T_g) of polymer particles in dry state as well as determination of minimal film-formation temperature (MFT) of aqueous polymer dispersions.

To determine the glass transition temperature of polymer colloids we used differential scanning calorimetry. The experimentally obtained T_g data are presented in Fig. 2. The T_g values decrease in linear order with increase of the BA content from 80 °C to 0 °C.

The drying process of low-T_g aqueous polymer dispersions is a complex process of coalescence of the individual latex particles and can be divided in different stages. As soon as particle dispersion is deposited on the solid substrate, water starts to evaporate. The effective concentration increases as the water evaporates and brings the latex particles into contact. Polymer particles form a compact structure and become deformed into hexagonal shape. After this stage the interdiffusion of polymer chains between deformed particles is possible if temperature exceeds T_g of polymer. Therefore, the temperature required for the formation of film by drying process is defined as minimal film-formation temperature (MFT). At temperatures below MFT no particle deformation and interdiffusion of polymer occurs. For majority of dispersions MFT is slightly higher then T_g, however plasticizing effects originating from presence of water or other additives can reduce MFT values considerably.

As shown in Fig. 2, measured minimal film-formation temperature (MFT) values are quite similar to T_g determined by DSC. The experimental data shown in Fig. 2 indicate that by varying the chemical composition of polymer colloids it is possible to adjust the film-formation temperature in a broad range.

3.2. Synthesis of hybrid colloids

To optimize in situ deposition of silver nanoparticles (AgNPs) on the surface of polymer colloids we selected sample containing 30 wt.-% BA with hydrodynamic radius $R_h = 140$ nm ($R_g = 115$ nm) (sample 3, Table 1). We used $AgNO_3$ as silver precursor and NaH_2PO_2 as reducing agent to form AgNPs [25]. The formation of AgNPs was studied at different temperatures (Table 2).

As shown in Table 2 the increase of reaction temperature increases dramatically the yield of AgNPs. The content of AgNPs in composite samples was increased from 2 wt.-% (synthesis at 80 °C) to 18 wt.-% (synthesis at 120 °C) at the reaction time 5 min. This indicates that the process of silver reduction is accelerated if temperature increases.

The evaluation of the particle morphology by SEM (Fig. 3a–f) indicates that at reaction temperature 120 °C more AgNPs are formed and they are localized exclusively on the surface of latex particles. At lower reaction temperatures secondary AgNPs and AgNPs aggregates can be detected beside hybrid colloids. It has been shown that the increase of the reaction temperature leads to increase of the nucleation rate and formation of AgNPs [26]. The design of the surface layer of polymer colloids with integrated carboxylic and β-diketone groups allows controlled formation of hybrid colloids. We assume that carboxylic and β-diketone groups complex Ag^+ ions and further induces formation of nucleation centres and growth of AgNPs on the polymer colloid surface during reduction process. Therefore, higher reaction temperature and increased concentration of Ag^+ ions in the surface layer of polymer colloids may lead to faster growth of AgNPs on the polymer particle surface compared to the growth in solution. The F-FFF experimental data shown in Fig. 3g indicate that the formation of the inorganic shell around polymer core took place only if synthesis was carried out at 120 °C. Determined radius of gyration for hybrid colloids is about 25 nm larger compared with the polymer template. The distribution curve is shifted to higher R_g values and only a little broadening of the particle size distribution can be observed. Contrary, samples prepared at 80 °C and 100 °C both exhibit a broad particle size distribution. The shift of the distribution curves to lower R_g values indicates formation of secondary AgNPs or AgNPs aggregates. So, the F-FFF results are in a good agreement with SEM results discussed above and we notice that reaction temperature is an extremely important parameter
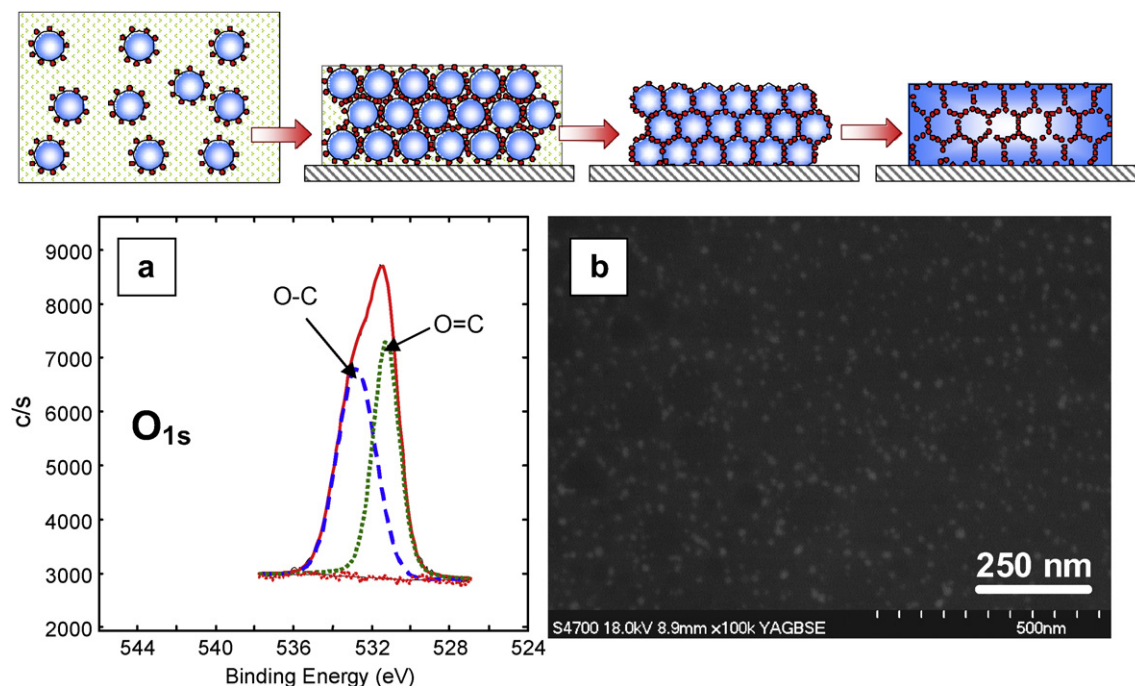
Fig. 5. O_{1s} XPS spectrum (a) and SEM image (b) of the film prepared from hybrid colloids containing 18.3 wt.-% AgNPs (inset shows simplified mechanism of the film formation from hybrid colloids).

that improves both the Ag^0 yield and deposition of silver nano-particles on the polymer colloid surface.

To optimize the amount of AgNPs deposited on the polymer colloid surface we varied amount of silver nitrate and reducing agent in the reaction mixture by keeping the ratio between both reagents and reaction temperature (120 °C) constant (Table 3). The theoretical silver content (assuming 100% conversion) in hybrid samples was varied from 10 wt.-% to 60 wt.-%. The experimentally determined silver content in hybrid samples is significantly lower compared with theoretical values. Interestingly the reaction yield increased significantly (from 50 to 60% to 90–95%) with the increase of the silver nitrate and reducing agent in the reaction mixture.

The deposition of the AgNPs reduces the colloidal stability of the hybrid particles. As shown in Table 3 the sedimentation velocity values determined at 3000 rpm increase with the increase of silver content in hybrid colloids. For the samples with silver content

above 45 wt.-% some particle aggregation was detected by F-FFF (data not shown).

The evaluation of the particle morphology was performed by SEM (Fig. 4). The increase of the AgNPs amount on the polymer particle surface is obvious; however we notice that the morphology of the silver shell is changing. At high silver loading (Fig. 4e,f) we detect increased amount of large Ag^0 clusters which lead to the formation of hybrid colloids with irregular shape. We assume that this phenomenon is responsible for the partial aggregation of hybrid particles and lost of the stabilization in aqueous medium.

3.3. Formation of composite films

Hybrid colloids with different AgNPs loading were used for the formation of films on glass substrates. Since the T_g and MFT for the polymer core was around 40 °C (Fig. 2), after particle deposition on the solid substrate and water evaporation samples were heated to
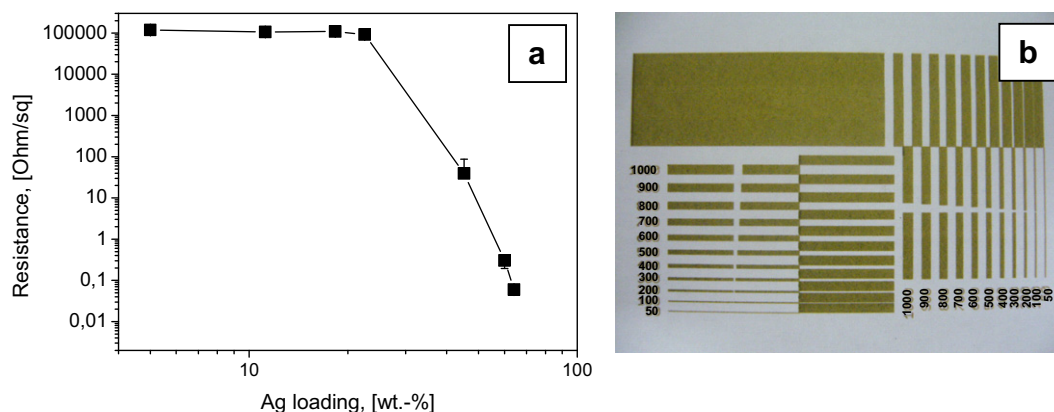

Fig. 6. Conductivity of composite films as a function of the AgNPs content (a). Array prepared by ink-jet printing of hybrid colloids containing 18.3 wt.-% AgNPs on paper substrate (the numbers labelled near each line indicate the widths of the lines) (b).

45 °C for 1 h to ensure the formation of composite film. The surface of composite films was evaluated by SEM and XPS. The HRXPS spectrum in Fig. 5a shows only the binding energy region of O_{1s} originating from carbonyl and ester groups of acrylates used for the particle synthesis. The O_{1s} spectra of hybrid film surfaces could be resolved into two components. The peaks at 531.4 eV and 533.1 eV were assigned to π-bonded oxygen (O=C) and σ-bonded (O–C) oxygen, respectively. The typical signals for silver-bonded oxygen (O–Ag) at binding energies between 529 eV and 530.5 eV could be not detected. This indicates that the oxidation of silver nanoclusters does not occur during film formation.

The microscopy studies indicate that the crack-free films were obtained with homogeneous distribution of AgNPs in polymer matrix. Fig. 5b shows back-scattered electron image of the composite film surface. The AgNPs appear as bright dots homogeneously distributed in polymer matrix.

Thin composite films were prepared by using hybrid colloids with variable AgNPs loading to investigate their electrical properties. The film resistance was measured by four-point method and the experimental data are summarized in Fig. 6a. For composite films with AgNPs content of 20 wt.-% rapid decrease of the resistance was detected. The increase of the film conductivity is due to the formation of conducting network out of AgNPs in polymer films. We assume that if the AgNPs loading on the polymer colloid surface is lower then 20 wt.-%, the metal nanoparticles become separated with insulating polymer layer during film formation process.

The big advantage of hybrid colloids as building blocks for the formation of conducting films is a combination of film-forming and conducting components in colloid form. This allows application of water-based particle dispersions as printing inks in ink-jet printers. Fig. 6b demonstrates the conducting patterns printed on paper by using hybrid particles with AgNPs shells by using DIMATIX DMP-2800 printer. The printed conducting arrays can find application as conducting elements in low-cost electronics for textiles or packaging.

4. Conclusions

Hybrid colloids with polymer core and inorganic shell consisting of silver nanoparticles (AgNPs) were synthesized and used as building blocks for the preparation of conducting composite films. Polymer colloids based on copolymer of ST and BA with variable film formation temperature and functional surface have been prepared by surfactant-free emulsion polymerization in aqueous phase. The variation of styrene:butylacrylate ratio in the monomer mixture led to the variation of the film formation temperature (10 °C–80 °C) and particle size (140 nm–220 nm). The deposition of AgNPs on polymer particle surface was performed by microwave-assisted reduction of silver precursors in aqueous medium. The increase of the reaction temperature from 80 °C to 120 °C improved both yield and deposition efficiency of AgNPs on the surface of polymer colloids. The loading of the AgNPs on the polymer particle surface was varied up to 60 wt.-%. Obtained hybrid colloids were used for preparation of composite films. Composite films with high electrical conductivity were obtained if AgNPs loading on the polymer particle surface was above 20 wt.-%.

References

[1] Kresge CT, Leonwicz ME. Nature 1992;359:710.
[2] Akolekar DB, Hind AR, Bhargava SK. J Colloid Interface Sci 1998;199:92.
[3] Förster S, Plantenberg T. Angew Chem Int Ed 2002;41:688.
[4] Kim JW, Lee JE, Kim SJ, Lee JS, Ryu JH, Kim J, Han SH, et al. Polymer 2004;45:4741.
[5] Chen CW, Serizawa T, Akashi M. Chem Mater 1999;11:1381.
[6] Zhang JG, Coombs N, Kumacheva E. J Am Chem Soc 2002;124:14512.
[7] Wang LM, Chen DJ. Chem Lett 2004;33:1010.
[8] Lu Y, Mei Y, Schrinner M, Ballauff M, Möller MW, Breu J. J Phys Chem C 2007;111:7676.
[9] Pol VG, Gedanken A, Moreno JC. Chem Mater 2003;15:1111.
[10] Pol VG, Grisaru H, Gedanken A. Langmuir 2005;21:3635.
[11] Dong AG, Wang YJ, Tang Y, Ren N, Yang WL, Gao Z. Chem Commun 2002;4:350.
[12] Zhang JH, Liu JB, Wang SZ, Zhan P, Wang ZL, Ming NB. Adv Funct Mater 2004;14:1089.
[13] Choi SH, Zhang YP, Gopalan A, Lee KP, Kang HD. Colloids Surf A 2005;25:165.
[14] Cheng DM, Zhou XD, Xia HB, Chan HSO. Chem Mater 2005;17:3578.
[15] Tamai T, Watanabe M, Hatanaka Z, Tsujiwaki H, Nishioka N, Matsukawa K. Langmuir 2008;24:14203.
[16] Tian CG, Mao BD, Wang EB, Kang ZH, Song YL, Wang CL, et al. J Phys Chem C 2007;111:3651.
[17] Mohammed HS, Shipp DA. Macromol Rapid Commun 2006;27:1774.
[18] Tsuji M, Hashimoto M, Nishizawa Y, Kubokawa M, Tsuji T. Chem Eur J 2005;11:440.
[19] Harpeness R, Gedanken A. Langmuir 2004;20:3431.
[20] Tuval T, Gedanken A. Nanotechnology 2007;18:255601.
[21] Hu B, Wang SB, Wang K, Zhang M, Yu SH. J Phys Chem C 2008;112:11169.
[22] Jensen DP, Morgan LW. J Appl Polym Sci 1990;42:2845.
[23] Guillaume JL, Pichot C, Guillot J. J Polym Sci A Polym Chem 1990;28:119.
[24] Santos AM, Countinho FMB. Polym Bull 1992;29:309.
[25] Mayer ABR, Grebner W, Wannemacher R. J Phys Chem B 2000;104:7278.
[26] Chen D, Qiao X, Qiu X, Chen J, Jiang R. Nanotechnology 2010;21:1.