Macromol. Symp. **2012**, 317-318, 137–141

DOI: 10.1002/masy.201100106

Spherical Polyelectrolyte Brushes as Templates for Stable Dispersions of Polyaniline Based Conducting Particles

A. N. Korovin,[*1] *V. G. Sergeyev,*[1] *O.A. Pyshkina,*[1] *L. Tsarkova*[1,2]

Summary: We prepare stable conducting core-shell particles using spherical polyelectrolyte brushes (SPB) as microreactor-templates. The polymerization of aniline is guided within the SPB shell so that no bulk polymerization proceeds up to 20% polyaniline (PANi) content in the resulting composite. The dispersions are electrostatically stabilized in a wide range of the ionic strength. The conductivity of the composite material reaches 0.1 S/cm which is comparable with the conductivity of bulk PANI obtained under comparable conditions.

Keywords: dispersions; microstructure; nanocomposites; polyaniline; polyelectrolyte brushes; template polymerization

Introduction

Modern technology searches for novel metal-free conducting materials for diverse applications ranging from microelectronics to anticorrosive coatings. Conductive polymers have proved to be promising building blocks in material science due to the unique combination of the metallic properties and the properties of macromolecular chains.[1–4]

Polyaniline (PANi) is the key representative of a class of conducting polymers and it possesses a number of attractive functional properties, such as stability to heating and external influences, relatively high conductivity (up to 500 S/cm), electrochromism, facile and low-cost manufacturing. However, the application of PANi is limited by its low solubility in the majority of known solvents, and by its poor mechanical properties. The production of dispersed core-shell particles by means of matrix polymerization of aniline is a widely used approach.[5] It allows significant facilitation and control over the synthetic procedure with respect to the particle size and composition, as well as for the design of the material, with appropriate, properties by the selection of a suitable core material. [6–12]However the application of PANI-based core-shell particles is frequently limited by their poor colloidal stability and irreversible aggregation due to the high surface energy of PANi. Typically, surfactants or steric stabilizers are used to improve the colloidal stability of PANI dispersions. Another limiting factor is related to a complexity of the polymerization reaction. As a result, a thin shell of PANi often possesses undesirable high roughness and non-uniform morphology.[6]

In this work we use spherical polyelectrolyte brushes (SPB) as templates for a matrix polymerization of aniline. Spherical polyelectrolyte brushes represent latex with densely grafted chains of polyelectrolytes. An important feature of SPB is that the majority of counter ions of polyelectrolyte chains are located within the brush, which leads to high osmotic pressure and causes strong swelling of polyelectrolyte chains up to almost their contour length.[13] This effect ensures a significant repulsion between particles and their electrostatic stabilization. At the same time, the poly-

---

[1] Polymer Division, Department of Chemistry, Moscow State University, 119991, Moscow, Russia
E-mail: alexnkorovin@gmail.com
[2] DWI an der RWTH, 52976 Aachen, Germany

electrolyte brushes interact with the charged reaction components which allows to improve the morphology of the conducting polymer.[14]

Experimental Part

The SPB particles consist of a monodispersed polystyrene core of 100 nm diameter to which linear sodium poly(styrenesulfonate) (PSS) chains with contour length around ~ 100 nm are densely grafted. The synthesis of SPB via photo-emulsion grafted-from polymerization has been described earlier.[15] As a reference template system, we used monodispersed latex particles (with a diameter of ~ 100 nm) stabilized by sodium dodecyl sulphate (SDS) which were precursors for SPB synthesis. Template-assisted polymerization of PANI was carried out for 12 hours at a fixed monomer- aniline hydrochloride (ANI) - and oxidating agent - APS - concentrations of 10^{-2} M, acidity of the reaction mixture (pH 2) was maintained by 0.01 M solution of HCl. The resulting dispersions were green colored due to the formation of the protonated emeraldine salt of PANI. After polymerization, all samples have been dialyzed against Millipore water. As we couldn't reliable determine contents of nitrogen less than 1% by elemental analysis the loading of the composite particles with PANishell (PANi loading) has been calculated assuming 100% conversion of monomer according to formila:

$$"PANi\,loading" = \frac{c_{ANi} \cdot M_{PANi}}{c_{ANi} \cdot M_{PANi} + 10 \cdot W_p\, \rho H_2O} \cdot 100\%,$$

where c(ANI) was concentration of monomer in mol/l, M_p– molar mass of PANimers assumed equal to 93.5 g/mol, ρ (H_2O) was assumed 1000 g/l, and resulted in PANI content up to 30%, the content of the template particles W_p has been varied in the range of 0–1 weight %.

The initiation time of the polymerization has been evaluated from the kinetic measurements of the UV-VIS spectra recorded on a Thermo Electron Corporation "Helios α" by analyzing the appearance of the absorption band around 700 nm. The morphology of the resulting core-shell particles have been examined by Zeiss 922 TEM microscop, ξ-potentials and hydrodynamic radia were measured by Malvern NanosizerZS. For the conductivity measurements with four-probe method, the composite suspension has been dried and pressed into pallets. Conductivity meassurements were performed using DC high resistivity meter Mitsubishi Chemicals Corporation "Loresta-GP MBBP–T610" with four probe electrode Loresta-PSP.

Results and Discussion

Polymerization of aniline hydrochloride in the presence of dispersions of modified latex led to green coloring of the latex dispersions. This observation indicates that, during polymerization the SPB dispersion did not lose their colloidal stability up to a content of loaded PANI of ca. 25%. For comparison, similar tests with a dispersion of standard latex discovered aggregation of composite particles already at 2% content of PANi.

The cryo-TEM microscopy revealed the presence of brush morphology at initial SPB particles (Figure 1a) and at composite SPB-PANI particles (Figure. 1b,c). In the case of the native SPB particles, the contrast of chains has been considerably improved by complexation with heavy metals (Cs^+) ions and bovine serum albumin.[16] The composite SPB-PANI particles were not contrasted additionally but still are clearly visible on the images (Figure 1b,c). Therefore the observed contrasting may be attributed to the formation of bunches of chains of PSS complexes in composite SPB-PANI particles.

To follow the structural changes in the shell due to the formation of PSS-PANI polyelectrolyte complex we performed measurements of size and electrophoretic mobility of initial SPB particles and

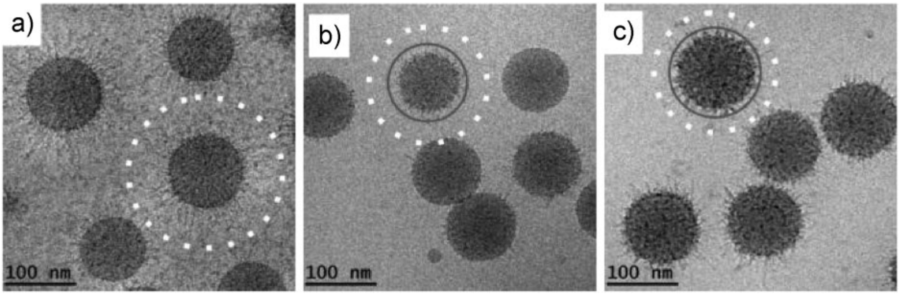

Figure 1.
Cryo-TEM micrograghs of (a) the native SPB particles (contrasted with bovine serum albumine), and of SPB-PANi particles with 7% (b) and 22% (c) of PANi loading. Dotted and solid line indicate hydrodynamic radia of particles (see below) at c(NaCl) □10^{-5} M and 10^{-1} M correspondingly.

dispersions of composite SPB-PANI particles in a wide range of ionic strengths (Figure 2).

Apparently from Figure 2a, the hydrodynamic sizes of particles gradually decrease with increase in content of PANIto 15% in all studied range of solution ionic strengths. Reduction in length of brushes reaches about 60–70 nanometers which is approximately 50% of the initial brush length. Thus, the free-brush thickness is considerably reduced as a result of the complexation of PANi with PSS chains. We note a slight tendency to increase the size of particles at high PANI content (above 22%), which presumably reflects the beginning of the aggregation instability due to the complexation of PANI with the whole PSS chains. Figure 2 summarizes the data on electrophoretic mobility μ of initial SPB and composite particles SPB-PANI versus PANI content at varied ionic strength. The increase of the ionic strength led to the decrease of electrophoretic mobility for all composite particles (in absolute values), while the increase of PANI content didn't make a significant effect. Estimated values of ξ - potentials are between −40 and −80 mV and provide high dispersion stability, which is confirmed by long-term visual observations (on a time scale of several months).We note that the content of PANI had no impact on the ξ – potentials of the particles. This observation can be attributed to two effects: On one hand, the collapse of brushes at increasing PANicon-

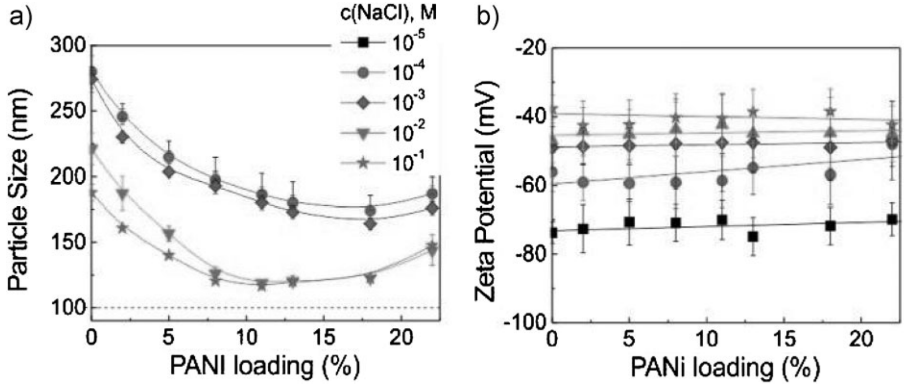

Figure 2.
Hydrodynamic diameter (a) and mobility (b) of SPB-PANi composite particles as a function of PANi loading calculated assuming 100% monomer conversion. The measurements on dialyzed dispersions have been done at indicated ionic strength.

tent should facilitate the diffusion of particles. On the other hand, the complexation of PSS chains with PANI led to a partial shielding of the surface charge which accordingly reduces the surface charge.

Thus, from the DLS data, combined with the electrophoretical mobility measurements, could be concluded that PANI formed complexes with PSS brush layer, while the free ends of PSS chains retained the brush morphology providing dispersions stability and sensitivity to external stimuli.

The ability of the SPB to concentrate charged species within the shell was used for the comparison of the polymerization kinetics of ANI in the presence of SPB and in the presence of the reference latex received by seed copolymerization of polystyrene and PSS. The reference latex possesses a high negative ζ- potential (nearby −60 mV). As it has been previously shown,[9] the induction time of ANI polymerization constantly decreases with increase in its concentration. Here we used this dependence for the estimation of the effective concentration of ANI in the reaction system. Figure 3a displays the evolution of UV spectra of the SPB dispersion in the course of the matrix polymerization of ANI. After the induction period, the growth of the adsorption at 680 nm is accompanied by the blue coloring of the dispersion followed by a band-shift to 720 nm. These observations are in accordance with the polymerization of ANI in solutions of linear PSS [17] and are attributed to the formation of nigraniline form of PANI and to the subsequent reduction to emeraldine, respectively. Figure 3b displays changes in the optical density of various latex dispersions as a function of the polymerization time. The induction period of the polymerization of ANI (at $c = 10^{-2}$ M) in the presence of SPB was about 7 minutes which is considerably shorter than that in the presence of reference latex (15 minutes) and under matrix-free conditions (20 minutes). Moreover, in the presence of SPB the polymerization proceeds at ANI concentration as low as 10^{-3} M which was not the case for other matrix systems. These results prove a high efficiency of SPB as a matrix to concentrate positively charged monomers.

The conductivity of the resulting composite particles from different dispersions (in the form of tablets) has been measured. The conductivity of samples from the stable SPB-PANI dispersions was ca.0.1 S/cm which is more than an order of magnitude larger than the conductivity of reference composite particles with the same content of PANI. Thus, the increase in conductivity of composite particles SPB-PANI could be particularly explained by concentration of monomers in brush environment.

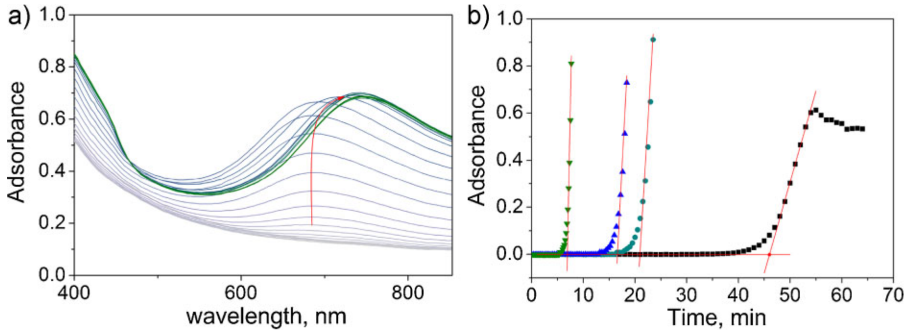

Figure 3.
Kinetics of polymerization of PANi: a) UV-vis spectra of SPB-PANI dispersion at different polymerization stage. Concentration of ANi = 0.001M Arrow indicates the increase of the polymerization time. b) Adsorbance of dispersion at 700 nm during PANi formation of SPB-PANi at ANi concentration 0.001 M (squares), SPB-PANi at ANi concentration 0.01 M (down triangles), PS-PSS-ANi at ANi concentration 0.01 M (up triangles), template free ANi concentration 0.01 M (circles).

Conclusion

Using spherical polyelecrolyte brushes as template allowes the fabrication of composite latex particles with improved properties of the PANi shell. Polymerization kinetic measurements suggested that SPB particles provide optimal conditions for matrix polymerization by both the localization of the ANi monomers within the finite volume of a polyelectrolyte brush and by the controlled delivery of the oxidizing reagent. Importantly, compared with traditionally prepared core–shell conductive particles, the SPB-PANi composites exhibit a remarkable long-term colloidal stability in aqueous phase, and significantly higher conductivity values in dried state. These results show significant improvements of material properties and a decisive perspective for designing novel composite conductive materials and coatings (a conductive ink).

Acknowledgements: The authors thank C. Hanske, A. Fery and A. Wittemann for providing the SPB samples and for fruitful discussions. The work has been done with the financial support by Federal target-oriented program "Scientific and educational research personnel of innovative Russia for 2009-2013" within the State contract No 02.740.11.5175 and the Ministry of Education and Science (Russian Federation)(Grant 16.513.11.3037).

[1] S. Bhadra, D. Khastgir, N. K. Singha, J. H. Lee, *Prog. Polym. Sci.* **2009**, *34*, 783–810.

[2] A. Pron, P. Rannou, *Prog. Polym. Sci.* **2002**, *27*, 135–190.

[3] A. G. MacDiarmid, *Angewandte Chemie International Edition* **2001**, *40*, 2581–2590.

[4] M. Thiyagarajan, L. A. Samuelson, J. Kumar, A. L. Cholli, *J. Am. Chem. Soc.* **2003**, *125*, 11502–11503.

[5] K. S. Ghosh, *Functional Coatings*, WILEY-VCH, **2006**.

[6] C. Barthet, S. P. Armes, S. F. Lascelles, S. Y. Luk, H. M. E. Stanley, *Langmuir* **1998**, *14*, 2032–2041.

[7] N. Kohut- Svelko, S. Reynaud, R. Dedryevre, H. Martinez, D. Gonbeau, J. Francois, *Langmuir* **2005**, *21*, 1575–1583.

[8] D. Li, R. B. Kaner, *J. Am. Chem. Soc.* **2006**, *128*, 968–975.

[9] C. F. Lee, H. H. Tsai, L. Y. Wang, C. F. Chen, W. Y. Chiu, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 342–354.

[10] Q. Wu, Z. Wang, G. Xue, *Adv. Funct. Mater.* **2007**, *17*, 1784–1789.

[11] M. G. Han, J. Sperry, A. Gupta, C. F. Huebner, S. T. Ingram, S. H. Foulger, *Journal of Materials Chemistry* **2007**, *17*, 1347.

[12] Y. Li, Z. Wang, Q. Wang, C. Wang, G. Xue, *Macromolecules* **2010**, *43*, 4468–4471.

[13] A. Jusufi, C. N. Likos, M. Ballauff, *Colloid Polym. Sci.* **2004**, *282*, 910–917.

[14] A. N. Korovin, V. G. Sergeyev, O. A. Pyshkina, C. Hanske, A. Fery, A. Wittemann, L. Tsarkova, *Macromol Rapid Comm* **2011**, *32*, 462–467.

[15] M. Schrinner, B. Haupt, A. Wittemann, *Chemical Engineering Journal* **2008**, *144*, 138–145.

[16] A. Wittemann, M. Drechsler, Y. Talmon, M. Ballauff, *J. Am. Chem. Soc.* **2005**, *127*, 9688–9689.

[17] Z. A. Boeva, O. A. Pyshkina, A. A. Lezov, G. E. Polushina, A. V. Lezov, V. G. Sergeyev, *Polymer Science Series C* **2010**, *52*, 35–43.