Electric Conductance of Films Prepared from Polymeric Composite Nanoparticles

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Summary: Novel polymeric particles of spherical shape consisting of an electrically insulating poly(styrene-*co*-acetoacetoxyethyl methacrylate) (PS/PAAEM) core and a conductive shell of poly(3,4-ethylenedioxythiophene) (PEDOT) were synthesized. Electric measurements showed a strong dependence of the conductivity on weight ratio of PEDOT to PS/PAAEM in the composite. As the PEDOT content varied from 2 to 31.4 wt.-%, resistivity of the resulting material changed exponentially from 12 GΩ cm to 100 Ω cm, depending also on the type of the used oxidation agent. Similar studies were performed on the basis of insulating poly(*N*-vinylcaprolactam-*co*-acetoacetoxyethyl methacrylate) (PVCL/PAAEM) microgel particles, which acted as microreactors for the synthesis of conductive PEDOT nanorods. In microgel systems, the conductivity was lower than in core-shell systems, when the PEDOT content was less than 5 wt.-%. Above this value of PEDOT concentration, the conductivities in the two systems became similar.

Keywords: coatings; composites; conducting polymers; core-shell particles; microgels

Introduction

Since the discovery of enhancing the electric conductance of polyacetylene by chemical or electrochemical doping more than 25 years ago, the investigations of conductive polymers (CPs) have attracted great scientific interest because of their high application potential.[1–3] CPs combine electric properties of metals due to their high conductance in the oxidized state with those of semiconductors or insulators in the reduced state. A well known example is poly[3,4-(ethylenedioxy)thiophene] (PEDOT) with a high thermal stability up to 280 °C.[4] Due to the low band gap and good environmental stability material seems to be a good candidate for many optoelectronic applications,[5,6] such as for electrodes, electromagnetic shielding, capacitors, sensors and antistatic and anticorrosion coatings. The high conductance and stability is attributed to the 3,4-substitution of the thiophene ring, which prohibits polymerization or crosslinking at the 3 or 4 position and leads to a high regularity of the PEDOT structure with less defects. The lack of solubility in most organic solvents is an aspect limiting the practical use of conducting polymers. One of the ways to processibility is their synthesis in the form of colloidal dispersions.[7] Many research groups have done a lot of work in this field, especially in the preparation of polyaniline[8] and polypyrrole.[9] The synthesis of PEDOT in aqueous solutions is difficult to realize due to the low solubility of the EDOT monomer, but many attempts have been done to overcome the solubility problem. Recently, the preparation of various PEDOT-based composites as core-shell structures[10,11] or nanorods has been explored.[12]

The aim of this work is to describe the synthesis of conductive poly(styrene-*co*-acetoacetoxyethyl methacrylate) (PS/PAAEM) core – PEDOT shell particles

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and poly(*N*-vinylcaprolactam-*co*-acetoacetoxyethyl methacrylate) (PVCL/PAAEM) microgel – PEDOT particles and present the values their electric conductance.

Experimental Part

Materials

The monomers *N*-vinylcaprolactam (VCL), 3,4-(ethylenedioxy)thiophene (EDOT) and styrene (ST) were obtained from Aldrich and purified by distillation. Acetoacetoxyethyl methacrylate (AAEM; Aldrich) was used as received. Crosslinker *N,N*′-methylenebisacrylamide (BIS) was purchased from Aldrich and added without any further purification. 2,2′-azobis(2-methylpropanimidamide) dihydrochloride (AMPA; Aldrich) was used as received and the oxidants $FeCl_3$ (Fluka), sodium phosphomolybdate ($Na_3Mo_{12}PO_{40}$), ammonium peroxodisulfate ($(NH_4)_2S_2O_8$) and tetrachloroauric(III) acid ($HAuCl_4$; Aldrich) were obtained anhydrous.

Synthesis of PS/PAAEM core-PEDOT-shell Particles

PS/PAAEM core particles were prepared according to ref.[13] The determined solid content of the latex was ca. 10 wt.-%. The PEDOT shell was prepared by oxidative polymerization of EDOT in the presence of PS/PAAEM core particles. 0.5 g EDOT was dissolved in 5 ml of an ethanol/water mixture (30 mol % EtOH) and the PS/PAAEM latex was added. The reaction mixture was stirred for 1 h at 60 °C. After the addition of $FeCl_3$ (0.57 g, mole ratio $FeCl_3$/EDOT 1:1), dissolved in 5 ml EtOH/H_2O, the dispersion was continuously stirred for 12 h. A change of colour from white to green and brown was observed. To deposit different amounts of PEDOT on the polymer core, the PS/PAAEM amount added to the reaction mixture was varied to achieve EDOT-to-PS/PAAEM weight ratios of 0.2, 0.5 and 1. In the cases where $Na_3Mo_{12}PO_{40}$ or $(NH_4)_2S_2O_8$ were used as oxidation agents instead of $FeCl_3$, the PS/PAAEM-to-EDOT weight ratio was 1.0 and oxidants were added in equimolar amount to EDOT. Purification was carried out by repeated washing with water and centrifugation of the produced composite.

Synthesis of PVCL/PAAEM Microgel PEDOT Particles

Microgel particles were prepared by dispersion polymerization according to ref.[14] The solid content of the dispersion was approx. 1 wt.-%. The PEDOT inclusions were prepared by *in-situ* oxidation of EDOT in the presence of the PVCL/PAAEM microgel particles. EDOT (0.5 g) was dissolved in 5 ml of an ethanol/water mixture (30 mol % EtOH) and the microgel dispersion was added. The reaction mixture was stirred for 1 h at 60 °C. After addition an equimolar amount of $FeCl_3$ (0.57 g) disolved in 5 ml EtOH/H_2O, the dispersion was continuously stirred for 12 h. A colour change from white to green, brown and blue could be observed. To deposit different amounts of PEDOT into the polymer microgel, the PVCL/PAAEM amount added to the reaction mixture was varied to achieve EDOT-to-PVCL/PAAEM weight ratios of 0.5, 2.5 and 5. Purification was carried out by repeated washing with water and centrifugation of the composite.

As we mentioned earlier, the synthesis of PEDOT both in the core-shell and the microgel systems was carried out in ethanol/water mixture. The addition of ethanol increased the solubility of EDOT in water. Simultaneously, the complexation of $FeCl_3$ with ethanol decreased its oxidation potential which resulted in the decrease in polymerization rate.[15] Due to the complexation effect, the conversion in the EDOT polymerization in the core-shell system was about 10%, but it also depended on the oxidant concentration, oxidant nature, temperature and ethanol content in the solvent mixture. In the case of microgel particles the conversion further decreased to ca. 1–2%, which was attributed to the hindered diffusion of EDOT into the network structure of the particles. The stability of the dispersion was not

Table 1.
Properties of thin films prepared from core-shell particles (1)...(6) and microgel composites (7)...(9).

Material	EDOT wt. ratio in the reaction	PEDOT content in composite	Film thickness	Resistance	Resistivity
		c (wt.-%)	L (μm)	R (Ω)	ρ (Ω cm)
		Core-shell particles			
(1)*	0.2	2.0	1.1	7.0×10^8	3.1×10^8
(2)*	0.5	7.0	8.0	2.1×10^7	6.7×10^7
(3)*	1.0	31.4	1.5	8.9×10^4	5.3×10^4
(4)†	1.0	26.9	4.8	5.3×10^1	1.0×10^2
(5)††	1.0	23.0	3.0	3.2×10^5	1.3×10^5
(6)†††	1.0	25.7	3.0	1.0×10^{10}	1.2×10^{10}
		Microgel composites			
(7)*	0.5	0.5	1.4	6.8×10^9	4.4×10^9
(8)*	2.5	5.0	1.7	3.3×10^8	2.6×10^8
(9)*	5.0	5.1	0.17	1.2×10^9	9.5×10^7

Oxidants: * $FeCl_3$, † $HAuCl_4$, †† $Na_3Mo_{12}PO_{40}$, ††† $(NH_4)_2S_2O_8$.

affected by the reaction conditions and was still maintained by the functional groups of polymer matrices which were introduced in the synthesis of polymer particles.[13,14] The contents of EDOT, the oxidant used and the resulting PEDOT determined by elemental analysis are summarized in Table 1.

Electric Conductance Measurements

Thin films were prepared by drop-casting from the particle dispersion onto glazed ceramic substrates with the interdigital gold electrode system. During solvent evaporation, a thin film over the electrode area was formed. Distances between the fingers of opposite electrodes were 50 μm, the thickness of the gold electrode was 1.1 μm. Resistivities ρ were calculated from the film resistance R (measured with Keithley 6517A electrometer), electrode geometrical factor l/g (l is the total length of the electrode pathway and g is the electrode distance) and film thickness L: $\rho = RlL/g$.

Results

The SEM and TEM images of the core-shell and microgel composite particles are shown in Figure 3. Two completely different particle morphologies can be seen. In the case of core-shell particles, a homogeneous and compact PEDOT shell was produced on the surface of the PS/PAAEM particles by *in-situ* polymerization of the EDOT monomer. When PVCL/PAAEM microgel particles were used as matrix for deposition of PEDOT, their porous particle structure led to the incorporation of PEDOT nanorods among polymer chains of the microgel, resulting in a different morphology compared with the core-shell structure.

As it follows from Figure 1 and Table 1, the amount of PEDOT in the particle strongly influences electric conductivities of both core-shell (1...3) and microgel (7...9) samples. The dependences of resistivities of films on the PEDOT content are shown in Figure 2. When the PEDOT content is low, resistivities of films prepared from core-shell particles are about 10 times lower than

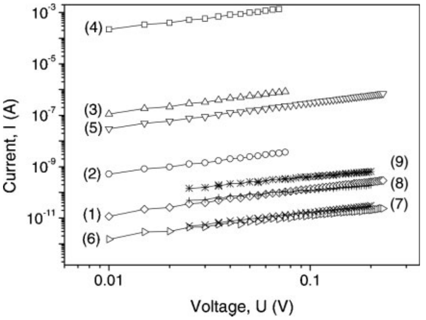

Figure 1.
Current-voltage characteristics of thin films prepared from core-shell (open symbols: (1...6)) and microgel composites (stars and crosses: (7...9)). The denoting corresponds to that in Table 1.

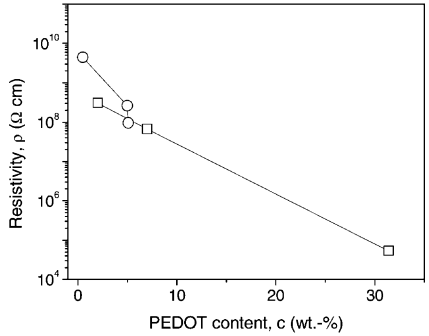

Figure 2.
The dependences of resistivities of thin films prepared from core-shell particles (squares) and microgel composites (circles). Oxidant: $FeCl_3$.

those prepared from microgel composites. This fact is understandable, because in the case of core-shell particles the conductive PEDOT layers are located on the particle surface; thus, their percolation threshold is lower than that of microgel composites, where PEDOT centers are separated by insulating chains of the PVCL/PAAEM copolymer. However, the resistivities of the two systems become almost the same as the PEDOT content approaches 5 wt.-%. Table 1 gives the summary of resistivities of the materials under study. Exceptionally low resistivity values have been measured for core-shell particles synthesized using $HAuCl_4$ as oxidation agent (line (4) in Figure 1 and Table 1). This could be explained by the presence of Au nanoparticles (AuNPs) formed by the aurate reduction simultaneously with the EDOT polymerization. Microscopy analysis (SEM, STM) indicated that AuNPs are present not only on the composite surface but also in the form of secondary particles (not shown here). The presence of AuNPs enhances an electric contact between core-shell composites and, consequently, film resistivity decreases. The other oxidation agents ($Na_3Mo_{12}PO_{40}$ and $(NH_4)_2S_2O_8$) used in this study showed a lower efficiency in producing conductive core-shell particles compared with $FeCl_3$ (see lines (5) and (6) in Figure 1 and Table 1). The resistivity achieved using $Na_3Mo_{12}PO_{40}$ was about 40 times higher and with $(NH_4)_2S_2O_8$ the resulting particles remained insulating.

Conclusion

Two polymer systems with different particle morphologies have been synthesized, one by coating PS/PAAEM latex particles with a conductive polymer layer of PEDOT and the other by modifying a microgel with PEDOT inclusions. Electric conductivities of the films based on composite core-shell and microgel particles strongly depend on the PEDOT content. Comparing the two systems, core-shell particles exhibit higher conductivity when the PEDOT content in both systems is low. This can be explained by higher percolation threshold in microgels because PEDOT nanorods are separated

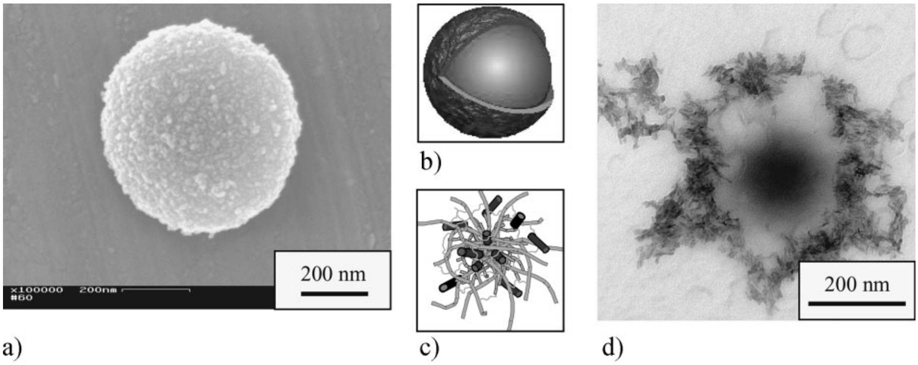

Figure 3.
SEM image of core-shell morphology (a) and its graphical structure model (b). TEM image of microgel composite particle (d) with its structure model (c).

by insulating chains of the PVCL/PAAEM copolymer. When the PEDOT content reaches about 5 wt.-%, the conductivity in both the systems becomes almost the same.

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