

Introduction of surface-modified Au-nanoparticles into the microflow-through polymerization of styrene

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Abstract

A microflow-through set-up consisting of three syringe pumps, a micromixer as well as a residence tube was used to introduce Au-nanoparticles with a hydrophobic surface into a emulsion polymerization of styrene. It was earlier shown, that this arrangement of a micromixer with a PTFE tube as residence unit is well suited for the emulsion polymerization process to obtain nanoparticles with diameters equal or smaller than 100 nm. Assemblies of Au-nanoparticles were observed after polymerization of a alkyl thiol-derived Au-nanoparticle containing styrene solution.

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Keywords: Microflow-through synthesis; Continuous emulsion polymerization; Polystyrene nanoparticles; Metal polymer composites

1. Introduction

Heterogeneous systems get more and more interest in microreaction technology. Thereby, liquid/liquid and gas/liquid flow-through systems are of particular importance due to the possibility of slug flow processes with well defined residence time, very narrow residence time distribution [1] and serial processing of samples [2]. Despite this advantages, the separated phases allows the use of the specific flow, wetting and solvation properties of different solvents and solutions. So, liquid/liquid two-phase processes give extended possibilities of handling of viscous media [3], cells [4] micro- and nanoparticles [5].

The synthesis and modification of polymers is of particular interest, but the use of microreactors for polymerization and polymer processing is connected with specific problems. So, the handling of polymers and polymerization in microchannels is difficult in case of the high and flow rate-dependent pressure drop due to the viscosity of polymer solutions or the viscosity increase during the polymerization. Although, the viscosity of polymer solutions is a serious problem it was possible to implement polymerization reactions in microreactors

[6]. A particular easy way for miniaturization is the emulsion polymerization, because the growing polymer chains are not dissolved and homogeneous distributed inside the process liquid, but are forming droplets or particles which are embedded as a colloid inside the low-viscous carrier solution. It could be shown in a previous study, that this long-known process could be transferred into a microflow-through system and lead to a continuous preparation of polymer nanoparticles [7].

Beside the formation of homopolymers, the fabrication of copolymers, block copolymers and composite materials in microreactors by a continuous process is of interest because of the possibility of precisely controlled mixing and reaction conditions. The incorporation of smaller inorganic particles into larger polymer particles is desirable in order to combine parameters of both materials. The incorporation of small metal nanoparticles is of particular interest due to their unique optical and electronic properties. The possibility of generation and handling of metal nanoparticles in microflow-through processes was already shown [8]. So, in principle flow-through two and multi step processes for the preparation of composite materials in microsystems should be realizable. Here, we report on investigations about the influence of gold nanoparticles on the flow-through polymerization process of styrene with and without a cross linking additive.

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2. Experimental

2.1. Procedure, devices and experimental arrangement

The gold nanoparticles (GNPs) were prepared in batch by reduction of 0.8 mmol/L tetrachloroauric acid trihydrate by 31.7 mmol sodium borohydride in water at ambient temperature in the presence of 12.4 mmol/L hexadecylamine (HDA) in 125 mL toluene under strong stirring. All solutions had to be prepared freshly and added in this succession: (1) dissolution of HDA in toluene, (2) addition of aqueous tetrachloroauric acid solution and (3) rapid addition of freshly prepared aqueous sodium borohydride solution. This reduction is accompanied by the transfer of the GNPs from the aqueous phase into the aprotic organic phase (toluene). After 30 min further stirring the organic phase with the GNPs was separated from the aqueous phase and cleaned by triple washing with particle-free water. After the last cleaning step the organic phase was evaporated at 60 °C till to a volume of about 20 mL. Afterwards the fivefold volume of cold ethanol was added and then the whole solution was stored over night at 4 °C. The obtained clear solution was digested from a red precipitate of GNPs. The GNPs were washed once with toluene, centrifuged and following dissolved in 100 mL toluene [9]. The ligand (0.8 mmol dodecanethiol) was added. During incubation over night at ambient temperature and under stirring the HDA shell of the GNPs is substituted by a shell of dodecanethiol (DDT).

The obtained colloidal solution of GNPs in the nonpolar solvent was then applied for the microflow-through process of polymerization. Two static micromixers (Statmix 6, IPHT Jena [10]) were used for the mixing of educts and for the formation of the emulsions. These mixers were prepared by a glass/Si/glass construction with two levels of liquid channels including a lamination of streaming liquids by splitting, deformation, twisting and recombination. The educts were actuated by syringe pumps. PTFE-tubings of 150 mm with an inner diameter of 0.3 mm were used as fluid connections from the syringes to the micromixers. Thirty-eight meter of PTFE-tube (1.0 mm inner diameter) were immersed as a residence loop in form of a tube coil inside

a thermostatic bath (Fig. 1). The resulting polymer latex was collected.

The residence time inside the micromixer was about 1 s at a volume flow rate of 27 mL/h. A residence time of about 70 min was realized in the thermo controlled tube loop at the same flow rate. It was expected, that the hydrophilic surface-modified GNPs were incorporated into the monomer droplets of the emulsion at beginning of the polymerization. Some of them could also be included in additional micelles formed of the applied surfactant. The GNPs should be exchanged between the monomer phases and the growing micelles during polymerization. In result, all lipophilic GNPs should be incorporated in the formed polymer micelles.

2.2. Characterization

In order to characterize the product, the obtained product emulsion as well as solid-like particles were investigated by UV/vis spectroscopy, centrifugal sedimentation spectroscopy as well as scanning electron microscopy (SEM). Optical spectra of GNP colloidal solution before and after surface modification as well as of resulting polymer lattices after polymerization were recorded by a UV/vis spectrophotometer (Specord 200, Analytik Jena, Germany). The size distribution of nanoparticle suspension was studied by centrifugal sedimentation spectroscopy (DSC20000, CPS Instruments, USA).

A part of formed lattices were deposited on single crystalline silicon chips in order to investigate the distribution of mate-

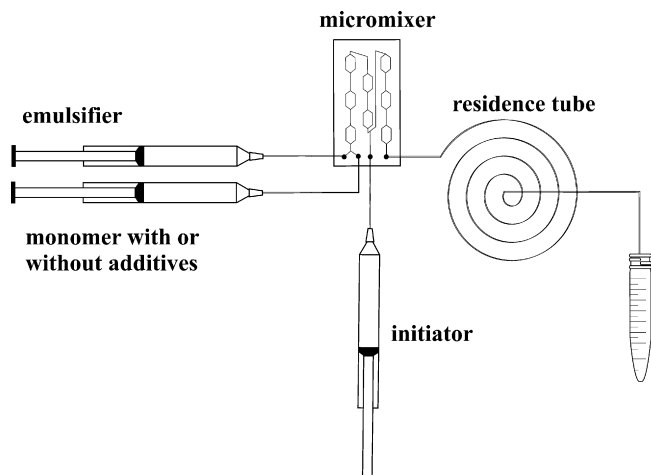


Fig. 1. Microfluidic experimental arrangement.

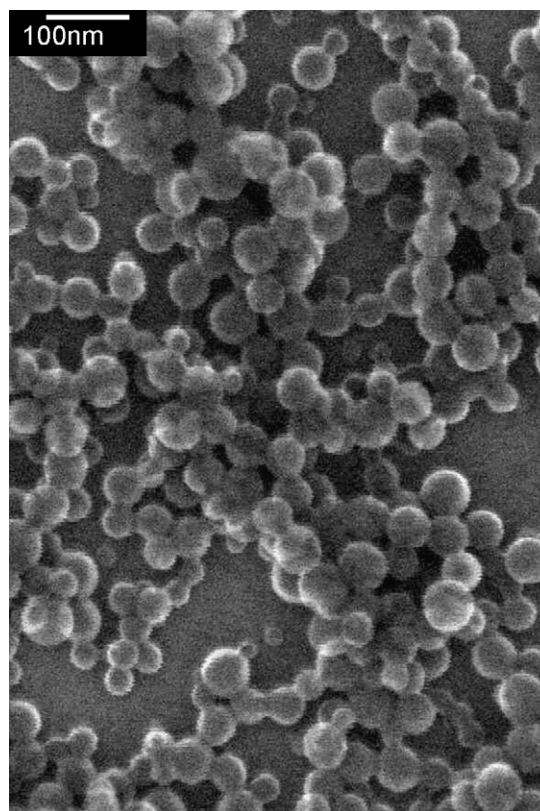


Fig. 2. Polystyrene nanoparticles, obtained by microflow-through emulsion polymerization (SEM image).

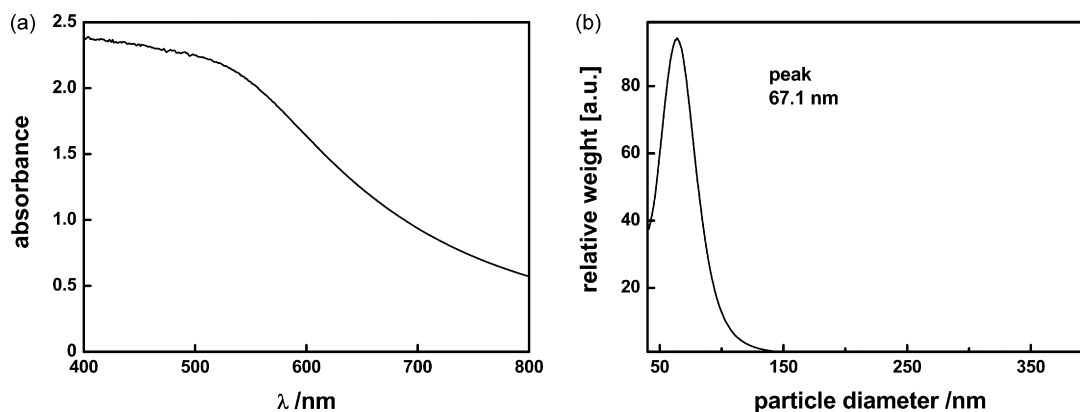


Fig. 3. Characterization of product suspensions: (a) UV/vis spectrum; (b) differential centrifuge spectra of polymer nanoparticles obtained by microflow-through process (polystyrene nanoparticles with diameters below 40 nm are influenced strongly by Brownian diffusion therefore these values are not shown in the diagram).

rial and to get a three-dimensional image of shape and size of particles. Therefore, about 3 μL of the latex was dispensed on the polished silicon surface. After short drying on air, the samples were further dried by blowing with nitrogen gas. Thereby, solid material and liquid components of low vapor pressure were deposited at the chip surface. Then, the samples were rinsed by water and solvent mixtures containing water as well as ethanol and dried again for two or three times. In result, all water soluble materials as well as low molecular weight educts and side products were removed, whereas polymer particles were kept at the surface.

A microscope (Zeiss Axioplan 2 Imaging) was used for dark field light microscopy of surface-adsorbed particles. Scanning electron microscopic images were obtained by use of a JEOL JSM6380 scanning electron microscope.

2.3. Chemicals and other materials

Tetrachloroauric(III) acid trihydrate (Carl Roth GmbH, Karlsruhe, Germany) with a purity of 99.5% and sodium borohydride (Merck KGaA, Darmstadt, Germany) with a purity of 96% were used to prepare GNPs. Hexadecylamine (Merck KGaA, Darmstadt, Germany, purity: 92%) as well as 1-dodecanethiol (Merck KGaA, Darmstadt, Germany, purity: 98%) were utilized to stabilize the GNPs. Fresh distilled styrene (Merck KGaA, Darmstadt, Germany, purity: 99%) was used for all polymerization experiments. Furthermore, distilled divinylbenzene (Merck KGaA, Darmstadt, Germany, mixture of 1,2-divinylbenzene and 1,4-divinylbenzene, purity: 95%) was used partially as cross-linker to reduce swelling of polymer nanoparticles in organic solvents. Sodium dodecylsulfat (SDS) (Merck KGaA, Darmstadt, Germany) was used as emulsifier and potassium peroxodisulfate (KPS) (Merck KGaA, Darmstadt, Germany, purity: 98%) as water soluble initiator.

3. Results and discussion

Polystyrene nanoparticles with diameters between 50 and 100 nm were obtained, if an emulsion of 0.906 g styrene together with an aqueous solution of 0.178 g SDS as well as 0.0068 g KPS was generated in the microfluidic system and then pumped

through the residence loop at 80 °C and a total flow rate of 26 mL/h. In several runs, always spherical polymer particles in the same size range were obtained (Fig. 2). The SEM images show single particles beside smaller and larger particle ensembles. In all cases, the particles possess a certain tendency of aggregation. This aggregation occurs during the adsorption at silicon surfaces and the following rinsing procedures and is due to the reduction of surfactant concentration and an increasing ability of hydrophobic interaction between the particles. This assumption is supported by the fact of rather high stability of product suspensions.

Beside ultramicroscopic imaging, the product suspension can be characterized by light microscopy as well as by optical and particle size spectroscopy. The optical spectrum (Fig. 3a) reflects the superposition of a typical absorbance spectrum of a light scattering emulsion (decreasing transmission at lower wave length due to higher scattering efficiency) with the plasmon absorption band of gold nanoparticles (around 529 nm). The centrifugal spectrum of the origin product emulsion (Fig. 3b) shows only the existence of single polymer particles with typical diame-



Fig. 4. Distribution of nanoparticles after surface adsorption of product suspension from styrene polymerization in presence of lipophilized gold nanoparticles; ensembles of gold nanoparticles embedded in a organic matrix at silicon chip surface; SEM image.

ters between 60 and 80 nm. This means that the centrifugal spectrum gives an additional information to the prevailing existence of dispersed single nanoparticles inside the origin product suspension.

The addition of metal nanoparticles leads to a certain inhibition of polymerization. So, the concentration of initiator was doubled by varying the flow rate of KPS solution. A polymerization took place in the microflow-through arrangement under these modified conditions. But, the polymer was not obtained in form of rigid nanospheres. In adsorption experiments, the product showed the formation of polymer spots at the chip surface. This behavior can be interpreted as the formation of polymers with lower molecular weight and by remaining monomer components inside the product micelles. Small bright dots were

identified inside the polymer nanospots (Fig. 4) in contrast to the polymer beads from synthesis without GNP addition, which look homogeneously in the SEM image (compare with Fig. 2). The SEM contrast of the bright spots inside polymer spots corresponds completely with the contrast of gold nanoparticles adsorbed at a silicon surface or embedded in a very thin polymer film.

The density of the GNPs inside the polymer spots is high, whereas nearly no GNPs could be detect outside polymer spots. So, it can be concluded that the polymer micelles, which are formed during the flow-through polymerization, accumulate the lipophilized GNPs. The relation between polymer micelle formation and extraction of modified GNPs by these micelles is also confirmed by a comparison of the obtained SEM images of

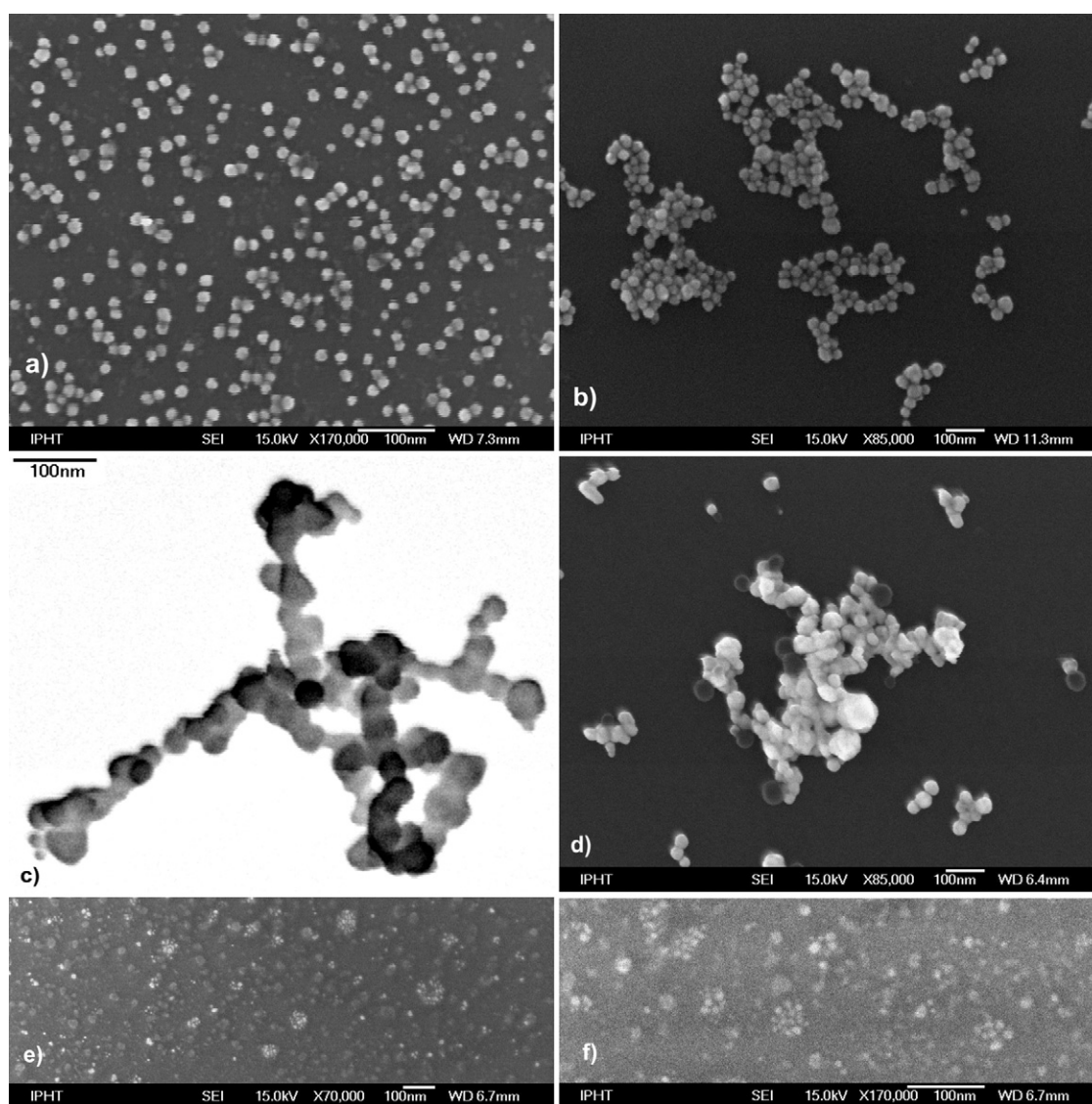


Fig. 5. Comparison between different aggregation behavior of gold nanoparticles from colloidal solutions at Si chip surfaces (SEM images): (a) preparation by reduction of tetrachloroaurate with presence of silicate (without aggregation), (b) preparation by reduction of tetrachloroaurate by ascorbic acid without further additives (with aggregation), (c) preparation by reduction of tetrachloroaurate by ascorbic acid in presence of aqueous PVA solutions (with aggregation), (d) chemical deposition of gold nanoparticles by reduction of tetrachloroaurate by ascorbic acid in presence of polystyrene nanoparticles from microflow-through polymerization in aqueous suspension, (e and f) products from introduction of lipophilic surface-modified gold nanoparticles into the microflow-through emulsion polymerization of styrene (vertical stage).

product particle adsorbates obtained under different conditions (Fig. 5).

Well dispersed single metal nanoparticles are obtained beside irregular aggregates by adsorption of product solution on chip surfaces (Fig. 5a). In some cases, an aggregation to network-like structures is observed (Fig. 5b). More complex aggregation pattern, sometimes in form of ensembles hierarchies and folded linear structures, are observed in presence of dissolved (hydrophilic) macromolecules, e.g. polyvinyl alcohol (PVA) in the colloidal gold solution (Fig. 5c). A mixed deposition of smaller GNPs between the larger polymer nanoparticles or sometimes a certain covering of polymer nanoparticles by metal particles was found, when the tetrachloroauric acid is reduced in the presence of polymer nanoparticles formed by a previous flow-through polymerization (Fig. 5d). All these adsorbate pattern differ significantly from the pattern found after the polymerization under feeding of surface-modified GNPs (Figs. 4 and 5e). All images of the adsorbates from these product liquids lead to round polymer spots with high concentration of accumulated gold particles. The images support the conclusion, that the modified gold is efficiently extracted from the monomer droplets into the polymer-containing product micelles.

4. Conclusions

The investigations have shown, that a microflow-through polymerization under presence of metal nanoparticles is possible. In result, small droplets – probably in form of micelle-like objects – containing aprotic polymer molecules as well as lipophilic gold nanoparticles were formed. The obtained material represents a nano composite of polymers and metal nanoparticles with a molecular shell. Further investigations will be addressed to the conditions of formation of rigid polymer

metal nanoparticle composites, on the introduction of different metals into the polymer material by the microflow-through polymerization, their characterization by additional methods like transmission electron microscopy and SPM techniques.

Acknowledgements

We would like to thank P. Miesen and M. Leich for experimental support, G. Mayer, J. Albert and M. Sossna from the Institute for Physical High Technology Jena (IPHT Jena) for the preparation of the micromixers. The financial support of the German Federal Environmental Foundation (DBU) is gratefully acknowledged.

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