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Complex Inorganic/Organic Core-Shell Particles by an Inverse Emulsion Technique

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Summary: Two synthetic approaches to modify the surface of inorganic particles are presented. In the first approach the inorganic particles are prepared in-situ in a confined space in inverse emulsions. The used amphiphilic statistical copolymers act not only as emulsifiers, but they also hydrophobize the remaining inorganic particles after the precipitation. This approach represents a versatile method to obtain various inorganic nanoparticles as well as more complex inorganic materials like core-multiple shell and perovskite-based nanoparticles. The second procedure uses preformed inorganic particles, as an aqueous dispersion, to modify them with surface active amphiphilic copolymers in a multicomponent solvent system. This method turns out to be a simple but highly efficient method to modify preformed inorganic nanoparticles. The particles are characterized by SEM, TEM and dynamic light scattering. The modified inorganic nanoparticles are suitable to be homogenously incorporated into a polymer matrix to form transparent nanocomposite materials.

Keywords: inorganic materials; inverse emulsion; multicomponent solvent system; nanocomposites; nanoparticles

Introduction

Hybrid organic-inorganic materials have attracted considerable attention in the past decade. The combination of two or more materials, organic or inorganic, leads to strong synergetic effects.[1–7] The incorporation of inorganic nanoparticles into polymer materials can significantly change the properties of the polymer matrix, such as stiffness[8], impact strength[9], absorption behavior[10], gas permeability[11] or refractive index[12]. The production of transparent nanocomposite materials is of great interest for industrial applications, especially for coating applications.[13] However, their preparation requires not only the control of particle size but also the homogeneous incorporation of the inorganic material in the polymer matrix.[14] The size of the incorporated particles has to be kept under 100 nm in order to obtain fully transparent nanocomposite materials. The achievement of the homogeneous distribution of the inorganic particles in the polymer matrix is still challenging. To suppress the formation of aggregates in the polymer matrix, full compatibility of the particles with the matrix is required. Numerous approaches[15] are described in the literature to modify the surface of inorganic particles in order to attain the this compatibility, e.g. the use of surfactants[16], grafting-from or -onto methods,[17,18] or emulsion techniques.[19,20] However, each of these methods suffers from certain drawbacks. Either they are synthetically demanding or they show a high tendency for the formation of larger aggregates, which leads to segregation of the particles after incorporation into a matrix.[21–23] The

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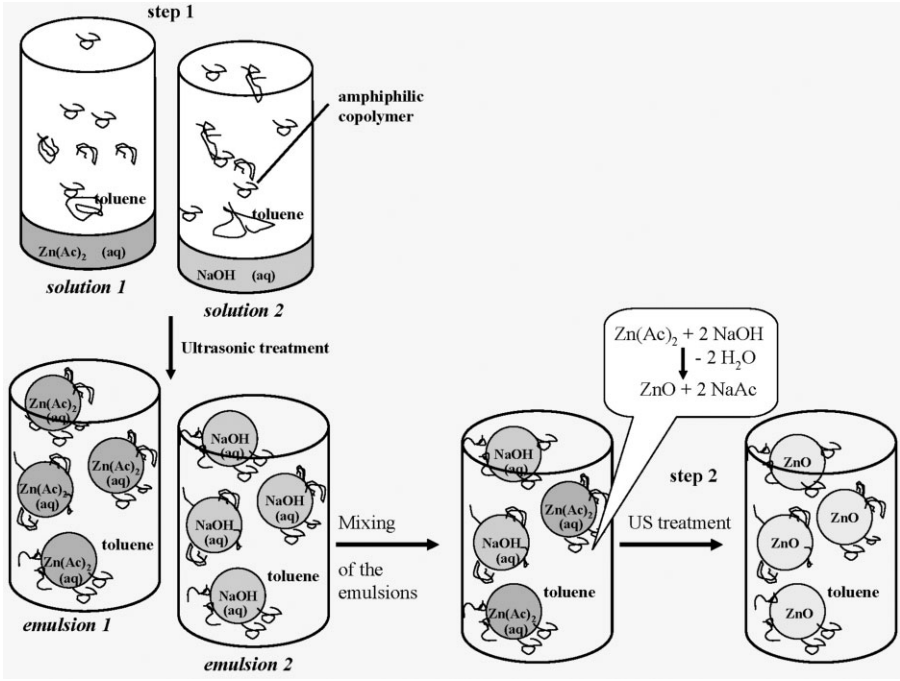
formation of aggregates is due to the high surface energy of the particles and their tendency to agglomerate. In addition, the hydrophilic particles and the hydrophobic polymer are not compatible in nature, which has to result in poor interfacial bonding.

This work reports two approaches to prepare surface functionalized inorganic particles overcoming these problems. The first approach (**method 1)** describes the use of statistical amphiphilic copolymers as surfactants in the preparation of inorganic nanoparticles in an inverse emulsion process.[24–27] This process offers a broad variety of nanosized inorganic particles, as metal oxides, chalcogenides, carbonates or free metals can be prepared from a saturated salt solution by a precipitation process. Furthermore, more complex inorganic-organic nanoparticles are accessible by this process, such as core-multiple-shell (ZnO-SiO_2-polymer particles) or perovskite-based particles. The second method (**method 2**) depicts the quantitative transfer of readily available inorganic particles from their aqueous dispersions into an unpolar environment by using a latent miscible multicomponent solvent system in combination with surface active amphiphilic copolymers.[28,29] Both methods allow the homogeneous incorporation of the functionalized particles into various polymer matrices.

Results and Discussion

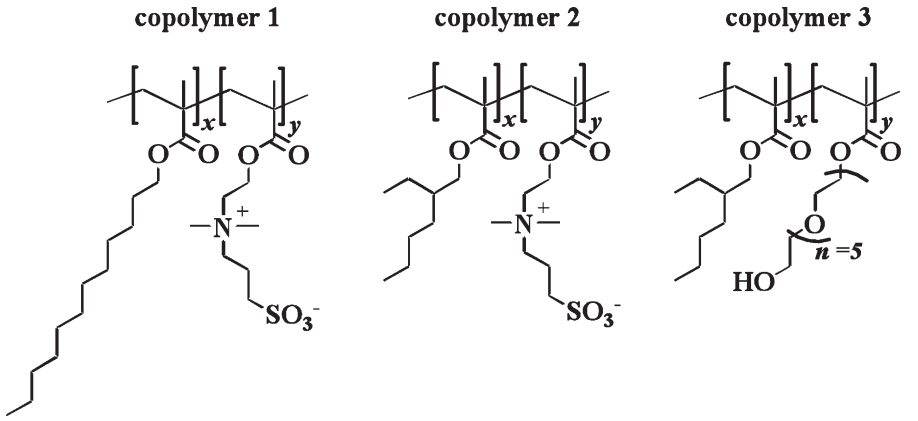
Surface Functionalization of Inorganic Particles by Method 1:

The first approach to synthesize hydrophobized inorganic nanoparticles is presented in Scheme 1. This method can be described as a four step synthesis. In step 1 two inverse emulsions were prepared from an aqueous solution of an inorganic salt and a



Scheme 1.

Preparation of inorganic particles, using an inverse emulsion to prepare surface functionalized inorganic particles by a precipitation process.



Scheme 2.
Amphiphilic copolymers used as surfactants and surface active compounds in **method 1**.

precipitation agent, e.g. $Zn(OAc)_2$ as the inorganic salt and NaOH as the precipitation agent to form ZnO particles, by ultrasonification of the aqueous salt solutions with a solution of the amphiphilic copolymer in toluene (Emulsion 1 and Emulsion 2). The amphiphilic copolymer serves as surfactant to stabilize both emulsions. In step 2 the two emulsions were combined and treated by ultrasound to ensure an appropriate mixing. The inorganic particles are formed inside the droplets, by the precipitation process. After removal of the solvents, the raw particles were isolated, purified by washing with water and in the final step redispersed in toluene.

The applied amphiphilic copolymers in this approach are displayed in Scheme 2. The copolymers **1**-**3** contained 95 mol-% of the hydrophobic monomers lauryl methacrylate (LMA), respectively 2-ethylhexyl methacrylate (EHMA) and 5 mol-% of the corresponding hydrophilic monomer.

Various inorganic particles were synthesized by this method, as listed in Table 1, which indicated the broad versatility of this process.

This process is not only useful for precipitation processes, but also to form metallic nanoparticles like Cu[26] and Ni[26] by means of reduction (Table 1).

The properties of the formed nanoparticles is illustrated in particular for ZnO due to the importance for the production of UV protective coatings, as ZnO shows a strong absorption at $\lambda < 400$ nm. As transparency of such coatings is required, any scattering effects, resulting from large ZnO particles, have to be avoided, requiring particle sizes below 100 nm. After the redispersion of the particles formed by the herein presented method in toluene, their characterization was conducted by X-ray diffraction (XRD), dynamic light scattering (DLS) and electron microscopy (TEM/SEM). XRD confirmed the existence of ZnO in a hexagonal crystallographic structu re of wurzite. DLS

Table 1.
Chemical reactions for the generation of the inorganic particles in **method 1**.

Reagent 1	Reagent 2	
$Zn(CH_3COO)_2$	$+2NaOH$	$\rightarrow$**ZnO**[24,26] $+ H_2O + 2Na(CH_3COO)$
$Cd(NO_3)_2$	$+Na_2S$	$\rightarrow$**CdS**[26] $+ 2NaNO_3$
$Mg(NO_3)_2$	$+(NH_4)_2CO_3$	$\rightarrow$**MgCO$_3$**[26] $+ 2NH_4NO_3$
$2Cu(NO_3)_2$	$+NaBH_4 + H_2O$	$\rightarrow 2$**Cu**[26] $+ NaNO_3 + 3HNO_3 + 2H_2 + H_3BO_3$
$2NiCl_2$	$+NaBH_4 + H_2O$	$\rightarrow 2$**Ni**[26] $+ NaCl + 3HCl + 2H_2 + H_3BO_3$

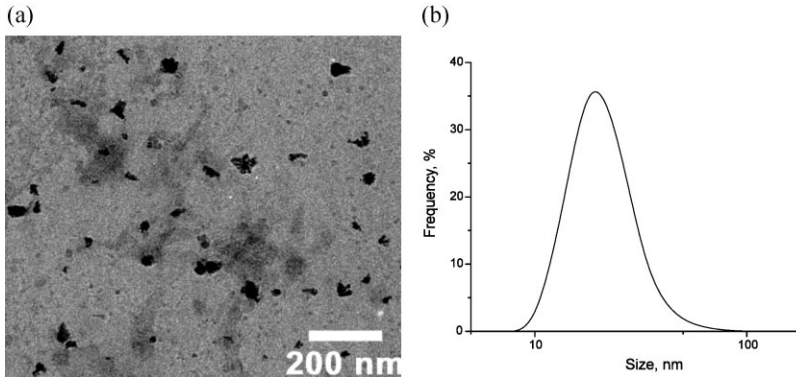


Figure 1.
a) TEM image of the ZnO particles, obtained after redispersion of the ZnO particles in toluene. b) Particle size distribution of the redispersed ZnO particles in toluene, measured by DLS.

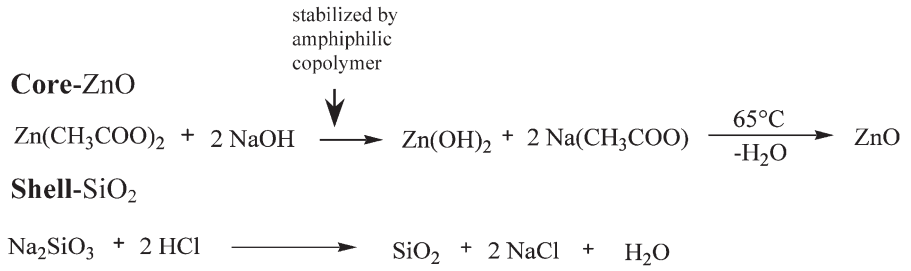
and TEM measurements (Figure 1) of the ZnO particles indicated a narrow monomodal size distribution and an average particle size of approx. 20 nm.

The possibility to redisperse these particles in an organic solvent without any further aggregation evidenced, that the amphiphilic copolymer remained adsorbed on the surface of the inorganic particles after the removal of the solvent. Furthermore, it revealed the presence of a polymeric shell surrounding the inorganic core protecting the particles from further aggregation in an unpolar environment. Incorporation of these functionalized ZnO particles in various polymer matrices (polymethylmethacrylate and poly(2-ethylhexyl methacrylate) lead to nanocomposite with full transparency in the range of $\lambda = 400$–800 nm and a sharp absorption below $\lambda = 400$ nm (transmittance $< 40\%$).

To further demonstrate the versatility of **method 1**, complex inorganic-organic nanomaterials were prepared. The incorporation of the photo catalytically active ZnO into a polymer matrix to produce UV protective coatings could result in the destruction of the matrix material.[30] Embedding the ZnO core inside a silica shell might resolve this problem. Applying the inverse emulsion technique, the ZnO core was enclosed in a SiO_2 shell, bearing a complete compatibilization of this ZnO/SiO_2 core with a polymer matrix due to the presence of copolymer **3** acting as a polymer shell around the multiple inorganic cores. The synthesis followed the protocol established for pure ZnO nanoparticles. After precipitation of the ZnO core inside the droplets of the inverse emulsion, the silica shell was formed by the subsequent addition of a third emulsion consisting of aqueous sodium silicate in toluene (Scheme 3).

The diffraction profile of the core-multiple-shell particles showed the typical reflections for hexagonal ZnO and a broad featureless halo, assigned to amorphous silica (Figure 2a).

A TEM image of the resulting core-multiple-shell particles (Figure 2b) clearly exhibited their core-shell structure, based upon different scattering power depending on the atomic number of zinc and silicon (Figure 2b). The completely redispersable particles showed a single core surrounded by a silica shell with particle sizes in the range of 20–40 nm. The DLS data of the redispersed particles in toluene yielded two maxima at 18 nm and 180 nm. The difference in the particle size maintained by TEM and DLS was due to the invisibility of the polymer shell in TEM. Therefore, the particle size in a TEM micrograph appeared smaller than the actual hydrodynamic diameters measured by DLS. The swelling of the polymer shell and the surrounding solvent further increases



Scheme 3.
Preparation of the core-multiple-shell particles (ZnO-SiO_2-polymer).

the value given by DLS. However, a slight tendency towards aggregation of the particles also leads to the higher values for the particle size by DLS.

In addition to core-multiple shell nanoparticles, it is also possible to generate perovskite-based nanoparticles by this inverse emulsion methodology. These materials are important due to their extraordinary dielectric properties and are widely used in non-linear optics or capacitors.[31] In case of hydrophobized perovskite-based nanoparticles, one emulsion consists of a mixture of hydrolyzed titanium (IV) chloride and barium or strontium chloride and the diluted amphiphilic copolymer. The addition of a second inverse emulsion carrying a very strong base (e. g. sodium hydroxide) in the water droplets resulted in the precipitation of $BaTiO_3$ or $SrTiO_3$ nanoparticles inside the droplets.

The X-ray diffraction patterns of these nanoparticles verified the perovskite structure of $BaTiO_3$ as well as $SrTiO_3$ without any by-products.

The size and the size distributions of these perovskite nanoparticles were investigated by DLS and scanning electron microscopy (SEM) (Figure 3).

Regarding the fact, that the polymer shell is not visible in the SEM images, the DLS measurements yielded larger particle sizes. In case of $BaTiO_3$ the observable aggregates in the SEM images were caused by the sample preparation via drop casting. This results in larger, irregular particles with a broader size distribution (Figure 3). In case of $BaTiO_3$, the hydrodynamic

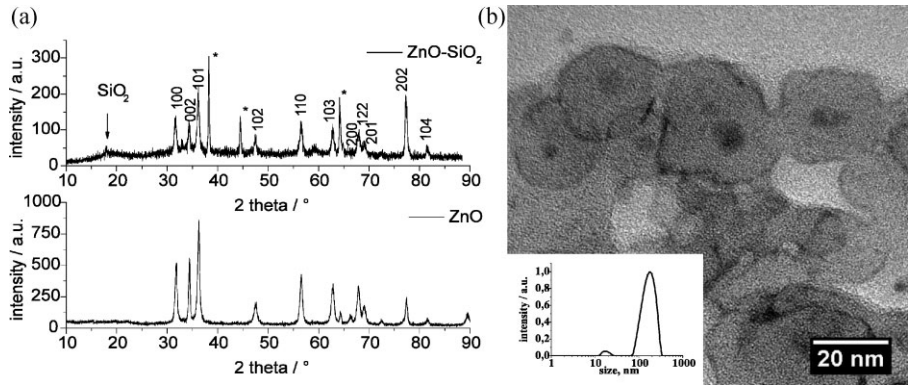


Figure 2.
a) X-ray diffraction patterns (Cu K_α radiation) of the synthesized core/shell ZnO/SiO_2 and pure ZnO nanoparticles (* aluminium support). b) TEM image and DLS of the ZnO-SiO_2-polymer particles, obtained after redispersion of the core-multiple-shell particles in toluene.

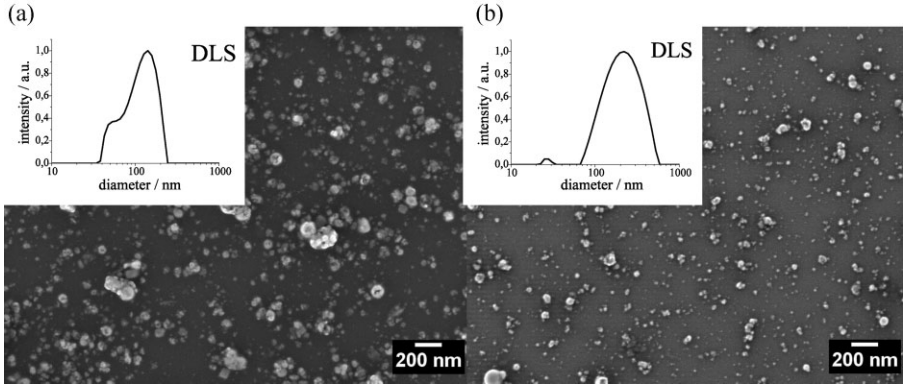


Figure 3.
SEM images of the samples (Si support, voltage a, 3 kV and b, 1 kV) and DLS of a) $BaTiO_3$ and b) $SrTiO_3$ dispersions, obtained after refluxing of 32 mg of the dried $BaTiO_3$ or $SrTiO_3$ powder in 20 ml toluene for 24 h.

diameter of the particles is approx. 160 nm which is in good agreement with the particle size calculated from the SEM image. The majority of the $SrTiO_3$ particles bear a hydrodynamic radius of approx. 250 nm. For both perowskite-based nanoparticles ($BaTiO_3$ and $SrTiO_3$) slightly bimodal particle size distributions were obtained. The size distribution of the $BaTiO_3$ particles showed a small shoulder towards smaller particle sizes, whereas in case of $SrTiO_3$ particles a second peak at about 25 nm appeared in the size distribution.

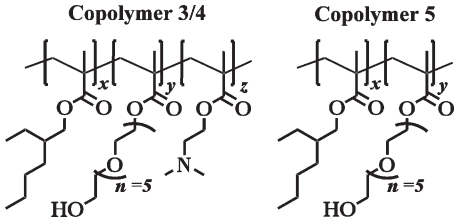
The synthesis of hydrophobized particles via an inverse emulsion technique has been reported for dense metal oxide, sulfides, carbonates and also metal nanoparticles. [24,26,27] More complex inorganic materials such as barium- and strontium based-perovskites and core-shell ZnO-SiO_2 nanoparticles are also accessible. As the post-hydrophobization of already existing particles will remain a challenge, the present approach offers a very fast and efficient method for obtaining functionalized nanoparticles. The inexpensive and easily accessible statistical amphiphilic copolymers, generally used as stabilizers, make this process attractive for industrial applications, especially when focusing on nanocomposites.

Surface Functionalization of Inorganic Particles by Method 2

Opposite to the first approach, the second method starts from preformed inorganic particles, since numerous inorganic nanoparticles are commercially available as aqueous dispersions. As a representative example for this method, an aqueous dispersion of SiO_2 nanoparticles was used (average diameter of the SiO_2 particles approx. 10 nm). The surface active amphiphilic copolymers, which were applied to functionalize the SiO_2 particles, were prepared by free radical polymerization of (EHMA), poly(ethylene oxide)methacrylate (PEOMA) and 2-(dimethylaminoethyl)methacrylate (DMAEMA) in various compositions (Table 2, Scheme 4).

Table 2.
Composition of the statistical amphiphilic copolymers used in method 2.

	EHMA [mol-%]	PEOMA [mol-%]	DMAEMA [mol-%]	M_n [$g \cdot mol^{-1}$]	PDI
Copolymer **3**	82	7	11	10300	1,6
Copolymer **4**	87	7	6	10600	1,6
Copolymer **5**	90	10	—	7100	1,7



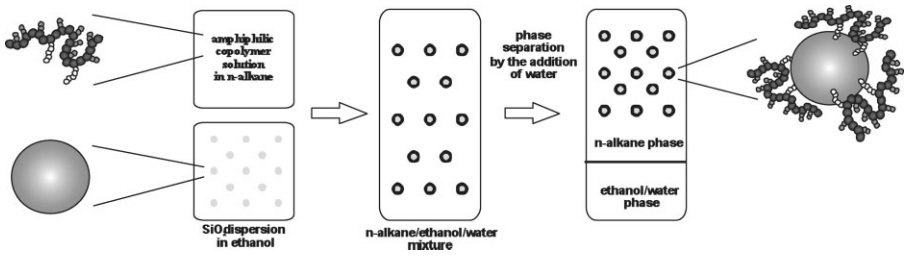
Scheme 4.
Statistical amphiphilic copolymers used as surface active compounds in **method 2**.

The surface functionalization of the SiO_2 particles was carried out in a multicomponent solvent system, which consisted of an unpolar solvent (*n*-alkane), a semi polar solvent (ethanol) and water (Scheme 5). The alcohol was vital in this approach, as it serves as a compatibilizer for the immiscible alkane and water.

The utilized surface active amphiphilic copolymers had to fulfill a basic requirement: solubility in the unpolar phase as well as in the solvent mixture. Therefore the amount of EHMA and PEOMA had to be adjusted in order to maintain solubility in the alkane and at the same time carrying a suitable amount of PEO anchor groups to achieve their necessary interaction with the surface of the SiO_2 nanoparticles.

The functionalization of the inorganic particles in such monophasic systems offers the possibility to isolate the resulting surface functionalized/hydrophobized particles in the unpolar phase by a subsequent phase separation process as illustrated in Scheme 5. This phase separation can be induced by changing the volumetric ratio of the solvents used. After dissolving the amphiphilic copolymers in the unpolar phase, this solution was combined with the aqueous dispersion of the SiO_2 particles, which had been preliminarily diluted with the alcohol. As a result, a clear monophasic solution was formed. After inducing the phase separation by increasing the amount of water, the functionalized SiO_2 particles were exclusively present in the unpolar phase. The functionalized SiO_2 particles were isolated by removing the polar phase, and were fully redispersible in common organic solvents without any further aggregation. DLS as well as SEM measurements of the redispersed particles (Figure 4) demonstrated single, non-aggregated particles as well as the fact that no agglomeration of the SiO_2 particles during the hydrophobization or the redispersion occurred.

The surface functionalized SiO_2 nanoparticles were incorporated into a polyurethane matrix. Polyurethane was chosen due to its relevance in industrial coating applications, e.g. in automotive lacquers.[32] The polyurethane was formed from a



Scheme 5.
The functionalization of inorganic nanoparticles in a multicomponent solvent system is a two step procedure. The quantitative transfer of the hydrophilic inorganic nanoparticles into the unpolar phase is achieved after the phase separation. The aqueous dispersion of SiO_2 nanoparticles was first diluted with ethanol before mixing with the copolymer solution. The role of ethanol is to suppress the miscibility gap between the unpolar phase and the aqueous dispersion of the particles. Further addition of water compensates this effect and leads to a phase separation.

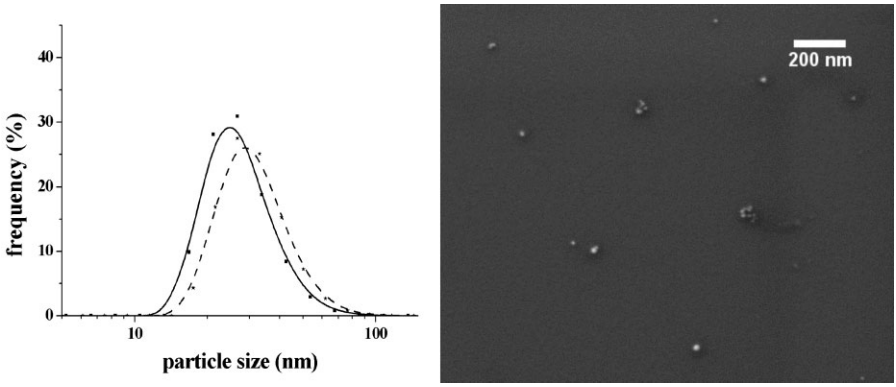


Figure 4.
Size distribution, obtained by dynamic light scattering, of the hydrophobized SiO_2 particles after phase separation (black curve) and after redispersion in n-heptane (dash-dot curve) using copolymer **3**. The SEM image shows the particles after redispersion.

commercially available two component system from Bayer Materials Science. The system consisted of hexamethylene diisocyanate derivatives (DD 3390 BA/SN) and a polyesterpolyol (DP 680 BA). To prevent any aggregation of the SiO_2 particles in the polyurethane matrix, a suitable interaction between the functionalized particles and the matrix was necessary. The used copolymer **5** provides no interaction between the particles and a PU matrix, therefore the third monomer DMAEMA was introduced in the amphiphilic copolymers. DMAEMA is capable to establish hydrogen bondings to the polyurethane matrix, offering the mandatory interaction. Transparent polyurethane/SiO_2 nanocomposites were formed only in case copolymer **3** was used to modify the SiO_2 particles as indicated by UV/VIS spectroscopy (Figure 5).

The polyurethane/SiO_2 nanocomposite films were analyzed by TEM to examine the homogeneity of the distribution of the SiO_2 particles in the matrix (Figure 5). In case of copolymer **3**, with the highest amount of DMAEMA, a homogeneous distribution of the particles was found within the polyurethane matrix. Additionally, the particle size was kept below 100 nm (Figure 5). Using copolymer **4**, with a lower amount of DMAEMA, to modify the SiO_2 particles, aggregation of the particles occurred. The aggregates were in the range of 200 to 500 nm in diameter (Figure 5B). For copolymer **3**, which contains only EHMA and PEOMA, aggregates in the range of several micrometers were formed in the polyurethane matrix, leading to opaque nanocomposite films (Figure 5).

These results supported our concept of a trifunctional surface active amphiphilic copolymer for the compatibilization of the inorganic particles with a polymer matrix. PEOMA provided the interaction of the amphiphilic copolymer with the SiO_2 surface, EHMA imparted the hydrophobicity of the particles and DMAEMA anchored the particles to the polymer matrix. In the absence of the monomer DMAEMA, a significant aggregation of the particles arised. After introducing the additional hydrophilic monomer DMAEMA the degree of aggregation was decreased and if the concentration of DMAEMA exceeded a certain threshold, aggregation of the SiO_2 particles was completely suppressed.

It should be noted, that other inorganic particles than SiO_2 could be functionalized by this method. However, a fine tuning of the amphiphilic copolymers, in regard to the surface characteristics of the inorganic particles, was necessary.

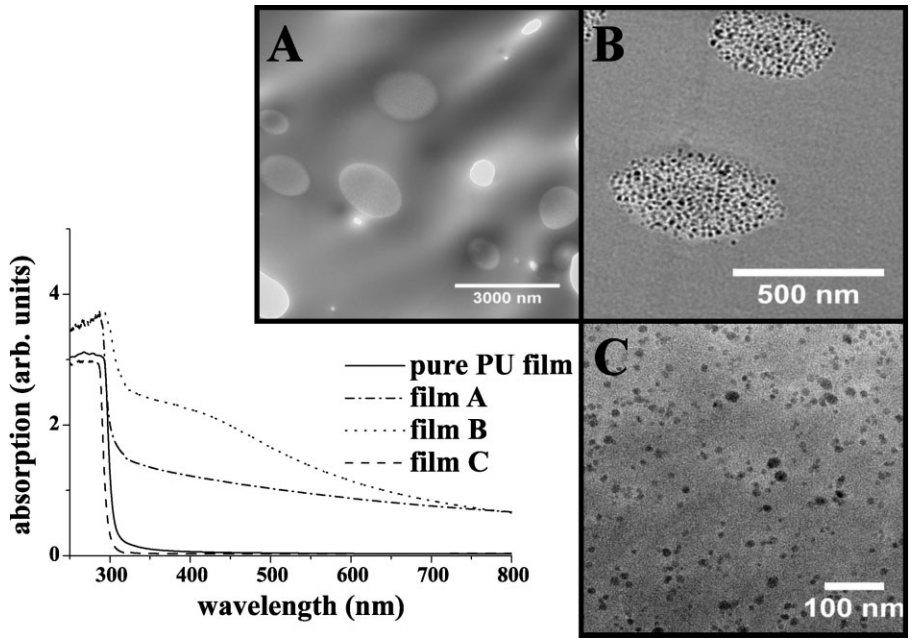


Figure 5.
UV/VIS spectra of the polyurethane/SiO_2 nanocomposites. Full transparency is observed only in case of copolymer **3** (dashed curve). Opaque polyurethane/SiO_2 nanocomposite films are observed if copolymer **4** (dash-doted curve) or copolymer **5** (doted curve) are used as emulsifiers for SiO_2. The thickness of these films is in the range of 300 to 500 μm. The black curve shows the UV/VIS spectra of a polyurethane film without any functionalized particles.

Conclusion

Two simple and highly efficient methods to functionalize inorganic nanoparticles have been developed. The main differences between these two approaches are the *in-situ* generation of the particles in an inverse emulsion versus the use of preformed inorganic particles.

The first method (**method 1**) generated the inorganic particles *in-situ* in an inverse emulsion by a precipitation process. The applied amphiphilic copolymers served as surfactants in these inverse emulsions as well as surface active compounds to modify the inorganic particles. As demonstrated, this method gave rise to a broad variety of inorganic particles, such as metal oxides, chalcogenides or free metals. The concept of the inverse emulsion technique had been successfully extended to more complex inorganic structures such as core-multiple-shell or barium- and strontium based perovskite nanoparticles.

In contrast to the first method, the second one (**method 2**) starts from preformed inorganic particles to functionalize these particles with amphiphilic copolymers. The key issue of this approach was the use of a multicomponent solvent system. These systems contained polar and unpolar solvents and were optimized to functionalize the hydrophilic particles with surface active amphiphilic copolymers in a homogeneous phase and prevent aggregation of the particles. This approach allowed the functionalization of readily available aqueous dispersions of inorganic particles in a simple and highly efficient way. It has also been demonstrated, that this approach tolerated the introduction of multiple functionalities in the amphiphilic copolymers, which were necessary for the homogeneous incorporation of the functio-

nalized particles into polymer matrices. This has been shown for the incorporation of SiO_2 particles into a polyurethane matrix. By this method, a versatile technique for the functionalization of inorganic particles, starting from their aqueous dispersions, has been presented.

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