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ORIGINAL CONTRIBUTION

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The formation of hydrophobic inorganic nanoparticles in the presence of amphiphilic copolymers

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Abstract The presented paper describes a novel procedure for the preparation of inorganic nanoparticles and their surface functionalization in situ dedicated to an application in technical polymers. Using an inverse emulsion technique and amphiphilic block or statistical copolymers as stabilizers, a broad variety of nanoparticles such as ZnO, CdS, $MgCO_3$, Ni, or Cu can be prepared. The amphiphilic polymers serve not only as surface active compounds in the emulsion but also to hydrophobize the inorganic particles as they remain adsorbed on the surface after the precipitation. As a consequence of the high degree of surface coverage by polymer chains, organic solvents are able to redisperse these particles in the aggregate free manner. The utilization of the block copolymers instead of statistical copolymers resulted in the formation of the particles, which were larger in size and possessed a much broader size distribution. The chemical nature of the adsorbed polymer layer on the particle surface is crucial to the preparation of polymer nanocomposites. The primary goal of this contribution is to demonstrate the universality of such a one-pot synthetic procedure, which was found to be relevant for industrial use.

Keywords Nanoparticles · Amphiphilic copolymers · Miniemulsions · Nanocomposites

Introduction

One of the most promising developments in the field of construction materials is the introduction of nanocomposites [1]. Even if the number of applications is still limited and focused on materials containing silica, a great future for these materials is predicted, as one can expect various synergistic effects from the combination of inorganic and organic materials [2–13]. As the polymer composite materials are inherently multiphase systems, a major drawback during their design is to achieve a full compatibility between the components. While preparing a polymer organic/inorganic nanocomposite, the compatibility is an important but not sufficient requirement. The inorganic phase must possess a polymer layer, which is able to entangle with the chains of the given polymer matrix [14]. Moreover, as the melt extrusion is the common way for the preparation of polymer composites, the properties of the surface-bound polymer layer must be carefully adjusted for homogenous particle incorporation during the extrusion process.

Many attempts have been described in the literature to overcome this challenge, all based on the hydrophobization of the inorganic surfaces [15–23]. These approaches can be divided into two different categories: the adsorption of surfactants onto already prepared particles and in situ functionalization during the particle formation. The synthesized particles are already successfuly applied in special high-price applications such as nanocomposites containing quantum dots or materials in photovoltaic, where very narrow distributed and well-defined particles are required and processing by film formation is used [24–27].

However, all these processes have various drawbacks for the preparation and processing of nanocomposites based on technical polymers such as PMMA, styrene etc. As in many cases, the particles are to costly, the dispersion in the matrix is not complete, or the hydrophobization is not stable during the extrusion. For example, in processes of the first category, preformed inorganic particles, which are prepared by hydrolysis or pyrolysis, are typically used [28–30]. These processes yield only particles with very broad size distributions. As they are aggregated, they have to be separated from each other by energy-consuming stirring, milling, or ultrasonication prior to the adsorption of the surfactants. The amphiphilic compounds used are typically fatty acids or long-chain alkylsulfonates. However, the bonding is relatively weak and desorption occurs not only during processing but also during the aging process. Furthermore, large amounts of fine dusts are produced, which are considered to be environmentally dangerous.

In the second approach, the particles are formed via a precipitation process in an inverse emulsion using low molecular organic surfactants as stabilizing compounds [15, 31]. Although these particles have a hydrophobic surface, full compatibility is not achieved. This can be attributed not only to the desorption of the surfactant but to the insufficient adhesion between the polymeric matrix and the surface-bound alkyl chains as well. To overcome such problems, various amphiphilic block copolymers have been applied in the inverse emulsion process [32]. Due to the adsorbed polymer chain, not only stronger adhesion interactions with the polymer matrix are expected, but also a more stable adsorption of the polar part on the surface of the inorganic particles. However, the block copolymers are very costly, and due to their complex phase behavior, it is sometimes difficult to obtain well-defined micelles [22, 33].

Recently, we have shown that in the presence of easily accessible amphiphilic statistical copolymers, ZnO nanoparticles of narrow size distribution can be obtained in inverse emulsion from zinc acetate and NaOH [34]. The obtained particles are completely hydrophobic and can be perfectly redispersed in organic media. These particles were also found to be homogeneously incorporated in PMMA as UV protector. The obtained films, featured by UV adsorption, were highly transparent in the region between 400 and 800 nm.

The primary goal of this study is to extend this work and to demonstrate the universality of this approach. By using the inverse emulsion technique along with easy accessible amphiphilic copolymers, a cheap and widely applicable method for the preparation of different core-shell inorganic/organic hybrid nanoparticles with well-defined size characteristics is presented. A comparative analysis of statistical and block copolymers as stabilizers of the emulsions is performed. The utilization of the amphiphilic copolymers as emulsion stabilizer allows an in situ hydrophobization of various inorganic particles.

Experimental part

Materials and analytical methods

Ethylhexylmethacrylate (95% purity) and dimethylaminoethylmethacrylate (97% purity), toluene, chloroform, AIBN, 1,3-propanesultone (97% purity), LiCl (99% purity), $NaBH_4$ (99% purity) and $Cd(NO_3)_2$* $6H_2O$ (98% purity) were purchased from Aldrich. $TiOCl_2$ solution (~15% Ti) in 37% w/w HCl was obtained from Fluka; $Cu(NO_3)_2$ was obtained from Merck. Monomers were distilled in vacuo ($5*10^{-1}$ mbar) before polymerization. Dry tetrahydrofuran was purchased from Acros. AIBN, 1,3-propanesultone and inorganic compounds were used as received.

NMR measurements were performed on a Bruker 250 spectrometer. IR spectra were recorded on a FT-IR spectrophotometer Nicolet-730. GPC measurements were performed on a chromatograph, equipped with a set of SD+ columns (MZ-Analysentechnik Mainz, Germany). THF was used as eluent. Molecular weights were calculated in respect to PMMA standards. For the preparation of the emulsions, a Brandson-250D sonifier, operating at a frequency of 20 kHz, was used. Thermogravimetric analysis was performed on a Mettler TGA851e apparatus. The measurements were carried out under nitrogen and heating rate of 10 K/min. The particle size was determined by means of electron microscopy on a transmission electron microscope Zeiss EM-902 and scanning electron microscope LEO 1530 Gemini as well as by dynamic light-scattering on a Zetasizer Malvern 3000.

Synthesis of amphiphilic copolymers

The detailed description of the synthesis of the statistical copolymer ***1*** as well as block copolymer ***2*** of ethylhexylmethacrylate (HexMA) and dimethyaminoethylmethacrylate (DMAEMA), depicted in Fig. 1, can be found elsewhere [35, 36].

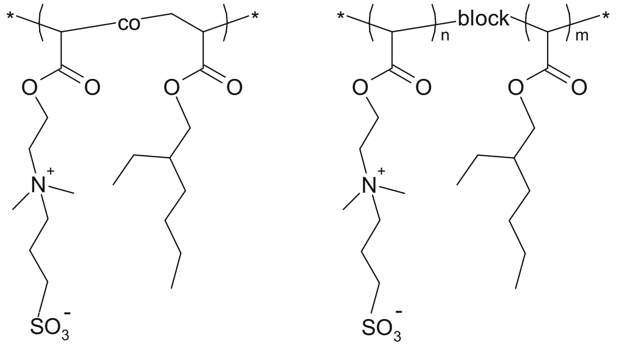

Fig. 1 Chemical structures of the amphiphilic copolymers used in this study

The statistical copolymer ***1*** was obtained by free radical copolymerization of a mixture of HexMA and DMAEMA in toluene. The polymerization was triggered by AIBN and carried out at 70°C. The block copolymer ***2*** was synthesized by living anionic polymerization, preformed in THF at −78°C. A mixture of diphenylethylene and *sec*-butyllithium was utilized as initiator. The obtained copolymers were purified by precipitation in methanol. For the conversion of the tertiary amine moieties into sulfobetain groups, the copolymers were reacted with 1,3-propanesultone in $CHCl_3$at 66°C. Table 1 summarizes the characteristics of the amphiphilic copolymers used in this study.

Preparation of emulsions and particles

The detailed procedure for particle preparation was described in our recent publication [34]. Two solutions, each containing 100 mg of the synthesized copolymer (***1*** or ***2***) in 11.7 g of toluene, were prepared. Two emulsions (Emulsion 1 and Emulsion 2) were obtained by addition of the corresponding aqueous phases to the toluene solution. (see Table 3). Emulsion 1 contains a salt, which is a precursor (further referred to as Reagent 1) of the inorganic solid being generated. Emulsion 2 contains the second reagent (referred to as Reagent 2), which is necessary for the precipitation. The obtained mixtures were stirred for 30 min at 1,000 rpm, followed by the sonication (power 70 W) for 3 min. Afterwards, both emulsions were combined and again treated with ultrasound (power 70 W) for 3 min. The solvents, water and toluene, were evaporated at 60°C under reduced pressure (100–150 mbar). The obtained solid was dried in vacuo (1×10^{-2} mbar), washed with water to remove side products and other possible impurities and dried in vacuo again. The particles were redispersed by refluxing 32 mg of the dried particles in toluene for 1 day. Inorganic particles such as ZnO, CdS, $MgCO_3$, Cu, and Ni were synthesized by this procedure. For formation of the inorganic phase, the following chemical reactions were used (Table 2).

Table 1 Molecular weight and composition of the synthesized copolymers

Copolymer	Copolymer type	Mn[a]	Mw[a]	Charged groups (sulfobetain), mol%[b]
1	Statistical	9,500	15,700	16
2	Block	14,300	15,900	15

[a] Measured by GPC. PMMA standards, eluent THF
[b] Determined by ^{1}H NMR

Table 2 Chemical reactions for the generation of the inorganic solids

Reagent 1	Reagent 2	
$Zn(CH_3COO)_2$	$+2NaOH$	$\rightarrow ZnO+H_2O+2Na(CH_3COO)$
$Cd(NO_3)_2$	$+Na_2S$	$\rightarrow CdS+2NaNO_3$
$Mg(NO_3)_2$	$+(NH_4)_2CO_3$	$\rightarrow MgCO_3+2NH_4NO_3$
$2Cu(NO_3)_2$	$+NaBH_4$	$+3H_2O\rightarrow 2Cu+NaNO_3+3NHO_3 +2H_2+H_3BO_3$
$2NiCl_2$	$+NaBH_4$	$+3H_2O\rightarrow 2Ni+NaCl+3HCl +2H_2+H_3BO_3$

Results and discussion

To show the broad versatility of the method, those particles were chosen which can be generated by different precipitation procedures. Therefore, a broad variety of particles was synthesized in the presence of the amphiphilic statistical copolymer ***1***. The characteristics of the obtained particles were then compared with those obtained by the same process, but by using the block copolymer ***2***.

Particles prepared with statistical copolymer ***1***

ZnO particles

It is important to note that many nanocomposite systems, described in the literature, are based on metal oxides. [1, 3, 9] Typically, they are prepared by hydrolysis of the corresponding metallorganic compounds. From the other side, one of the most facile ways to obtain such materials is the decomposition of the corresponding hydroxides. As an example of the preparation of this type of inorganic materials, we investigated the synthesis of ZnO. Nanocomposites containing ZnO are especially interesting for making UV protective films and coatings due to its strong UV absorption [37]. As such nanocomposites are mainly applied as coatings, they have to be highly transparent, and scattering due to the presence of larger ZnO particles has to be strictly avoided. Therefore, it is mandatory to have ZnO particles smaller than 100 nm and perfectly redispersable in a polymeric matrix. We generated the particles by the inverse emulsion technique, combining a $Zn(CH_3COO)_2$ solution with aqueous NaOH in the presence of the statistical copolymer ***1***. It is important to say that the reaction between an inorganic salt and a base (e.g., NaOH) is a general way towards metalloxides.

The formed particles were isolated and dried at 60°C *in vacuo* to trigger the formation of ZnO (see Experimental part).

Table 3 Compositions of the emulsions and characteristics of the prepared inorganic particles

Sample	Inorganic material/polymer	Aqueous phase of emulsion 1		Aqueous phase of emulsion 2		Inorganic content[a]	Particle size, D [1,0]±σ nm[b]
		Aqueous phase, g	[Reagent 1], mol/l	Aqueous phase, g	[Reagent 2] mol/l		
ZnO (1)	ZnO/***1***	0.5	0.3	0.5	0.6	8.6	22±14
ZnO (2)	ZnO/***1***	1	0.3	1	0.6	12.6	29±19
ZnO (3)	ZnO/***1***	2	0.3	2	0.6	16.6	45±32
CdS (1)	CdS/***1***	0.5	0.3	0.5	0.3	15	30±21
$MgCO_3$(1)	$MgCO_3$/***1***	0.5	0.3	0.5	0.3	11.1	12±8
Ni (1)	Ni/***1***	0.5	0.5	0.5	0.5	12.4	30±20
Cu (1)	Cu/***1***	0.5	0.5	0.5	0.5	15	30±20
CdS (2)	CdS/***2***	0.5	0.3	0.5	0.3	13.8	66±52
$MgCO_3$(2)	$MgCO_3$/***2***	0.5	0.3	0.5	0.3	8.8	30±20
Ni (2)	Ni/***2***	0.5	0.5	0.5	0.5	14	79±44
Cu (2)	Cu/***2***	0.5	0.5	0.5	0.5	15	32±23

[a] Determined by TGA

[b] Determined by dynamic light scattering; analysis by number

X-ray diffraction proved that the hexagonal crystallographic structure of wurzite was obtained. Due to adsorption of the polymer chains on the particles surface, ZnO can be redispersed in toluene. The obtained dispersion was characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS). A TEM image of the obtained dispersion is presented in Fig. 2a.

According to the dynamic light-scattering studies, the average particle size of the redispersed ZnO(1) material was 22 nm. The quite narrow particle-size distribution proved the complete absence of aggregated particles. This also indicates the good steric stabilization and hydrophobization of the inorganic materials. It is important to note that inside of one emulsion droplet many crystallization centers can form. In the course of growing stage, various particles merge and lead to the observed irregular form resulting in a broader distribution than it can be expected from the approaches used for quantum dots [38].

While designing a composite material, it is often necessary to control the ratio between inorganic and organic components. Therefore, the influence of the zinc oxide–polymer ratio on the particle size was investigated.

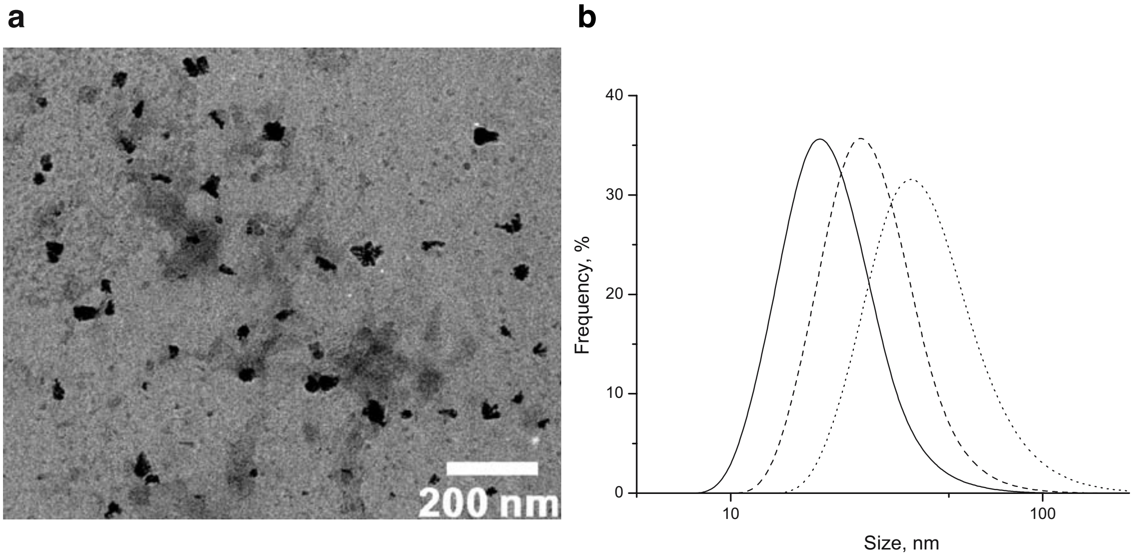

Fig. 2 **a** TEM image of the ZnO dispersion, obtained after refluxing of 32 mg of the dried ZnO(1) material in 20 ml toluene for 24 h. **b** Particle size distribution of ZnO dispersion measured by DLS: — ZnO(1), - - - ZnO (2) ··· ZnO(3). Particles were obtained by refluxing 32 mg of the corresponding material in 20 ml of toluene for 24 h

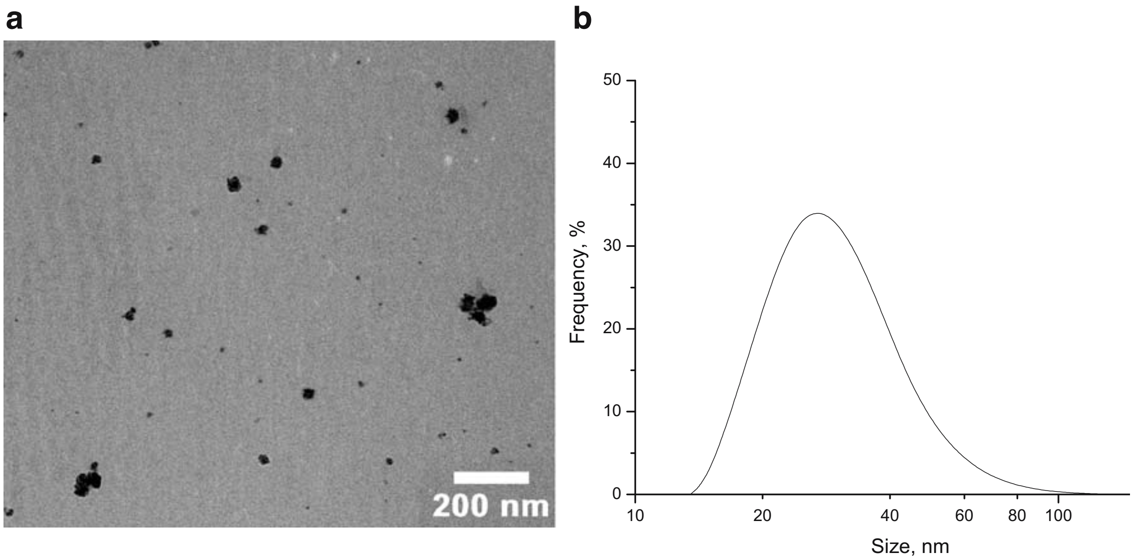

Fig. 3 **a** TEM image of the CdS dispersion, obtained after refluxing of 32 mg of the dried CdS (1) material in 20 ml toluene for 24 h. **b** Particle size distribution of the CdS dispersion measured by DLS. Particles were obtained by refluxing 32 mg of the dried CdS (1) material in 20 ml of toluene for 24 h

For example, the inorganic content in the particles could be varied by increasing the amount of the aqueous solutions of Zn($CH_3COO)_2$ and NaOH, respectively, while keeping the amount of the polymer constant. The average particle size and its distribution were found to increase upon increasing the amount of aqueous solutions. In the case of ZnO(3) some large particles were observed. In respect to the particle formation mechanism, the preparation of inorganic particles in inverse emulsion is very similar to the suspension polymerization. Actually, the size of emulsion droplets is defined by the solubilizing capability of the copolymer used. The increase of the amount of an aqueous solution, which must be stabilized with a given quantity of a copolymer, must result in the increase of the size of the emulsion droplets and, thus, of the inorganic particles.

CdS

Other materials, which attract a large interest in the field of nanocomposites, are chalcogenides of various heavy metals. Many of these materials are semiconductors and can be interesting for the preparation of nanocomposites with special optical or electro-optical properties. For example, CdS nanoparticles have been investigated as the inorganic component in nanocomposites for light filters [39, 40]. Again, a high transparency of the polymeric material is desired, which makes the synthesis of perfectly stabilized small CdS particles necessary. Applying the statistical copolymers in the particle formation of CdS by precipitation in the presence of sulfides results in non-aggregated CdS nanoparticles (Fig. 3). The investigation by X-ray diffraction has demonstrated that the hexagonal crystallographic structure of greenockite was obtained. Figure 3b shows the particle-size distribution obtained by evaluation of the electron microscopy and dynamic light scattering curves. Similar to the ZnO particles, DLS reveals particles with an average diameter of 30 nm.

The obtained dispersion of CdS was found to be stable over a long period. After 4 weeks, no sedimentation or agglomeration was detected by DLS. As in the case of ZnO, the adsorbed polymer chains provide good steric stabilization of the CdS nanoparticles. It is clear that the size of the particles, in comparison with the methods described, for example, by Alivisatos, is quite high.

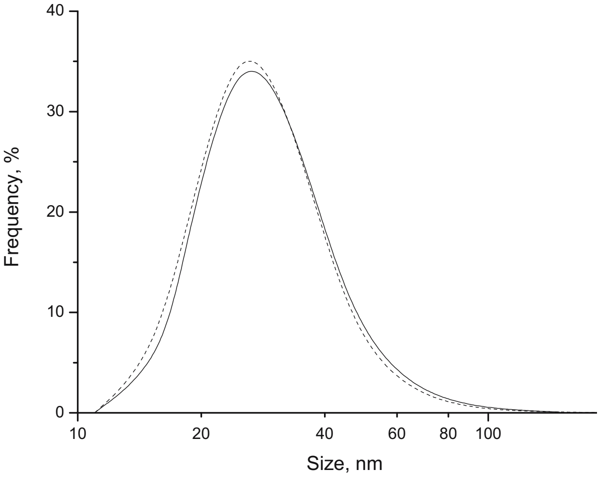

Fig. 4 Particle size distribution of Cu (—) and Ni (- - -) dispersions measured by DLS. Particles were obtained by refluxing 32 mg of the dried Cu (1) or Ni (1) materials in 20 ml of toluene for 24 h

$MgCO_3$

In a third example, the synthesis of surface-functionalized carbonates was investigated. Especially $MgCO_3$ is of interest for obtaining nanocomposites with improved flame resistance. Usually, the application of inorganic materials as flame retardants is quite restricted because it is hard to achieve their homogeneous and aggregate-free incorporation into a polymer. As a result, the mechanical or optical properties are affected in undesirable ways. To achieve the desired flame inhibition effect, it is necessary to incorporate large amounts (about 10 wt%) [41]. The use of nanocomposites in this field is very promising; it is expected that the required amount of the flame inhibitor can be reduced to 1–3 wt% [42, 43].

Therefore, we prepared surface-modified $MgCO_3$ nanoparticles by precipitation in the inverse emulsion, stabilized by the statistical copolymer ***1***. The obtained $MgCO_3$ particles were completely redispersed with an average size of 12 nm (see Table 3). The investigation of the obtained particles by X-ray diffraction has elucidated a formation of the amorphous form of $MgCO_3$. However, from literature it is known that in the case of low-temperature synthesis, some carbonates ($MgCO_3$ or $CaCO_3$) are amorphous [44]. The redispersability of the magnesium carbonate particles in toluene demonstrates that the adsorbed polymer chains protect the particle against attractive interactions between each other. From the literature, it is also known that utilization of the silica nanoparticles, grafted with polymer chains, results in their homogeneous and aggregate-free incorporation into a corresponding polymer matrix [45]. From the particle morphology point of view, this nanosized silica, prepared by a multi-step procedure, is similar to the synthesized $MgCO_3$. As the polymer layer on the surface is responsible for a homogeneous distribution of the particles in a polymer matrix, it is expected that the obtained $MgCO_3$ can also be incorporated into a suitable polymer in a homogeneous manner, without formation of aggregates.

Free metals

To demonstrate that the procedure for particle generation is not limited to precipitation reactions, we have studied the synthesis of metal particles by a reduction process. In this procedure, again two emulsions are mixed, the first one containing a precursor salt, the second one a reducing agent. As examples, the preparation of polymer-modified metal particles of nickel and copper were investigated. Nanocomposites containing free metals are expected to show a high thermoconductivity [46]. Another potential application is as coatings for protection from electromagnetic irradiation. However, especially nickel is technically of low importance as it has a high allergic potential. One possibility to overcome this fundamental problem might be a coating process for the metal beads. This makes these systems ideal candidates for the herein presented approach of an in situ surface functionalization of particles.

From emulsions of $NiCl_2$ or $Cu(NO_3)_2$, small nanoparticles with the size of around 30 nm were obtained by the standard procedure. Figure 4 shows the particle-size distributions of the corresponding toluene dispersions, obtained by dynamic light-scattering.

Also, these particles are completely redispersable in toluene. This result indicates again a high degree of surface functionalization and hydrophobization. The surrounding

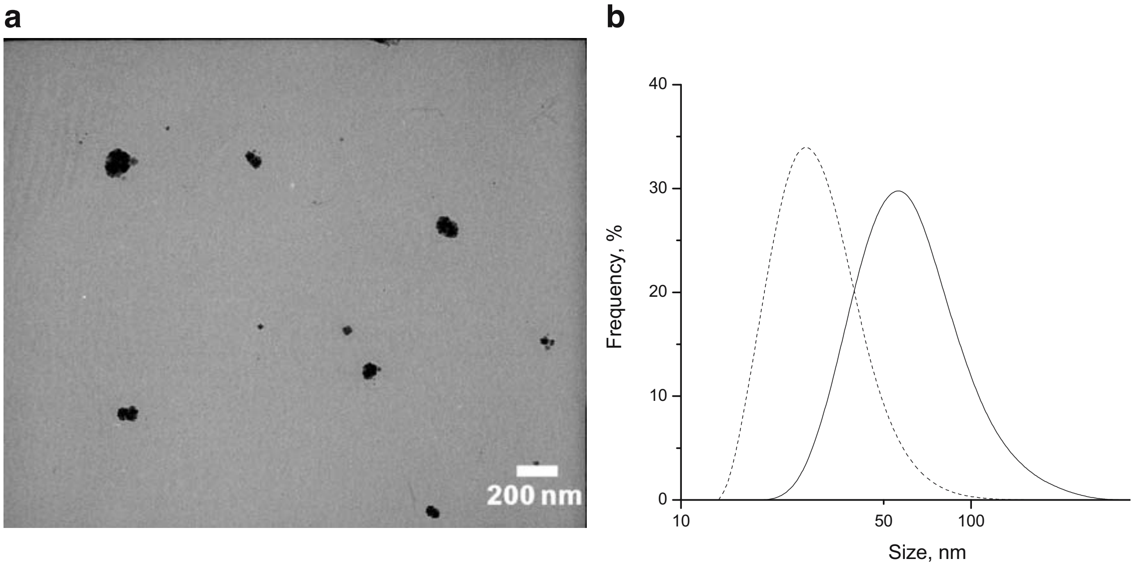

Fig. 5 **a** TEM image of the CdS dispersion, obtained after refluxing 32 mg of the dried particles in 20 ml of toluene for 24 h. Sample CdS (2). **b** Particle size distribution of CdS dispersions measured by DLS: - - - CdS(1). — CdS(2). Particles were obtained by refluxing 32 mg of the dried CdS(1) or CdS (2) materials in 20 ml of toluene for 24 h

of the particles by a polymeric shell gives not only the possibility to incorporate metal particles into a hydrophobic matrix but it may also diminish the allergic effect of the metals by a shielding effect. In this case, applications, e.g., as wrapping or coatings, wherein the contact with the human skin is possible are not excluded anymore [47–50].

Particles prepared with the block copolymer *2*

Block copolymers have often been used for the preparation of polymer-stabilized inorganic nanoparticles. They can be used for surface modification of already prepared inorganic particles or as stabilizers in the inverse emulsion process, similar to our approach [21, 26]. Obviously, the question is raised as to whether the more defined block copolymers have an advantage over the statistical amphiphilic structures. For this purpose, the block copolymer ***2*** was synthesized and applied for the preparation of particles such as CdS, $MgCO_3$, Cu, and Ni. For the ability to compare the particle-size characteristics with those prepared with the statistical copolymer ***1***, the composition and the molecular weight of the block copolymer ***2***, as well as the formulations of the inverse emulsions, were designed to be equal. The particles obtained in the presence of block copolymer ***2*** were also found to be redispersable in toluene. However, in comparison with those prepared with the statistical copolymer ***1***, the particle-size distributions were much broader and the average particle sizes were usually almost doubled. Figure 5a, for example, presents a TEM Image of the CdS dispersion in toluene.

The analysis of the particle-size distribution of the obtained dispersion by dynamic light-scattering revealed an average particle size of 66 nm, whereas, the CdS particles prepared with statistical copolymer ***1*** are 30 nm in diameter (Fig. 5b).

A similar effect was seen for $MgCO_3$ particles. When they were prepared in the presence of the block copolymer ***2***, they were redispersable in toluene. The average size of the $MgCO_3$dispersions stabilized by the block copolymer ***2*** was 30 nm, whereas, in the case of statistical copolymer ***1***, particles of 12 nm in diameter were obtained (see Table 3). Again, it is obvious that utilization of the block copolymer ***2***, instead of the statistical copolymer ***1*** results into an increasing of the average particle size and a broadening of the particle-size distribution.

The metal particles could also be obtained if the block copolymer ***2*** is used. The metal particles, prepared in the presence of the statistical copolymer ***1***, in comparison with the block copolymer ***2***, were smaller in size and possess an improved smaller particle-size distribution. For example, in the case of nickel, the utilization of the block copolymer ***2*** resulted in the formation of particles with an average size of 72 nm. The statistical copolymer ***1***, however, yields particles of 30 nm in diameter.

When using the block copolymer ***2***, a major reason for the increase of particle size and broadening of size distribution might be related to a different emulsion formation process. Amphiphilic block copolymers in mixtures of polar/nonpolar solvents are able to form micelles. It is well-known that their aggregation behavior is quite complex, and well-defined micelles are difficult to achieve, mainly due to their slow dynamics in comparison with low molecular weight surfactants. This restricts the equilibration of the number of surfactants between micelles. As a result, the micelle formation becomes kinetically controlled, which is described in the literature as “frozen micelles” [22]. As the size distribution of the micelles should directly correlate with the size of the inorganic particle formed inside the micelles, a broadening of the distribution of the particles can be expected. However, for the particle-formation process in the presence of statistical copolymers, a different model is suggested as they cannot form micellar solutions. Due to the ultrasonication in the organic phase, small water droplets are formed, which are afterwards stabilized by the statistical copolymer. Similar to the suspension polymerization, the size of the droplets should be controlled by the ultrasonication and the ratio between the organic and aqueous phase, and not by preformed micelles.

Conclusions and outlook

The preparation of nanocomposites in the industrial scale is still difficult to achieve. There are many methods for their preparation, but a universal cheap and efficient process allowing a perfect distribution of the inorganic particles in a polymeric matrix is a challenge. This is mainly due to the difficulties in fulfilling all necessary requirements, such as good compatibility and high degree of entanglement between the polymeric matrix and the polymer chains attached to the surface of the inorganic particle. In this paper, it is demonstrated that an excellent surface functionalization can easily be achieved by preparing inorganic nanoparticles in an inverse emulsion process using easy accessible amphiphilic statistical copolymers as stabilizers. It has been shown that not only oxide particles but also carbonates, sulfides, and metal particles can be obtained by this procedure. As it has also been demonstrated by some examples, the size of the particles can be controlled by the nature of the amphiphilic copolymer and by the ratio between the aqueous phase and the oil phase. As the polymer remains absorbed on the particles, an in situ functionalization of the beads is achieved. As a consequence of a high degree of surface coverage by polymer chains, organic solvents are able to perfectly redisperse these particles.

For comparison, in a similar approach more defined but also more expensive block copolymers were applied as stabilizer in the inverse emulsion process. Also, in this case, surface-functionalized particles could be obtained but remarkably with a larger size and a much broader distribution. This result is of great industrial relevance as the easier accessible statistical amphiphilic copolymers are not only significantly cheaper but also give better-defined nanoparticles.

This article focuses on the synthesis of the particles only. The thorough investigation of the incorporation of these hydrophobic particles in various polymer matrices such as acrylates, polystyrene, or rubbers by blending or by adding them during the polymerization process is already performed and will be published elsewhere. The influence of the chemical nature of the polymer layer which is adsorbed on the particle surface, as well as the influence of the nanoparticles on the properties of the nanocomposites is currently systematically investigated in cooperation with Merck KGaA, the DKI Darmstadt, and the IVW Kaiserslautern. With this new procedure, we have created an easy tool to obtain a broad range of new inorganic/organic hybrid materials in a very cheap and elegant way [51].

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