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Silica/Polyethylene Nanocomposite Particles from Catalytic Emulsion Polymerization

Vincent Monteil,[†] Jörg Stumbaum,[†] Ralf Thomann,[‡] and Stefan Mecking*,[†]

Lehrstuhl für Chemische Materialwissenschaft, Fachbereich Chemie, Universität Konstanz, Universitätsstr. 10, D-78457 Konstanz, Germany, and Freiburger Materialforschungszentrum (FMF), Stefan-Meier-Str. 21, D-79104 Freiburg, Germany

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ABSTRACT: Catalytic emulsion polymerization of ethylene with nickel catalysts in the presence of silica nanoparticles affords stable dispersions of silica/polyethylene nanocomposite particles. The modification of the surface of silica particles by grafting upon their surface of octenyl- or octylsilanes is a prerequisite for obtaining composites. Different morphologies of composites particles were observed depending on the microstructure and crystallinity of the polyethylene part, controlled by different catalyst precursors. Composite structures consisting of silica spheres at the surface of lentil-like crystalline polyethylene particles were formed with a nickel(II) phosphinoenolate catalyst precursor or with the Ni(II) salicylaldiminato complex [{κ^2-*N,O*-6-C(H)=NAr-2,4-$I_2C_6H_2O$}NiMe(tmeda)] (Ar = 2,6-{3,5-$(F_3C)_2C_6H_3$}$_2C_6H_3$). In contrast, silica particles homogeneously embedded in an amorphous polyethylene matrix are observed by TEM when another Ni(II) salicylaldiminato catalyst precursor (Ar = 2,6-{3,5-$Me_2C_6H_3$}$_2C_6H_3$) was used in the presence of a copolymerizable octenyl-modified silica.

Introduction

Polymer nanocomposites with inorganic materials are of strong interest. The presence of disperse nanoscale inorganic particles can improve polymer properties (such as mechanical strength or thermal stability) and introduce novel properties (such as scratch resistance) which cannot be obtained by a simple macroscopic mixing of polymer with a bulk inorganic material. However, obtaining a high degree of dispersion of submicron inorganic particles in a polymer matrix remains a challenge. Among a great variety of syntheses of organic−inorganic nanostructured materials, heterophase polymerization offers particularly suitable synthetic routes for the preparation of particulate nanocomposites with controlled compositions, sizes, shapes, and surface properties.[1] By performing heterophase polymerizations in aqueous systems (e.g., suspension, dispersion, or emulsion polymerization) in the presence of inorganic particles, polymer−inorganic nanocomposite particles with various morphologies can be prepared.[1] These methods generally imply a premodification of the surface of inorganic particles to increase their compatibility with the polymer. For example, modification may involve the covalent attachment of hydrophobic and/or polymerizable organic fragments on the particle surface.

Emulsion polymerization allows for the synthesis of composite particles with various morphologies[2,3] (most frequently core−shell or raspberry-like structure) depending on the surface chemistry and the size of the inorganic particles (generally silica). Miniemulsion polymerization was found to be a particularly suitable method for the synthesis of nanocomposite particles with a controlled morphology.[4] Indeed, particle nucleation occurred in miniemulsion monomer droplets (containing dispersed inorganic particles) which represents a simplification in comparison with classical emulsion with complex nucleation mechanisms. Inorganic materials such as pigments, calcium carbonate, silica, or magnetite were successfully encapsulated by polymer.[5] Colloidal silicas were also used to (co)stabilize oil miniemulsions as Pickering stabilizers.[6]

Other polymerization processes such as "surfactant free" heterophase polymerization[7] or dispersion polymerization[8] were used to prepare composite particles with inorganic particles (generally silica) with various morphologies.

However, these controlled organic−inorganic nanocomposite particle architectures obtained by heterophase polymerization are restricted to polymers accessible by free radical polymerization (such as polystyrene or PMMA) to date. Recent studies have demonstrated the feasibility of non-free-radical routes in polymerization in aqueous systems.[9−11] Catalytic polymerizations are of particular interest, as they enable a broad control of polymer microstructures. The catalytic emulsion polymerization of olefins, using late transition metal catalysts, gives access to polyolefin latices of variable microstructures and crystallinities, consisting in some cases of unusually small particles <20 nm.[12]

Polyolefins are of great technical importance, but the synthesis of polyolefin nanocomposites is particularly challenging. Two principal strategies have been investigated to date.[13] The first one is the melt intercalation of a (modified) polyolefin into modified layered clays.[14] The second is the in situ polymerization of olefin by a catalyst supported on inorganic materials or intercalated in modified silicates.[15] These two routes produce nanocomposites of a solid polyolefin matrix that is embedded with inorganic nanoparticles.

In this paper we report a new route for the synthesis of silica/polyolefin nanocomposites. Our method involves catalytic emulsion polymerization of ethylene with nickel catalysts in the presence of modified silica nanoparticles.

Results and Discussion

1. Synthesis of Modified Silica Nanoparticles. Using the Stöber method,[16] silica dispersions in ethanol of two different particle sizes[17] (Table 1, Figure S1 in Supporting Information) were prepared. Solid-state ^{13}C CPMAS NMR spectroscopy and

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[†] Universität Konstanz.

[‡] Freiburger Materialforschungszentrum.

* Corresponding author: Fax +49 (0) 7531 88-5152; e-mail stefan.mecking@uni-konstanz.de.

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Table 1. Dispersions of Silica Nanoparticles

silica	particle size: diameter (nm) DLS (PDI)[a]	TEM[b]	C (wt %)	specific area (m^2/g)[c]
Si1	125 (0.03)	87	2.65	27
Si2	67 (0.08)	41	3.41	50

[a] Volume average particle diameters and polydispersity (PDI) determined by DLS. [b] Volume average particle diameters determined by TEM. [c] Estimated from the particle size (DLS) on the assumption of spherical silica particles with a density of 1.8 g/cm^3.

elemental analysis show the presence of unhydrolyzed ethoxy groups (Figure 1a).

As already mentioned, for the synthesis of silica−polymer nanocomposite particles the surface of hydrophilic silica particles usually needs to be modified to enhance the compatibility with the hydrophobic polymers. This can be achieved by grafting of organosilanes at the silica particle surface.[18] Methacryloxy(propyl)trimethoxysilane (MPS) is usually used, and a covalent attachment between silica and polymer is observed by copolymerization between the grafted silane and monomer (such as styrene or MMA) via a free radical mechanism.[8a] In our case we aimed to polymerize ethylene in the presence of silica nanoparticles by catalytic polymerization. For this purpose we used an organosilane with a terminal double bond suitable for catalytic polymerization: trimethoxy(7-octen-1-yl)silane (**1**). For comparative purposes, a second organosilane, trimethoxy(octyl)silane (**2**), was also grafted with the effect to only hydrophobize the silica surface without the possibility of covalent incorporation by copolymerization. Silica dispersions in ethanol (Si1 and Si2) were modified with a large excess of the two different organosilanes respective to the estimated surface silanol concentration (Table 2 and Experimental Section).[19] The excess of silane was removed by centrifugation. Redispersion in ethanol afforded stable dispersions of modified silica particles. Attempts to redisperse these silica particles in toluene led to dispersions of low stability which sedimented rapidly, as also observed with MPS-modified silicas.[18] Redispersion in water was not possible.

Grafting of organosilanes upon the silica particle surface was evidenced by ^{13}C and ^{29}Si solid-state CPMAS NMR spectroscopy (Figure 1 and Figure S2). In the case of trimethoxy(7-octen-1-yl)silane (**1**) the ^{13}C spectrum indicates the presence of remaining unreacted ethoxy groups and of six new signals, which can be attributed to the grafted silane. The signal at 12.6 ppm ($R-\mathbf{C}H_2-Si\equiv$) indicates a covalent binding between the silane and the silica surface. Indeed, it appears at higher chemical shift than the corresponding signal for the free organosilane (9.3 ppm), as already observed for MPS grafting.[8a] For trimethoxy(octyl)silane the same features were observed (Figure 1c). The ^{29}Si NMR confirms the covalent attachment of silanes on the silica surface with the characteristic signals for T^2 and T^3 (and a small amount of T^1) silicon atoms (Figure S2 in the Supporting Information).[20]

The amount of grafted silane was estimated according to the Berendsen equation[21] (Table 2 and Experimental Section). It was found to be between 7 and 16 μmol of silane per m^2 of silica (corresponding to 4−10 silane molecules per nm^2). These estimated grafting efficiencies and ^{29}Si NMR observations (with the predominance of the T^2 signal) indicate the presence of partially cross-linked organosilanes on the silica surface.[8a]

No significant modifications of the sizes and the shapes of silica particles were observed upon the functionalization of their surface (Figure S1 in Supporting Information).[22] This indicates that no interparticle cross-linking or other undesired agglomeration occurs.

2. Nanocomposite Dispersions of Semicrystalline Linear Low-Molecular-Weight Polyethylene and Silica Obtained with Ni^{II} Phosphinoenolate Catalysts. Dispersions of silica/polyethylene composite particles were synthesized using a modification of the procedure for catalytic polymerization of ethylene in emulsion developed in our laboratory. A nickel(II) phosphinoenolate complex **3** (obtained in situ by reacting a mixture of triphenylphosphine and chloranil with bis(1,5-cyclooctadiene)nickel was used as a catalyst precursor, affording low-molecular-weight linear semicrystalline polyethylenes.[12d] The first step of the catalytic polymerization of ethylene in emulsion is the preparation of a fine initial dispersion of the catalyst in the form of a miniemulsion of a solution of the catalyst precursor in a small amount of a hydrocarbon solvent (toluene). For the synthesis of composite dispersions the silica dispersion in ethanol is added to the catalyst miniemulsion components (water, surfactant (SDS), hydrophobic agent (hexadecane), and a solution of **3** in toluene). This mixture is exposed to high shear by means of ultrasound, generating a fine dispersion of toluene droplets (containing the nickel catalyst precursor) and of silica particles. At this stage, to obtain nanocomposites particles during the subsequent polymerization, it is crucial to have a close interaction between silica particles and toluene droplets. The hydrophobization of silica particles should make this interaction more effective.

Table 3 summarizes the results after exposure to ethylene pressure of these dispersions of **3**/silica with various sizes and surface modifications.

In the presence of silica modified with octenylsilane **1** (Si1-1^{octen}, diameter ∼ 110 nm), the nickel catalyst is able to polymerize ethylene, and a stable SiO_2/polyethylene composite dispersion is obtained (Table 3, entry 1). An overview transmission electronic microscopy (TEM) image of this latex reveals a good dispersion of silica particles among polyethylene particles (Figure 2A). A more precise observation shows that silica particles are not isolated but belong to composite objects consisting of one (or two) silica sphere(s) at the periphery of lentil-like polyethylene particles (Figure 2B−D). This particular nonspherical structure of polyethylene particles is due to polymer crystallization, as already observed.[12e]

To investigate the effect of surface functionalization of silica particles, polymerizations were conducted with an unmodified hydrophilic silica (Table 3, entry 2) and with a silica modified with a nonpolymerizable silane **2** (Table 3, entry 3). In the first case, TEM clearly shows the formation of lentil-like polyethylene particles separately from silica particles (Figure 3A). There is no evidence for an interaction between the polymer and the silica particles, which tend to agglomerate. By contrast with the silane **2** the silica particles are dispersed among the polymer particles; no clear differences appear in comparison with silane **1** (Figure 3B).

These observations are confirmed by quantitative analyses of the dispersions (Table 3, entries 1−3 and Experimental Section). Silica/polyethylene composite particles were separated by ultracentrifugation from free polyethylene particles and were analyzed by thermogravimetric analysis. (Free silica particles would also be collected with the composite particles; however, the aforementioned TEM images can rule out the presence of free silica particles.) In the case of the unmodified silica, the amount of "composite" is very low (7 wt %) with a high residual SiO_2 content (69 wt %), corresponding mostly to the amount and the nature of the silica introduced before the polymerization (which contains ∼85 wt % residual SiO_2 by thermogravimetric analysis, TGA). The analyses of the dispersions obtained with modified silicas show quite different results with a higher

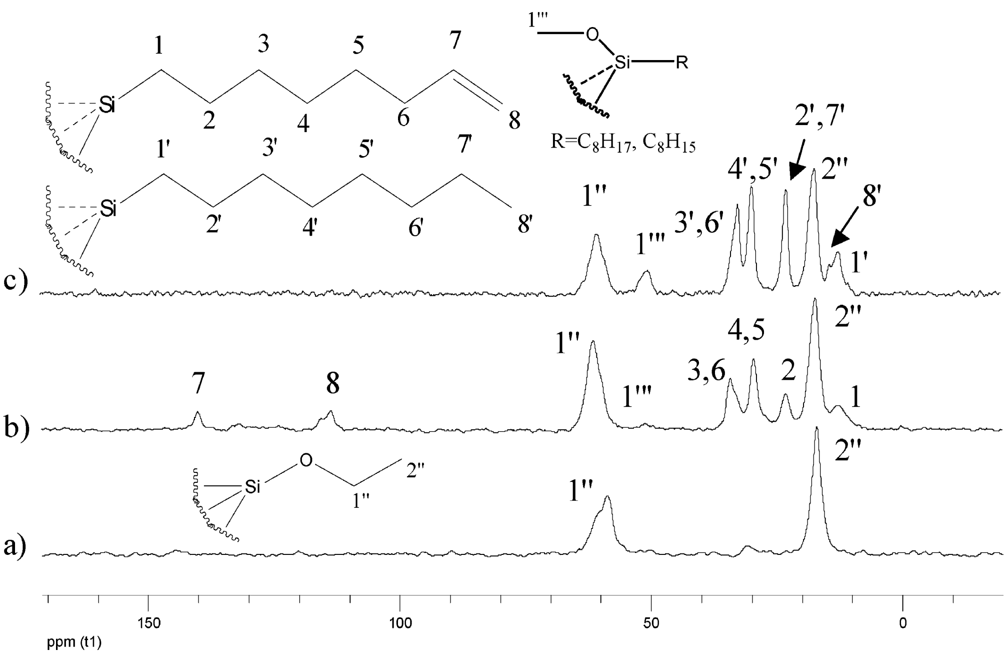

Figure 1. ^{13}C CPMAS NMR of silica before (a) and after grafting with **1** (b) and **2** (c).

Table 2. Dispersions of Modified Silica in Ethanol

		particle size^b			
silica	silane^a	diameter (nm)	PDI	C (wt %)	grafted silane (μmol/m^2)
Si1-1$^{\text{octen}}$	**1**	109	0.2	4.43	7.3
Si1-2$^{\text{octan}}$	**2**	113	0.2	4.93	9.4
Si2-1$^{\text{octen}}$	**1**	54	0.12	8.27	11.5
Si2-2$^{\text{octan}}$	**2**	66	0.2	9.93	16.2

[a] **1**: trimethoxy(7-octen-1-yl)silane; **2**: trimethoxy(octyl)silane; 6 equiv/silanol. [b] Volume average particle diameters and polydispersity (PDI) determined by DLS.

amount of composite (up to 57 wt %) containing a lower amount of residual SiO$_2$ (~40 vs ~85 wt % for the modified silica introduced before the polymerization). Once again no dramatic differences appear between the two different silanes **1** and **2** (Table 3, entry 1 vs 3).

By using smaller silica particles (diameter ~ 60 nm), similar features were observed with the difference that the average number of silica particles per polyethylene particle is greater in the composite structures (Table 3, entry 5, and Figure S3 in the Supporting Information). Analyses by TGA of the composite portion of the dispersions show the same clear difference between the dispersions obtained with or without a modification of the silica surface (Table 3, entry 4 vs 5).

To simplify the initial system, it could be advantageous to use modified silica directly dispersed in toluene as the catalyst is also dissolved in toluene. Despite the lack of stability of the modified silica dispersions in toluene, a polymerization of ethylene was performed following the procedure described previously with a dispersion of modified silica in toluene (Table 3, entry 6). No differences were observed in comparison with the corresponding more stable dispersions of modified silicas in ethanol as observed by TEM (Figure S4) and quantitative analysis of the resulting composite dispersion (Table 3, entry 6). We assume that ethanol is present in the aqueous phase in the initial dispersion of the catalyst (dissolved in toluene) and does not affect the interactions between the toluene phase and the hydrophobic modified silica particles.

Differential scanning calorimetry (DSC) measurements were performed on the composite dispersions and on the isolated solids obtained by precipitation from the latices. It is known that catalyst **3** polymerizes ethylene to linear low-molecular-weight polyethylenes also in aqueous emulsion.[12d,e] By comparison, melting points observed (T_m = 120−127 °C for isolated polymers and T_m = 116−123 °C for the dispersions) indicate that linear low-molecular-weight polyethylenes are formed also in the presence of inorganic particles.

Mechanism of Formation of the Composite Particles. To better understand the mechanism of formation of the composite particles, the initial complex system (resulting from the preparation of the catalyst miniemulsion in the presence of silica particles) was investigated by dynamic light scattering (DLS). Figure 4 shows the droplets size distribution of a catalyst miniemulsion in the presence or in the absence of modified silica particles (Si1-1$^{\text{octen}}$, diameter ~ 110 nm). The addition of the silica dispersion increased the droplet size of the corresponding miniemulsion, resulting from the interaction between the lipophilically modified silica particles and the toluene phase (Figure 4).

We assume that some of the toluene droplets generated during the miniemulsification process are in interaction with silica particles (one or more depending on the silica size). This interaction is only effective when the silica surface has been modified hydrophobically. When exposed to ethylene pressure, polyethylene particles are growing from this initial state, incorporating silica particles. Composites particles (and also to a lesser extent separate free polyethylene particles) are generated. Because of the crystallization of polyethylene, the nanocomposite particles cannot achieve a complete core−shell structure (with a silica core and a polyethylene shell) and dissymmetric structures are formed, as observed by TEM. The crystallinity of the polymer is probably also responsible for the formation of free polyethylene particles. Indeed, for latices of crystalline polyethylene prepared with a catalyst miniemulsion, a large increase in the number of particles in the course of the polymerization has been observed.[12c] This is explained by the growing polymer chains precipitating from the organic droplets (toluene), generating a crystalline polymer particle, and leaving a liquid droplet which can generate further polymer particles.

Table 3. Synthesis of Silica/Polyethylene Composite Dispersion with Ni^{II} Catalyst 3[a]

			particle size[c]			
entry no.	silica (g)	solids cont (wt %)[b]	diameter (nm)	PDI	wt % composite[d]	wt % SiO_2[e]
1	Si1-1^{octen} (0.7)	2.3	152	0.08	57	43
2	Si1 (0.2)	2.9	280	0.05	7	69
3	Si1-2^{octan} (0.35)	2.1	170	0.08	30	37
4	Si2 (0.3)	9.1	206	0.22	3	64
5	Si2-1^{octen} (0.75)	2.8	111	0.06	61	33
6	Si1-1^{octen} (0.5)	5.4	157	0.11	20	37

[a] Polymerization conditions: $T = 60$ °C; p(ethylene) = 40 bar; 1 g of SDS, 0.3 mL of hexadecane, silica dispersion in EtOH (in toluene for entry 6), H_2O; catalyst **3**: 100 μmol of PPh_3, 100 μmol of chloranil, 110 μmol of $Ni(cod)_2$, 1 mL of 2-propanol, 5 mL of toluene; total volume: 100 mL; reaction time = 2 h. [b] Solids cont: solids content of the dispersion determined with moisture analyzer; masses of surfactant and hexadecane are subtracted (accuracy of the method was confirmed by isolation of the polymer by precipitation of the dispersion). [c] Volume average particle diameters and polydispersity (PDI) determined by DLS. [d] Determined after ultracentrifugation. [e] Wt % silica in composite (determined by TGA).

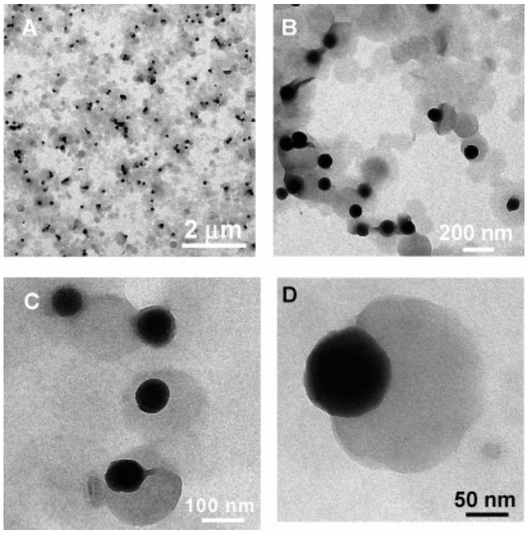

Figure 2. TEM images of silica/polyethylene composite dispersions using an octenyl-modified silica (Table 3, entry 1).

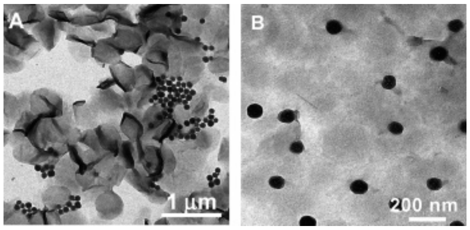

Figure 3. TEM images of silica/polyethylene composite dispersions prepared with (A) an unmodified silica (Table 3, entry 2) and (B) an octyl-modified silica (Table 3, entry 3).

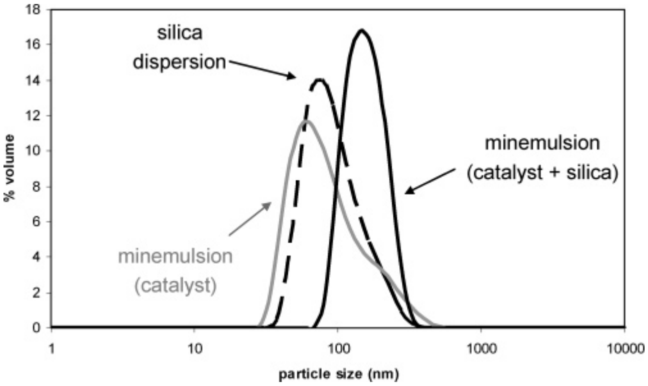

Figure 4. Volume-weighted size distribution of a catalyst miniemulsion in the presence or absence of a modified silica dispersion (Si1-1^{octen}, dashed line).

Concerning the nature of the interaction between silica and polyethylene in the composite structures, our results with this nickel catalyst **3** allow us to assume that a physical interaction (with a possible cocrystallization of polyethylene chains and of alkyl chain at the surface of silica) is sufficient to afford composite structures in this case. Whether an additional copolymerization occurs for the octenyl-modified silica particles remains open. A hydrophobization of the silica particles surface, as provided with the alkyl- and alkenylsilane, is a prerequisite for obtaining composites.

At this stage it is also of interest to verify that the synthesis of such SiO_2/polyethylene nanocomposite particles could not be obtained by simply mixing a polyethylene latex and a dispersion of a hydrophobized silica. For this purpose a dispersion in ethanol of a modified silica was slowly added to a polyethylene latex (obtained with a miniemulsion of **3**). This addition first caused a partial coagulation of the latex. TEM images of the resulting latex show agglomerations of silica particles among polyethylene particles without the formation of composite structures as observed when ethylene is polymerized in the presence of silica.

3. Nanocomposite Dispersions of Silica and Polyethylenes with Variable Crystallinity Obtained with Ni^{II} Salicylaldiminato Catalysts. To vary the morphology of the polyethylene part of the nanocomposites particles, other nickel catalyst precursors were used. In contrast to Ni^{II} phosphinoenolate precursors such as **3**, Ni(II) salicylaldiminato complexes, such as $[\{\kappa^2\text{-}N,O\text{-6-C(H)=NAr-2,4-I}_2\text{C}_6\text{H}_2\text{O}\}\text{NiMe(tmeda)}]$ (Ar = 2,6-$\{3,5\text{-Me}_2\text{C}_6\text{H}_3\}_2\text{C}_6\text{H}_3$ (**4**) or 2,6-$\{3,5\text{-(F}_3\text{C)}_2\text{C}_6\text{H}_3\}_2\text{C}_6\text{H}_3$ (**5**)), are known to afford polyethylenes of variable molecular weight and branching (and thus crystallinity).[12f] Whereas **4** affords low-molecular-weight highly branched amorphous polymer ($M_n \sim 10^3$ g mol^{-1}; 80 branches/1000 C), with **5** higher molecular weight semicrystalline polyethylene is formed ($M_n \sim 2 \times 10^4$ g mol^{-1}; 10 branches/1000 C).[12f]

Using a similar procedure as previously described for phosphinoenolate Ni^{II} catalysts, ethylene was polymerized with salicylaldiminato Ni^{II} catalysts in the presence of silica dispersions. The results are summarized in Table 4. The behavior of the catalyst precursor **4** was studied (Table 4, entries 1−3). In the presence of various silica dispersions with different surface modifications, this catalyst is able to polymerize ethylene. In the case of octyl-modified silica (Table 4, entry 3), a very low productivity was observed in comparison with unmodified and octenyl-modified silica (probably due to the presence of some impurities in the silica dispersion which cause the deactivation of the catalyst).

Observations by TEM show a homogeneous dispersion of silica particles in an amorphous polyethylene matrix when silica modified by octenylsilane **1** is used (Figure 5B and Table 4, entry 2). In the case of unmodified silica the stability of the dispersion is low, and TEM analyses reveal that the hydrophilic inorganic particles are aggregated and excluded from the

Table 4. Synthesis of Silica/Polyethylene Composite Dispersions with Ni^{II} Salicylaldiminato Catalysts 4 and 5

			particle size[c]			
entry no.	silica (g)	solids cont (wt %)[b]	diameter (nm)	PDI	wt % composite[d]	wt % SiO_2[e]
1	Si1 (1.0)	7.2	675[f]		11[g]	58[g]
2	Si1-1^{octen} (0.9)	13.1	118	0.18	7	51
3	Si1-2^{octan} (0.8)	2.2	146	0.05	64	77
4	Si1 (0.5)	3.0	63	0.18	17	84
5	Si1-1^{octen} (1)	6.7	127	0.17	16	37

[a] Polymerization conditions: $T = 20$ °C; p(ethylene) = 40 bar; 1 g of SDS, 0.3 mL of hexadecane, silica dispersion in EtOH, H_2O; catalyst: **4** (40 μmol, entries 1−3), **5** (20 μmol, entries 4−5), 2 mL of toluene; total volume: 100 mL; reaction time = 2 h. [b] Solids cont: solids content of the dispersion determined with moisture analyzer; masses of surfactant and hexadecane are subtracted. [c] Volume average particle diameters and polydispersity (PDI) determined by DLS. [d] Determined after ultracentrifugation. [e] Wt % silica in composite (determined by TGA). [f] Low stability of the dispersion. [g] Analysis of the colloidally stable part of the dispersion.

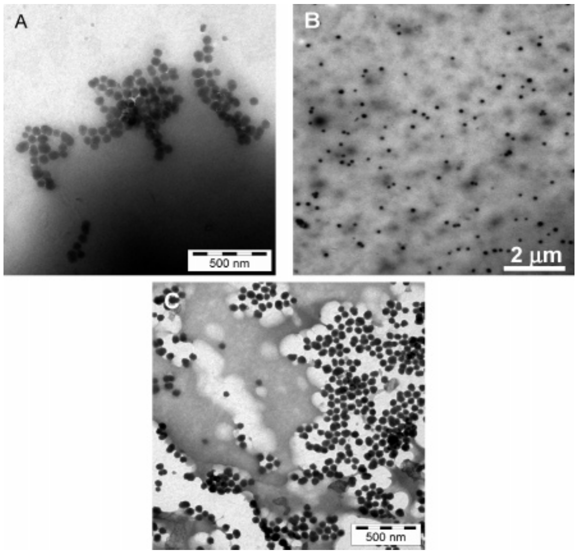

Figure 5. TEM images of silica/polyethylene composite dispersions obtained with catalyst **4** using (A) an unmodified silica, (B) an octenyl-modified silica, and (C) octyl-modified silica (Table 4, entries 1−3, respectively).

hydrophobic polyethylene matrix (Figure 5A and Table 4, entry 1). A similar behavior is observed with the octyl-modified silica which differs from observations with Ni^{II} phosphinoenolate catalysts (Figure 5C and Table 4, entry 3). Because of the amorphous character (as confirmed by DSC: no melt transition is detected) and the low molecular weight of the polyethylene generated with this catalyst, a coalescence of the polymer particles occurs during the evaporation of water for the preparation of TEM samples. This impedes the observation of separated polymer particles and especially core−shell structures.

The quantitative analyses of the dispersions (Table 4) must be compared with some caution due to the lower catalyst activity and amount of polymer formed in entry 3 (with octyl-modified silica). Nevertheless, in the latter case the SiO_2 content of the "composite" portion isolated is close to that of the starting silica (∼85 wt % residual SiO_2 from TGA), which is in accordance with the TEM observations of silica particles separated from the polymer phase. The observation of true composite particle formation for the copolymerizable silica (51 wt % residual SiO_2 from TGA, Table 4, entry 2) is in line with the TEM observations. For unmodified silica, composite particles seem to be formed according to TGA analysis (58 wt % SiO_2). On the other hand, the sample has a lower colloidal stability, as evidenced by formation of coagulate during the polymerization, which can disturb the separation process during the centrifugation. As pointed out, the TEM micrographs reveal agglomerated silica particles and do not evidence a significant silica/polyethylene interaction. The comparison between octyl- and octenyl-modified silica indicates that a copolymerization, that is a covalent linkage between the inorganic and organic particle phase, is a prerequisite for the formation of composite particles with the amorphous polyethylene.

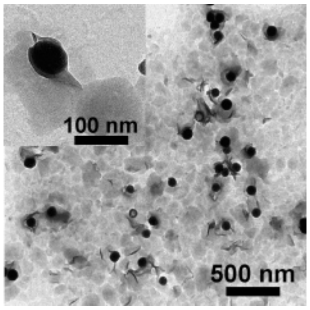

Figure 6. TEM image of silica/polyethylene composite dispersions obtained with catalyst **5** using an octenyl-modified silica (Table 4, entry 5).

With catalyst precursor **5**, which is known to afford high-molecular-weight semicrystalline polyethylene with a low degree of branching (vide supra), ethylene was also polymerized in the presence of unmodified and octenyl-modified silica dispersions. Stable SiO_2/polyethylene composite dispersions were obtained (Table 4, entries 4 and 5). TEM images reveal, in the case of octenyl-modified silica, the presence of composite particles with a similar structure as observed with Ni^{II} catalyst **3** (Figure 6). Free PE particles are formed additionally. The crystallinity of the polyethylene formed with this catalyst (T_m ∼ 130 °C) is responsible for the formation of such composite structures, as already observed with Ni^{II} catalyst **3**. Quantitative analyses show a clear difference of the composite portion of the dispersions obtained with or without a modification of the silica surface (Table 4, entry 4 vs 5). The composition of the material obtained with the unmodified silica corresponds to the starting silica (84 wt % from TGA); that is, composite particles are formed only with the lipophilic silica.

Summary and Conclusion

The polymerization of ethylene in aqueous emulsion in the presence of appropriately functionalized silica particles was found to afford dispersions of nanocomposite organic/inorganic particles. Lipophilic silica particles with octenyl (or octyl) surface functionalities were prepared for this purpose.

Polymerizations were carried out with various lipophilic catalyst precursors, dispersed in the initial reaction mixture in the form of a miniemulsion of a catalyst solution in a small amount of toluene. DLS studies confirm that a strong interaction between lipophilically modified silica particles and these miniemulsion droplets occurs in the initial reaction mixture.

The formation of nanocomposite particles and their structure depends on the microstructure and crystallinity of the polymer formed, which is controlled by the catalyst precursor employed. For all systems studied, formation of nanocomposite particles to a significant extent required lipophilically modified silica particles. With unmodified particles directly from classical Stöber synthesis, separate polymer and silica particles were formed as evidenced by TEM studies of particle morphology and quantitative analysis of dispersions by centrifugation and TGA analysis.

In polymerization with catalyst **3**, affording low-molecular-weight linear semicrystalline polyethylene (T_m ~125°C), nanocomposite particles are formed, consisting of a silica particle embedded at the periphery of a (lentil-shaped) polyethylene particle. This structure can be related to the crystallinity of polyethylene which does not enable formation of a PE shell on the curved surface of the silica particles. No significant difference is observed between copolymerizable (octenyl-modified) and octyl-functionalized silica. Obviously, a physical interaction is sufficient and controls the particle structure. A similar structure was observed for nanocomposite particles with octenyl-modified silica prepared with catalyst **5**, which polymerizes ethylene to high-molecular-weight semicrystalline polyethylene (T_m ~ 130 °C).

With catalyst **4**, affording highly branched amorphous low-molecular-weight polyethylene, a different behavior was evidenced. Clear formation of nanocomposite particles was observed only with copolymerizable silica particles, whereas the use of octyl-modified silica particles resulted in formation of separate silica and polyethylene particles. In TEM micrographs of the nanocomposite dispersions, continuous films of polyethylene (which is amorphous and above T_g) are observed with homogeneously dispersed nonaggregated silica particles.

Experimental Section

General Considerations. All manipulations (except for silica synthesis and modifications) were performed using standard Schlenk techniques under an inert atmosphere. ^{13}C and ^{29}Si solid-state CP/MAS NMR of silicas were recorded at the Institute of Macromolecular Chemistry at Freiburg University on a Bruker Avance 500 solid-state NMR spectrometer operating at 125.775 MHz for ^{13}C and 99.375 MHz for ^{29}Si. The samples were spun at the magic angle at 8 kHz using 4 mm rotors. Cross-polarization was employed with a contact time and a relaxation delay of 3 ms and 3 s (^{13}C) or 4 s (^{29}Si), respectively. Dynamic light scattering (DLS) on diluted latex samples was performed on a Malvern Nano-ZS ZEN 3600 particle sizer (173° backscattering). The given average particle sizes are volume means. The polydispersity (PDI) is directly calculated from the signal intensity. Miniemulsion droplet sizes were measured as undiluted samples. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 F1 at a heating rate of 10 K/min. The polymers were investigated in the temperature range 25−160 °C. DSC data reported are second heats. Thermogravimetric analysis (TGA) was performed under an O_2 atmosphere on a Netzsch STA 429 at a heating rate of 10 K/min. The composites were investigated in the temperature range 20−1250 °C. Transmission electron microscopy (TEM) was carried out on a LEO 912 Omega apparatus using an acceleration voltage of 120 kV. Samples were prepared by applying a drop of the dispersion to a carbon-coated grid.

Materials. Ethylene of 3.5 grade supplied by Gerling, Holz + Co. was used without further purification. Tetraethyl orthosilicate (TEOS) was distilled prior to use. Ethanol and ammonia solution (25% NH_3 in water) were purchased from Riedel-de Haen and used as received. Toluene was dried over Na and distilled under argon. 2-Propanol and hexadecane were degassed by repeated freeze−pump−thaw cycles. Deionized water was degassed by distillation under nitrogen prior to use. The organosilanes trimethoxy(7-octen-1-yl)silane and trimethoxy(octyl)silane were purchased from Aldrich and used as received. Sodium dodecyl sulfate (SDS) was purchased from Fluka and degassed under argon prior to use. 2,3,5,6-Tetrachloro-1,4-benzoquinone (chloranil) and triphenylphosphine were purchased from Aldrich and degassed under argon prior to use. Bis(1,5-cyclooctadiene)nickel ([Ni(cod)$_2$]),[23] [(tmeda)NiMe$_2$],[24] and salicylaldimine ligands[12f] (corresponding to complexes **4** and **5**) were prepared according to literature procedures.

Preparation and Modification of Silica Particles. The silica particles were prepared according to the Stöber method. 400 mL of ethanol and 21 mL (Si1) or 15 mL (Si2) of an ammonia solution (25% NH_3 in water) were mixed in a 1 L flask. After 5 min strong stirring and 30 min slower stirring, 16 mL of TEOS was added and stirred again for 12 h at room temperature. The silica dispersion obtained was then concentrated (to 0.2−1 g in 10 mL) and degassed by bubbling argon prior to use for polymerization (ammonia is removed during concentration of the silica dispersion). Modification of the silica surface was achieved by mixing the silica dispersions (directly after synthesis) and the corresponding organosilane (**1** or **2**) and stirring 2 h at room temperature. Organosilanes were added in excess: 48 μmol/m^2 (corresponding to ca. 6 times the silanol surface concentration estimated to be equal to 8 μmol/m^2).[8a] The dispersions of modified silica were then purified from excess organosilane by series of centrifugations (2 h at 6500 rpm) and redispersions in ethanol (0.3−1 g in 10 mL). They were degassed by bubbling argon prior to use for polymerization. For analysis purpose (elemental analysis and solid-state NMR) the silica dispersions were dried 12 h at 50 °C under vacuum.

Characterization of Modified Silica Particles. Elemental analysis (wt % C) was carried out on dried silica samples. From the difference between the carbon weight percentage before and after grafting the quantity of organosilane grafted on the silica surface was estimated according to the Berendsen equation.[21] Direct evidence of grafting of organosilane was also obtained by solid-state CP/MAS NMR. ^{29}Si NMR: (a) silica before modification: −109 (Q^4 Si), −101 (Q^3 Si); (b) silica after modification: −109 (Q^4 Si), −101 (Q^3 Si), −64 (T^3 Si), −56 (T^2 Si), −49 (T^1 Si) (T^x, Q^x notations[20a] see Figure S2). ^{13}C NMR: (a) silica before modification: 17.1 ($Si{-}O{-}CH_2{-}\mathbf{C}H_3$), 58.7 ($Si{-}O{-}\mathbf{C}H_2{-}CH_3$); (b) silica grafted with **1**: 12.6 ($Si\text{-}\mathbf{C}H_2{-}(CH_2)_5{-}CH{=}CH_2$), 16.8 ($Si{-}O{-}CH_2{-}\mathbf{C}H_3$), 22.6 ($Si{-}CH_2{-}\mathbf{C}H_2{-}(CH_2)_4{-}CH{=}CH_2$), 28.9 ($Si{-}(CH_2)_3{-}\mathbf{C}H_2{-}\mathbf{C}H_2{-}CH_2{-}CH{=}CH_2$), 33.5 ($Si{-}(CH_2)_2{-}\mathbf{C}H_2{-}(CH_2)_2{-}\mathbf{C}H_2{-}CH{=}CH_2$), 50.3 ($Si{-}O{-}\mathbf{C}H_3$), 60.6 ($Si{-}O{-}\mathbf{C}H_2{-}CH_3$), 112.2 ($Si{-}(CH_2)_6{-}CH{=}\mathbf{C}H_2$), 138.5 ($Si{-}(CH_2)_6{-}\mathbf{C}H{=}CH_2$); (c) for silica grafted with **2**: 12.5 ($Si{-}\mathbf{C}H_2{-}(CH_2)_6{-}CH_3$), 14.3 ($Si{-}(CH_2)_7{-}\mathbf{C}H_3$), 17.2 ($Si{-}O{-}CH_2{-}\mathbf{C}H_3$), 22.8 ($Si{-}CH_2{-}\mathbf{C}H_2{-}(CH_2)_4{-}\mathbf{C}H_2{-}CH_3$), 29.6 ($Si{-}(CH_2)_3{-}\mathbf{C}H_2{-}\mathbf{C}H_2{-}(CH_2)_2{-}CH_3$), 33.4 ($Si{-}(CH_2)_2{-}\mathbf{C}H_2{-}(CH_2)_2{-}\mathbf{C}H_2{-}CH_2{-}CH_3$), 50.2 ($Si{-}O{-}\mathbf{C}H_3$), 60.3 ($Si{-}O{-}\mathbf{C}H_2{-}CH_3$).

Synthesis of SiO_2/Polyethylene Composite Dispersions. Catalyst **3** was prepared according to a literature procedure:[12d] equal molar amounts of 2,3,5,6-tetrachloro-1,4-benzoquinone and PPh_3 were dissolved under argon in a mixture of the given amounts of toluene and 2-propanol. After stirring for about 20 min, the solution obtained was transferred to a 1.1-fold molar excess of bis(1,5-cyclooctadiene)nickel.

Catalysts **4** and **5** were prepared by mixing [(tmeda)NiMe$_2$] and the corresponding salicylaldimine ligand in toluene.[12f]

Polymerization procedure (also cf. Tables 3 and 4): To the catalyst solution (**3**−**5**) in toluene was first added hexadecane (0.3 mL), then the dispersion of silica (10 mL ethanol; 0.2−1 g of silica), and one-third of an aqueous solution of surfactant (1 wt % SDS). The resulting biphasic mixture was ultrasonified (Bandelin HD 2200 with a KE76 tip, operated at 120 W) to afford the "catalyst/silica miniemulsion". The remaining two-thirds of SDS solution and the "catalyst/silica miniemulsion" were then introduced into a mechanically stirred 250 mL pressure reactor equipped with a heating/cooling jacket controlled by a temperature sensor dipping into the reaction mixture. The reactor was flushed and pressurized with ethylene (p = 40 bar), while rapidly heating to the specified temperature (T = 60 °C (**3**) or T = 20 °C (**4**, **5**)) under stirring (1000 rpm). The pressure was kept constant during the entire polymerization by feeding monomer. After the desired reaction time

(2 h) the reaction was stopped by cooling and releasing the gas pressure. The dispersions obtained were filtered through a funnel with glass wool prior to further workup and analysis. Solids contents were determined with a moisture analyzer. After polymerization, the free PE particles were separated from the composite particles by centrifugations of dispersions at 40 000 rpm (40 min) on a Beckman L8-55M ultracentrifugation apparatus (it was verified by TGA that the surpernatant contains only polyethylene). The composite particles (solid residue) were dried and analyzed by thermogravimetric analysis (TGA) to determine the weight percentage of SiO_2.

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Supporting Information Available: TEM images of silica dispersions and of silica/polyethylene composite dispersions; ^{29}Si CP/MAS NMR spectra of silicas. This material is available free of charge via the Internet at http://pubs.acs.org.

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