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Synthesis of poly(ε-caprolactone)–silica nanocomposites: from hairy colloids to core–shell nanoparticles

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The synthesis of structurally well defined poly(ε-caprolactone) (PCL)–silica nanocomposites was performed following two synthetic routes:(1) "graft from" anionic ring opening polymerization of CL initiated from the surface of silica nanoparticles that have been previously modified by grafting of hydroxyl groups, and (2) dispersion polymerization of CL in the presence of OH-functionalized silica beads. In both strategies, yttrium or aluminium alkoxides were used as catalysts. In the first case, the influence of the catalyst, the OH to Al molar ratio and the monomer concentration on the amount of grafted polymer was studied. TEM analysis revealed the formation of a dense and uniform polymer brush around the silica nanoparticles. In the second case, "core–shell" particles with a silica core and a PCL shell were successfully obtained. The grafting of a small quantity of polymer on the silica surface during the first stages of the dispersion polymerization process appeared to be a prerequisite condition for encapsulation to succeed. When raw, un-modified silica beads were used, encapsulation failed to occur.

Introduction

Over the last few years, organic–inorganic hybrids have attracted particular attention in various areas due to the multifunctional character conferred by their starting components on the macroscopic scale. When these materials are made for instance of an inorganic core coated by a polymer shell, the polymer layer renders the inorganic filler compatible with a binder and promotes dispersion of the inorganic particles into polymer matrices, resulting consequently in better performances of the host material. To achieve optimum control over the composite nanostructure and to tailor the surface properties of the inorganic filler, a large number of synthetic strategies based on *in situ* heterophase polymerization,[1] controlled precipitation of preformed latexes on seed minerals (so-called heterocoagulation)[2] or grafting of polymer chains onto inorganic particles have been developed.[3] In the latter approach, three main routes are currently reported: chemisorption of polymer end groups to reactive sites on the surface ("graft to" method),[4–8] copolymerization with polymerizable groups grafted to the surface ("graft through" method)[9–12] and growth of polymer chains from chemically attached initiators ("graft from" method).[13–17] The latter technique is of particular interest as it ensures the formation of organic–inorganic materials with controlled nanostructures by exploiting the features of controlled/"living" polymerization systems. The benefits of such an approach were clearly demonstrated by von Werne *et al.*[16,17] who reported the grafting of polystyrene and polymethyl methacrylate using Atom Transfer Radical Polymerization (ATRP) initiators supported onto silica nanoparticles. The ATRP process confers perfect control over the molecular weight and the molecular weight distribution of the grafted polymer chains and therefore ensures subsequent control over the structure of the hybrid material on the nanoscale. Various "living" processes such as Nitroxide Mediated Polymerization,[18] Reversible Addition–Fragmentation Transfer,[19,20] or ionic polymerizations[13,21,22] have been reported in the recent literature using a variety of inorganic materials. Although successful for specific applications, for instance the elaboration of (co)polymers with controlled architectures, these "graft from" techniques are limited however to low polymer contents and low grafting efficiencies and do not allow the formation of large amounts of surface polymer.[23]

We thus decided to investigate an alternative approach based on *in situ* heterophase polymerization which seems to be an attractive solution to overcome the above mentioned limitations in view of the recent literature in this field.[3] Indeed, in this technique, a large proportion (if not all) of the total amount of polymer synthesized is located at the surface of the inorganic particles at the end of polymerization. However, the lack of affinity between inorganic nanoparticles and polymers requires adaptation of the polymerization procedure in order to promote polymer formation on the inorganic surface. This is generally achieved by adsorption of monomers,[2,24] macromonomers[25] or initiators[26,27] or by grafting of convenient silane molecules on the mineral surface before polymerization.[28,29] Bourgeat-Lami *et al.*[28,29] have developed for instance a process based on dispersion polymerization of styrene in the presence of silica nanoparticles coated with a silane coupling agent carrying a methacrylate functionality. They demonstrated that the presence of the coupling agent was essential in order to achieve a successful encapsulation. The authors suggested that the grafted polymer chains formed in the earlier stages of polymerization rendered the silica surface hydrophobic which process promoted capture of the growing radicals and shell formation by growth of polymer chains in the vicinity of the silica surface. The shell thus resulted in entanglements between free and grafted polymer chains. By tuning the experimental conditions, not only were all the silica beads surrounded by polymer but no free polystyrene latex particles were produced separately from the silica seed particles.[29]

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On the other hand, we recently reported the synthesis of poly(ε-caprolactone)–silica hybrid materials by the "graft from" technique.[30] Alcohol groups were introduced onto the silica particles surface in order to co-initiate the anionic ring-opening polymerization (ROP) of ε-caprolactone in the presence of metal alkoxides. We observed that restricted mobility of the alcohol moieties on the silica surface affected exchange reactions between the grafted alcohol and the metal alkoxide and that, consequently, free polymer chains were mostly formed at the expense of grafted polymer. The polymer content (and therefore the grafting efficiency) could be tuned nevertheless from a few percent to 70% by mass by varying the polymerization rate, that is by changing the alcohol to catalyst molar ratio. However, the silica nanoparticles used in this previous work were composed of large aggregates which did not allow any morphological characterization of the resulting hybrid material. Thus, the strategy described in our previous work is extended in the present paper to colloidal silica particles with a predetermined particle size. The polymerization process is studied as previously and particular attention is paid to characterization of the nanocomposite morphology. This "graft from" process is next extrapolated to dispersion polymerization. We hope that *in situ* grafting of polymer chains can increase the affinity between the silica surface and the growing polymer and promote therefore PCL-encapsulation of the silica particles.

Experimental

Materials

Reagents for the synthesis and modification of the silica sol. Tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS, Fluka 86578) was distilled under reduced pressure before use. Absolute ethanol (Prolabo 20821.321), ammonium hydroxide (28%, Carlo-Erba reagent, 314863) and dimethylformamide (99%, Acros Organics 116220010) were used without any purification. Titration indicated an ammonia concentration of 10.5 M. The coupling agent, 3-glycidoxypropyltrimethoxysilane (GPS, Gelest SIG.5825,0) was used as supplied.

Reagents for the "graft from" and dispersion polymerizations. ε-CL (99%, Aldrich 24,129-6) was stirred with calcium hydride, purified upon distillation under reduced pressure and stored under dry nitrogen over molecular sieves (3 Å, Aldrich 20,857-4). Toluene (>99.5%, Fluka 89681), heptane (99%, Carlo-Erba reagent 339385) and 1,4-dioxane (99%, Acros Organics 117110025) were distilled over sodium and stored under dry nitrogen over molecular sieves. Yttrium isopropoxide ($Y(O^iPr)_3$, 20–25% in toluene, Strem 39-3000) was used as supplied. Aluminium isopropoxide ($Al(O^iPr)_3$, >98%, Aldrich 22,041-8) was dissolved either in toluene or heptane depending on the synthetic route. In both cases, the aluminium concentration was 0.1 M and the solutions were stored under dry nitrogen over molecular sieves.

Reagents for synthesis of the copolymer stabilizer. 1,3-Dicyclohexylcarbodiimide (DCCI, 99%, Aldrich D 8,000-2), 4-dimethylaminopyridine (DMAP, 99%, Aldrich 10,770-0), triethylamine (>99.5%, Aldrich 47,128-5) and 2,2′-azo-bis-isobutyronitrile (AIBN, >98%, Fluka 11 630) were used as received. Dodecyl acrylate (>90%, Aldrich 2156-97-0) was purified from the inhibitor by washing with an aqueous basic solution (pH = 12).

Synthesis

Silica alcosol preparation and GPS grafting. A silica nanoparticle dispersion in a mixture of alcohol, ammonia and water (so-called alcosol) was prepared according to Stöber *et al.*[31] This "sol–gel" process allows the preparation of monodisperse silica beads, with radii ranging from 20 nm to several μm, at room temperature. In a typical experiment, absolute ethanol (670 g), ammonia (10.5 g), deionised water (95.8 g) and TEOS (41.6 g) were mixed in a 2 l reactor under mechanical stirring (300 rpm) at room temperature during 60 h. The silylation procedure was adapted from the recipe of Philipse and co-authors.[32] Ethanol, ammonia, water and residual monomer were distilled and replaced by DMF. Care was taken to keep a constant volume. The procedure was continued until the temperature of the head of the distillation column was equal to 152 °C corresponding to the boiling point of DMF. Then, the silica dispersion (400 g) was cooled down to room temperature before addition of the GPS organosilane (1.8 g). The reaction mixture was heated to 100 °C with an oil bath during 24 h. The separation of free GPS from the GPS-grafted silica was achieved by successive centrifugation-redispersion cycles in ethanol (Bioblock Scientific, 10 500 g, 30 minutes). The organophilic silica sol was then dried for 24 h at room temperature under dynamic vacuum. The epoxy groups of the GPS-grafted silica were converted into diol molecules by treating the functionalized silica with a 94 : 6 (v/v) mixture of ethanol (96%) and concentrated HCl solution. The resulting white powder was treated at 150 °C under dynamic vacuum and stored under dry nitrogen before characterization. The grafting density expressed in μmol m^{-2} of grafted diol per square metre of silica surface was determined by thermogravimetric analysis (TGA) using eqn (1):

$$\text{grafting density} = \frac{\left(\frac{W_{200-1100}}{100-W_{200-1100}}\right)\times 100 - W_{\text{silica}}}{M \times S_{\text{spec}} \times 100} \times 10^6 \quad (1)$$

where $W_{200-1100}$ is the TGA weight loss between 200 and 1100 °C and M is the molecular weight of the grafted diol molecule ($M = 195.6\ \text{g mol}^{-1}$). S_{spec} ($\text{m}^2\ \text{g}^{-1}$) and W_{silica} are, respectively, the specific surface area and the percentage weight loss of silica determined before grafting. S_{spec} was calculated using eqn (2):

$$S_{\text{spec}}/\text{m}^2\ \text{g}^{-1} = 3000/(\delta * R) \quad (2)$$

where R (nm) is the radius of the silica particles determined by dynamic light scattering (DLS) and δ is the density of silica ($\delta = 2\ \text{g cm}^{-3}$).

The silica particles size and the diol grafting density are reported in Table 1.

"Graft from" polymerization procedure. All the polymerizations were performed in a Schlenck-type flask under dry nitrogen. The monomer to polymer conversions were determined by gas chromatography (GC HP 5840, column HP-5, N_2: 0.7 bar, detector: 250 °C, injector: 180 °C, oven: 150 °C) using a calibration curve. Polymerization times were between 15 minutes and several days depending on the catalytic system used, on the OH to metal ratio, and on the targeted (theoretical) number-average degree of polymerization, DP_n. We

Table 1 Characteristics of raw and OH-functionalized silica nanoparticles

Samples	D_p/nm[a]	Specific surface area/m^2 g^{-1}[b]	Weight loss (%)[c]	Diol grafting density/ μmol m^{-2}[d]
Raw silica	108 ± 3	28	5.7	—
OH-functionalized silica	149 ± 11	20	9.1	7.93

[a] Determined by DLS in ethanol. [b] Determined using eqn (2). [c] Weight loss between 200 °C and 1100 °C determined by TGA. [d] Determined using eqn (1).

Table 2 Effect of the OH to catalyst molar ratio and of the monomer concentration on the properties of the PCL-grafted silica particles

Runs[a]	Catalyst	OH/Al[b]	[ε-CL]/g L^{-1}	Reaction time/h	Conversion (%)	Weight loss (%)[c]	Γ/mg m^{-2}[d]	Grafting efficiency (%)[e]	Hydrodynamic diameter/nm[f]
1	$Y(O^iPr)_3$	0.5	89.0	0.5	>99	12	2.9	0.20	—
2	$Al(O^iPr)_3$	0.5	89.0	16	>99	17.1	5.4	0.3	182 ± 9
3	$Al(O^iPr)_3$	0.5	133.5	17.5	>99	23.1	8.8	0.4	237 ± 11
4	$Al(O^iPr)_3$	0.5	178.1	19	92	34.2	16.7	0.6	264 ± 8
5	$Al(O^iPr)_3$	0.95	52.8	18	>99	18.2	5.9	0.6	—
6	$Al(O^iPr)_3$	1.9	32.7	240	32	29.2	12.8	6.8	—

[a] [OH-functionalized silica] = 2 g L^{-1}. $DP_{n\ \mathrm{theoretical}}$ = [ε-CL]/([grafted diol] + 3 × [metal alkoxide]) = 253 except for runs 3 and 4 for which $DP_{n\ \mathrm{theoretical}}$ is equal to 380 and 506, respectively. Polymerization temperature = 50 °C. [b] Grafted alcohol to aluminium molar ratio assuming that only the primary alcohol of the grafted diol molecule can participate to the polymerization. The OH concentration thus corresponds to the diol concentration: [OH] = [grafted diol] = 8 μmol m^{-2}. [c] TGA weight loss measured between 200 °C and 1100 °C. [d] Determined using eqn (3). [e] Determined using eqn (4). [f] Determined by DLS in toluene.

assume that only one OH group per grafted diol molecules is able to initiate the polymerization, the secondary alcohol being too basic to initiate the ROP. The alcohol groups of the silylated silica surface were activated using metal alkoxides. Theoretical DP_n were thus determined from the monomer and the total initiating groups concentration according to: DP_n = [monomer]/(3 × [metal alkoxide] + [grafted diol]). In a typical run (run 2, Table 2), the OH-functionalized silica powder (0.2 g), toluene (92 mL) and ε-caprolactone (9 g) were introduced into a reaction flask. The suspension was heated to 50 °C with an oil bath before addition of 0.2 mL of a 0.1 molar aluminium triisopropoxide solution. After polymerization, the "free" non-grafted polymer chains were removed from the suspension medium by successive centrifugation–redispersion cycles. The washings were repeated until no polymer was detected in the supernatant solution. The polymer-grafted silica particles were dried under vacuum at 50 °C for 15 h. The PCL grafting density, denoted Γ (mg m^{-2}), was evaluated by TGA using eqn (3):

$$\Gamma/\mathrm{mg\,m^{-2}} = \frac{\left(\frac{W_{200-1100}}{100-W_{200-1100}}\right)\times 100 - W_{\mathrm{silica}}}{S_{\mathrm{spec}}\times 100}\times 10^{3} \qquad (3)$$

where $W_{200-1100}$, W_{silica} and S_{spec} have the same meaning as previously.

The grafting efficiency, which corresponds to the weight fraction of grafted polymer, was determined using eqn (4):

$$\text{Grafting efficiency} = \frac{\text{Grafted polymer}}{\text{Total polymer formed}}\times 100 \qquad (4)$$

Synthesis of the poly(dodecyl acrylate)-*g*-poly(ε-caprolactone) (PDA-*g*-PCL) graft copolymer stabilizer. We first synthesized a methacrylate end-capped poly(ε-caprolactone) macromonomer as follows: 60 mL of dry toluene, 3.4 mmol of ethanol, 0.34 mmol of yttrium triisopropoxide and 0.135 mol of ε-caprolactone were added in a Schlenck-type flask under dry nitrogen. The reaction mixture was stirred for 10 min at room temperature and the reaction was stopped by adding 3 mL of ethanol. PCL (15 g) was recovered by precipitation from heptane. The average molecular weight and polydispersity index were 2000 g mol^{-1} and 1.3, respectively, as determined by SEC using polystyrene standards. PCL was then esterified with methacrylic acid using the dicyclohexylcarbodiimide (DCCI) method.[33] According to ^1H NMR analysis, each PCL chain was quantitatively end-capped with a methacryloyl unit. Copolymerization of the PCL macromonomer with dodecyl acrylate was carried out using the recipe of Slomkowski *et al.*[34] The molar mass, M_n, of the graft copolymer stabilizer determined by SEC was 35 000 g mol^{-1} in equivalent polystyrene and the weight fraction of PCL, determined by ^1H NMR, was 0.25.

Dispersion polymerization. All the polymerizations were performed in a Schlenck-type flask under dry nitrogen. The monomer to polymer conversions were determined by gas chromatography. The polymerisation conditions were adapted from the recipe of Slomkowski *et al.*[34] In a typical procedure, a 4 : 1 (v/v) mixture of heptane and 1,4-dioxane (94.5 mL) was introduced into a Schlenck-type flask and the desired quantity of the PDA-*g*-PCL graft copolymer (from 0.2 g to 0.4 g) was dissolved in the reaction medium. Then, 5.5 mL of ε-caprolactone was added under magnetic stirring (60 rpm.). For the synthesis of the composite latex particles, the suspension contained a known amount of silica or OH-functionalized silica corresponding to a concentration of 1.6 g L^{-1} and the required quantity of stabilizer. After complete dissolution of the stabilizer, the silica suspension was left under magnetic stirring for 1.5 h and immersed in an ultrasonic bath for 30 min to ensure the production of a colloidally stable silica dispersion. The desired volume of the catalyst solution corresponding to a final $Al(O^iPr)_3$ concentration of 0.63 × 10^{-2} mol L^{-1} was finally added to the silica suspension to initiate polymerization.

Measurements

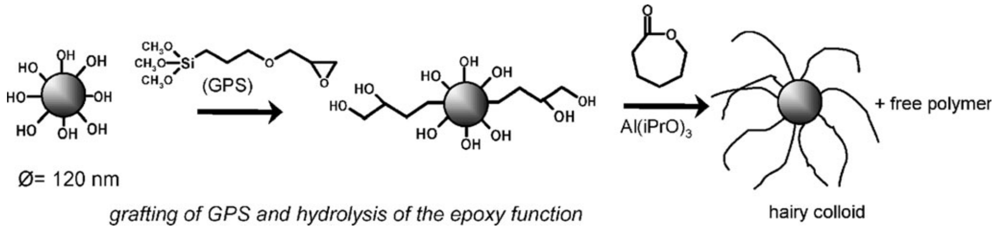
FTIR spectra were recorded on a Nicolet 20 SXB FTIR spectrometer equipped with a Spectra-Tech 'Collector' diffuse reflectance accessory, using KBr pellets. Thermogravimetric analyses (TGA) were performed using a SETARAM apparatus (TGA, 10 °C min^{-1} from 30 °C to 1100 °C, air). Transmission Electron Microscopy (TEM) experiments were performed on a Philips CM200 transmission electron microscope. A drop of the diluted dispersion (about 0.01 wt%) was spread on a carbon film supported by a calibrated copper grid (45 μm) and allowed to air dry before analysis. Particle size was measured by dynamic light scattering with a Coulter N4+ instrument. The particle number per unit volume of solvent was calculated using eqn (5):

$$N_{\mathrm{p}}\,\mathrm{L^{-1}} = \frac{C}{\rho\frac{\pi}{6}D_{\mathrm{p}}^{3}}\times 10^{19} \qquad (5)$$

where C (g L^{-1}) is the total solid concentration, ρ (g cm^{-3}) is the density of either the polymer, the silica or the composite particles, and D_p (nm) is the particle diameter.

Results and discussion

Our article is divided in two parts: (1) synthesis of SiO_2–PCL hairy colloids by the so-called "graft from" technique, and (2) combination of this technique with a heterogeneous dispersion polymerization process in order to produce PCL-encapsulated silica particles.



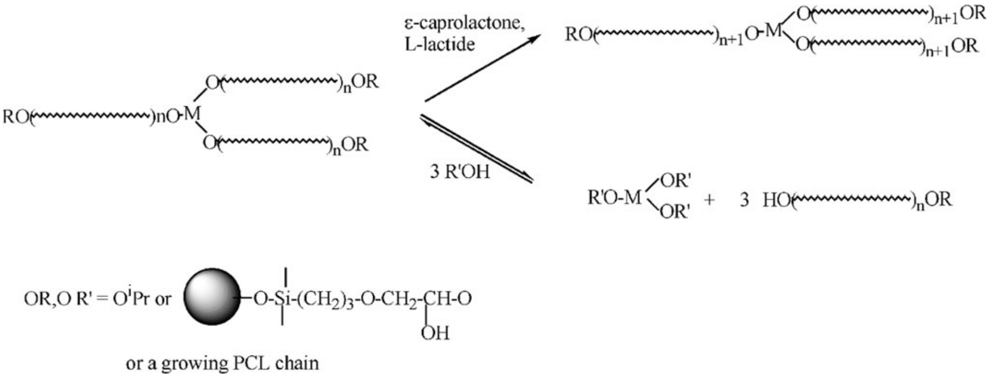
Scheme 1 Synthetic strategy for the graft anionic coordinated ring-opening polymerization of ε-caprolactone "from" OH-functionalized silica particles using Al or Y alkoxides as catalysts.

Synthesis of SiO_2–PCL hairy nanoparticles using the "graft from" technique

The "graft from" procedure, described in our previous report for fumed silica,[30] is extended in the present work to well defined colloidal silica beads with a radius of 54 nm and a diol grafting density of 7.9 μmol m^{-2} (Table 1, Scheme 1). PCL grafting on the inorganic nanoparticle surface occurs thanks to exchange reactions taking place between the grafted alcohol molecules and the metal alkoxide. The alcohol groups thus play the role of co-initiators in the ROP of CL leading consequently to the concurrent formation of grafted and free PCL chains as depicted in Scheme 2. For steric and reactivity considerations, we assume that only the primary alcohol of the grafted diol molecule is able to initiate the polymerization. The maximum number of polymer chains that can potentially grow from the surface is thus directly given by the surfacic diol concentration.

The grafting was characterized by DRIFT, DSC measurements and TGA analysis. The DRIFT spectrum (not shown) exhibits vibration bands characteristic of both components with a band at 1735 cm^{-1} attributed to the ester group of the polymer and a large band at 1100 cm^{-1} corresponding to silica. DSC measurements also supported the grafting, as we have already reported an increase in the T_g of the grafted polymer chains as compared with a commercial polymer of similar molecular weight.[30] The influence of the catalyst, the OH to metal alkoxide molar ratio and the monomer concentration on the polymer content was studied in a systematic way in order to optimize the process of formation of the SiO_2–PCL hybrids (Table 2). In view of the results given in Table 2, the nature of silica seems not to have a great influence on the grafting process. In agreement with our previous work on fumed silica, the polymer contents ranged from 12 to 34% by mass depending on the polymerization rate, which in turn, can be tuned either by the OH to metal molar ratio or by the choice of the catalyst. Indeed, decreasing the polymerization rate allows interchange reactions between dormant and growing polymer chains to proceed in a better way which promotes PCL grafting onto silica. In the case of $Y(O^iPr)_3$ for instance, which is known to exhibit high polymerization rates compared to $Al(O^iPr)_3$, the weight loss is close to that of un-functionalized silica and the PCL-grafting density is two times lower than that obtained for $Al(O^iPr)_3$ for the same monomer conversion. In the case of aluminium isopropoxide, the OH : Al molar ratio appears to have a great influence on the amount of grafted polymer. The higher the OH to metal ratio, the lower the polymerization rate and the more efficient therefore the exchange process which results in an increased polymer content. It is worth noticing however that changing the OH : Al molar ratio from 1 to 2 has only a small influence on the polymer content (compare run 2 and run 5 in Table 2). We presume that, for large aluminium concentrations (*i.e.*, for low OH : Al ratios), some catalyst molecules are aggregated on the silica surface which reduces the effective number of active aluminium groups.[35] Nevertheless, when this ratio is increased further (run 6), the polymer content increases and reaches one of the highest values of the series in spite of a low conversion. As expected, an increase in the initial monomer concentration for a constant OH : Al molar ratio also resulted in higher polymer contents (runs 2, 3 and 4).

Attempts to determine the diameter of raw and alcohol-functionalized silica particles in toluene by DLS was unsuccessful due to the hydrophilic character of the silica surface leading to particle aggregation and sedimentation. In contrast, this analysis was performed with success after grafting of PCL chains which indicates significant improvement of the colloidal stability of the silica suspension upon grafting *via* presumably a steric stabilization mechanism promoted by the hairy PCL layer formed around the silica particles. It should be noticed that the higher the polymer content, the larger the hydrodynamic diameter of the nanocomposite particles. This suggests that the polymer chains adopt an extended brush conformation at the silica surface which assumption is supported by the high polymer grafting density between 2.9 and 16.7 mg m^{-2}. In order to gain further insights into the polymer chain conformation on the silica surface, we have compared the shell thickness determined by DLS to the mean average end-to-



Scheme 2 Competition between the propagation step and the exchange reaction in the catalytic ROP process.

Table 3 Width, l_i, of the hairy shell layer of a series of PCL-grafted silica particles. Comparison with theoretical predictions

Runs[a]	[ε-CL]/g L^{-1}	Γ/mg m^{-2} [b]	$DP_{n\ theoretical}$	$DP_{n\ calculated}$ [c]	Shell thickness/nm[d]	l_i/nm[e]	Estimated DP_n[f]	PCL grafting density/μmoles m^{-2} [g]
2	89.0	5.4	253	6.0	37	3.8	58	0.8
3	133.5	8.8	380	9.7	64.5	6.2	102	0.76
4	178.1	16.7	506	18.5	78	11.7	123	1.2

[a] [OH-functionalized silica] = 2 g L^{-1}. Temperature = 50 °C. OH/Al molar ratio = 0.5. [b] Determined from the weight loss data of Table 2 using eqn (3). [c] DP_n of the grafted polymer chain determined from the diol grafting density and the weight loss data assuming that one hydroxyl group per grafted diol molecules initiates the polymerization. [d] Determined from the hydrodynamic diameter before and after grafting. [e] Calculated from the theoretical brush model according to: $l_i = 5DP_n \times L_{C\text{–}C} \times \sin(\theta/2)$ with $L_{C\text{–}C} = 1.54$ Å and $\theta = 112°$. [f] Estimated from the experimental shell thickness according to: DP_n = shell thickness (Å)/($5L_{C\text{–}C} \times \sin(\theta/2)$). [g] Calculated according to: [PCL] (μmol m^{-2}) = DP_n (calculated) × [diol grafting density]/DP_n (estimated).

end distance, l_i, of a fully extended chain according to: $l_i = 5DP_n\ L_{C\text{–}C} \sin(\theta/2)$ where $L_{C\text{–}C}$ designates the length of the C–C bond ($L_{C\text{–}C} = 1.54$ Å), $5DP_n$ is the number of C–C bonds, and θ (in radians) is the bond angle ($\theta = 112°$ for carbon chains). The results are reported in Table 3.

The data in Table 3 indicate that the shell thickness is much larger than that estimated from the extended coil model. This is not surprising since the calculation assumes that every grafted primary alcohol molecule (*e.g.*, 8 μmol m^{-2} silica surface) can initiate one polymer chain. However, given a cross-sectional area of 60 Å^2 for GPS, we can calculate that the maximum GPS grafting density corresponding to a monolayer is only 2.75 μmol m^{-2}. Our results thus suggests the formation of a multilayer coverage. Indeed, it is known from the literature that in acidic conditions, GPS molecules first hydrolyze and react in solution to produce oligomers that adsorb and condense on the surface.[36] Under such conditions, it is likely that an irregular multilayer coating rather than a monolayer coverage was formed on silica. Consequently, because of steric hindrance limitations, we can reasonably assume that only a fraction of the grafted alcohols will effectively participate in the polymerization. If we make the assumption of an extended brush conformation on the surface and given the shell thickness determined by DLS, we can calculate the DP_n of the grafted polymer chains and the corresponding polymer grafting density. The results indicate a PCL grafting density of the order of 1 μmol m^{-2} and a molecular weight of the grafted polymer chains in the range 6000–14 000 g mol^{-1} (Table 3). Although these results appear plausible, the possibility that much longer (and consequently less numerous) grafted polymer chains would adopt a random coil conformation on the surface also cannot be completely ruled out.

The hypothesis of formation of an homogenous and dense PCL coating on the silica surface is supported by TEM analysis. Fig. 1 represents TEM micrographs of raw silica and PCL-grafted silica particles (runs 2, 3 and 4) cast from dilute ethanol and toluene suspensions, respectively. For hybrid particles with a low polymer content, identification of the polymer shell by TEM is not obvious. This is presumably due to the low DP_n of the grafted PCL and collapsing of the polymer chains in the vicinity of the silica surface upon drying. In contrast, the polymer layer is clearly identified for the materials with higher polymer contents. It is noteworthy that the higher the polymer content, the more ordered the silica particles within the polymer film after solvent evaporation. Indeed, a regular hexagonal array of silica particles with interparticulate domains filled with polymer can be clearly identified in the TEM pictures of Fig. 1c and 1d. According to Patten[16] and Auroy,[37] two conditions are necessary for crystalline packing of polymer-grafted colloidal spheres. First, the molar mass of the grafted polymer chains must be sufficiently high and, second, their polydispersity index must be close to 1. In our case, we cannot ensure that these two conditions are fulfilled since we cannot isolate the grafted PCL from the silica surface as chemical etching of silica with acid treatment by HF would immediately damage the polymer chains. However, estimation of the polymerization degree as described above indicates that the molecular weight of the grafted polymer chains is larger than 10 000 g mol^{-1} (see Table 3) which value is of the same order of magnitude as that reported in the work of von Werne and Patten.[16] In summary, TEM analysis suggests a controlled growth of the grafted polymer chains and we can reasonably assume that well defined hybrid nanoparticles consisting of a silica core surrounded by a dense hairy polymer layer have been synthesized by our process.

Using such a technique, we obtained nanocomposites having polymer content (<35%) higher than that obtained by other authors[38,39] using cationic polymerization of CL from the surface (<19%) but the coating efficiency was still low. We thus decided to perform the "graft from" polymerization in dispersed media in order to synthesize PCL-coated silica nanoparticles involving a larger amount of PCL.

Synthesis of SiO_2–PCL core–shell hybrid particles through dispersion polymerization

In this section, we first optimized the experimental conditions in order to synthesize poly(ε-caprolactone) latex particles by dispersion polymerization in the presence of aluminium alk-

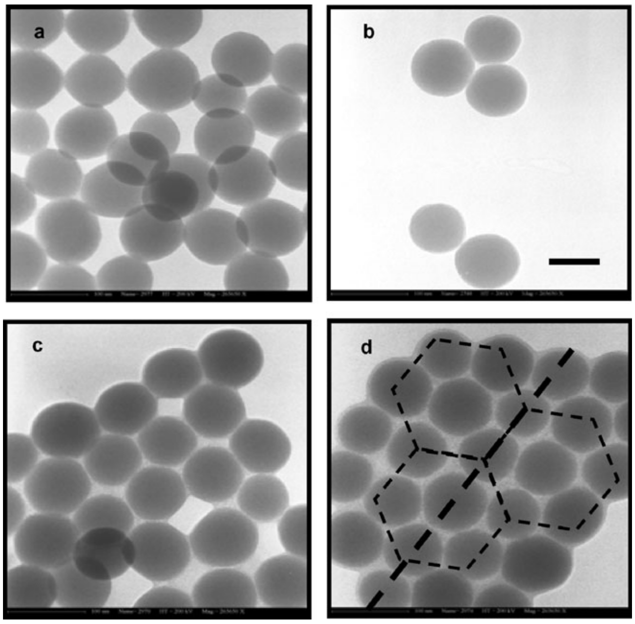
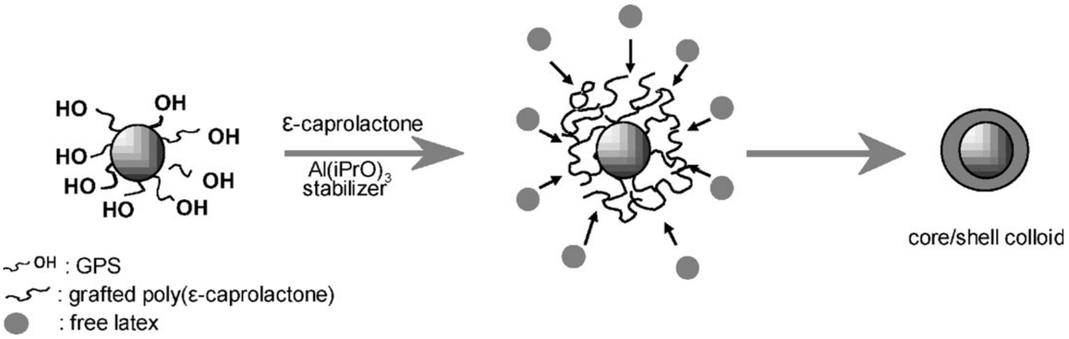


Fig. 1 TEM micrographs of (a) raw silica and (b)–(d) PCL-grafted silica particles: (b) run 2, (c) run 3 and (d) run 4 (see Table 2). Scale bar: 100 nm.



Scheme 3 Synthetic strategy for the encapsulation of OH-functionalized silica particles by dispersion polymerization of ε-caprolactone.

oxide. We next extrapolated this polymerization technique to the encapsulation of silica nanoparticles and we examined the effect of the nature of the silica surface on the encapsulation process (Scheme 3).

Dispersion polymerization of ε-caprolactone. To our knowledge, dispersion polymerization is the only way to obtain PCL latex particles by *in situ* heterophase polymerization. Dispersion polymerization of ε-caprolactone has been extensively studied by Slomkowski *et al.*[34,40,41] in a 4 : 1 (v/v) mixture of heptane and 1,4-dioxane using a graft copolymer, poly(dodecyl acrylate)-*g*-poly(ε-caprolactone), as steric stabilizer. According to this author, polymerization is initiated in solution until the formation of stable primary particles. The polymerization then continues within the polymer microspheres into which monomer molecules diffuse from solution, the active catalytic center being mostly contained within the monomer-swollen particles. On the basis of these pioneering works, a series of blank experiments, *i.e.*, polymerizations conducted in the absence of silica beads, were performed by changing the concentrations of the initiator and of the steric stabilizer, until monodisperse, stable polymer nanoparticles were obtained. The only difference with Slomkowski's previous studies is the nature of the catalyst. In the present work, we used aluminium triisopropoxide instead of aluminium diethylethoxide in order to compare our results with those obtained in the "graft from" process. The results, including initiator concentrations, monomer conversions and particle size are given in Table 4. While polymerization performed with large amounts of initiator and low copolymer concentrations systematically afforded unstable latexes, a colloidally stable milky dispersion could be obtained by decreasing the initiator concentration and increasing the amount of stabilizer (run 10). This can be regarded as a consequence of the diminution of the number of primary polymer particles. It is known that in the early stage of dispersion polymerization, the polymer chains grow and reach a molecular weight at which they are no longer soluble. They associate with other growing polymer chains in the continuous phase to form small aggregates which assemble with other aggregates until mature stable latex particles are formed when the amount of stabilizer adsorbed on their surface is sufficient to prevent their aggregation. These particles constitute the nuclei of the final latex particles. For a given stabilizer concentration, the number of polymer nuclei depends on the initiator concentration.[42] Indeed, increasing the amount of initiator leads to an increase in the number of primary polymer particles. The data in Table 4 thus demonstrate that for initiator concentrations larger than 0.63×10^{-2} mol L^{-1}, the amount of stabilizer is not sufficient to stabilize all the nuclei formed, resulting therefore in aggregation and sedimentation of the polymer latex particles.

Given the results of Table 4, the optimal conditions of run 10 were selected in the following experiments in order to synthesize SiO_2–PCL composite particles through dispersion polymerization. An important issue to be addressed before performing the polymerization is the colloidal stability of the suspension medium. Indeed, as mentioned above, neither raw silica nor OH-functionalized silica were stable in organic solvents due to their hydrophilic character which resulted in sedimentation of the silica suspensions. Attempts were made therefore to stabilize the silica suspension by addition of an appropriate amount of graft copolymer prior to polymerization. In the range of concentrations studied, the PDA-*g*-PCL stabilizer presented appropriate properties to stabilize the silica beads in the selected continuous phase (Table 5). This result can be attributed to potential hydrogen bonding interactions between the ester groups of the pendant PCL chains and the silanol groups of silica. Similar observations were reported in the literature by von Werne *et al.*[43] who used PCL macroinitiators adsorbed onto silica surfaces in apolar solvents in order to initiate the free radical polymerization of styrene from the silica surface. Whatever the initial stabilizer concentration, the mean silica particle diameter increased from 108 nm (for raw silica in ethanol) to 234 nm (after adsorption of the graft copolymer) indicating a slight aggregation phenomenon (Table 5). The amount of adsorbed copolymer reached a constant value of 6 mg m^{-2} (*e.g.*, 0.2 μmol m^{-2}) whatever the initial copolymer concentration. This value probably corresponds to the amount of polymer adsorbed at saturation. At this stage,

Table 4 Dispersion polymerisation of εε-CL in a 4/1 (v/v) mixture of heptane and 1,4-dioxane using aluminium isopropoxide as catalyst and PDA-*g*-PCL as steric stabilizer

Runs[a]	[PDA-*g*-PCL]/g L^{-1}	$[Al(O^iPr)_3]$/mol L^{-1}	Reaction time/h	Conversion (%)	Latex stability	Particle diameter/nm[b]	Particle number/L^{-1}[c]
7	2.2	2.56×10^{-2}	5	—	Unstable	—	—
8	2.2	1.26×10^{-2}	5	—	Unstable	—	—
9	2.2	0.63×10^{-2}	10	89	Stable	Polydisperse	—
10	4.4	0.63×10^{-2}	10	93	Stable	362 ± 12	2.2×10^{15}

[a] [ε-CL] = 56 g L^{-1}; $[Al(O^iPr)_3] = 0.63 \times 10^{-2}$ mol L^{-1}; polymerization temperature = room temperature. [b] Determined by DLS in a 4 : 1 (v/v) mixture of heptane and 1,4-dioxane. [c] Determined using eqn (5).

Table 5 Adsorption isotherm of PDA-*g*-PCL onto OH-functionalized silica particles in a 4/1 (v/v) mixture of heptane and 1,4-dioxane

[PDA-*g*-PCL]/g L^{-1}	Weight loss (%)[a]	Adsorbed copolymer (%)[b]	Adsorbed copolymer/mg m^{-2}[c]	Silica particle diameter/nm[d]
2	19.0	9.5	5.5	227 ± 14
4.2	20.1	5.2	6.2	234 ± 11
6.9	19.8	3.0	6	218 ± 14

[a] Weight loss measured by TGA between 200 °C and 1100 °C. [b] Mass of adsorbed copolymer × 100 divided by the total mass of copolymer. [c] Determined using eqn (2). [d] Determined by DLS in a 4 : 1 (v/v) heptane–1,4-dioxane mixture. $[SiO_2] = 1.6$ g L^{-1}.

Table 6 Dispersion polymerisation of ε-CL in presence of raw and OH functionalized silica in a 4 : 1 (v/v) mixture of heptane and 1,4-dioxane using aluminium isopropoxide as catalyst and PDA-*g*-PCL as steric stabilizer

Runs[a]	Silica	[PDA-*g*-PCL]/g L^{-1}	Reaction time/h	Conversion (%)	Latex stability	Particle diameter/nm[b]	Particle number/L^{-1} [c]
11	Raw silica	4.4	9	92	Stable	350 ± 15 and 1500 ± 41	—
12	OH-functionalized silica	4.4	11	95	Stable	772 ± 8	2.2×10^{14}

[a] [OH-functionalized silica] = 1.6 g L^{-1}. [ε-CL] = 56 g L^{-1}. $[Al(O^iPr)_3] = 0.63 \times 10^{-2}$ mol L^{-1}. Temperature = room temperature. [b] Determined by DLS in a 4:1 (v/v) mixture of heptane and 1,4-dioxane. [c] Determined using eqn. (5).

all the conditions were fulfilled to start polymerization and perform a successful encapsulation.

Dispersion polymerization of ε-caprolactone in the presence of raw and OH-functionalized silica beads. Run 10 was repeated in the presence of raw and OH-functionalized silica beads. Table 6 summarizes the experimental conditions and the properties of the resulting composite latexes. DLS analysis revealed that the success of the encapsulation was highly dependent on the nature of the silica surface. When raw silica beads were engaged in the process, particle size measurements suggested that the encapsulation failed. Indeed, DLS indicated the presence of two populations with mean diameters of 350 nm and 1500 nm, respectively. The diameter of the first population is close to the diameter of the latex particles obtained under similar conditions without silica beads while the second population can be attributed to aggregates of polymer latex particles and silica beads. In contrast, when OH-functionalized silica particles were used as the seeds, DLS measurements indicated only one population of particles whose diameter was twice that of the PCL microspheres produced in run 10. This result, together with TEM analysis, suggests a successful encapsulation. The TEM micrograph of the corresponding hybrid particles is shown in Fig. 2. The silica particles (in dark) are easily identified by their contrast. They are surrounded by a diffuse polymer halo with badly defined contours. This is believed to be related to the low T_g of PCL ($T_g = -65$ °C) that promotes particle coalescence on the TEM grid. When the coalescence is important, as in the central part of the TEM picture, we can no longer distinguish the particle shape and determine their size. However, considering solely isolated particles, a rough estimation of their size on the TEM image indicates a mean diameter in the range 400–900 nm (see inset). Most of these composite particles (the smallest ones) contain only one silica bead although we can also distinguish a few particles with two (and sometimes three) silica beads. These silica doublets (or triplets) may result from aggregation occurring before polymerization when the functionalized silica particles are introduced into the heptane–1,4-dioxane suspension medium. As a matter of fact, the diameter of these silica aggregates determined by DLS (*e.g.*, 234 nm, see Table 5) agrees well with the size of a doublet or a triplet. It is known however that DLS is more sensitive to large particles than to smaller ones and we cannot completely exclude therefore the presence of a certain proportion of individual non-aggregated silica particles in the original silica suspension. It should be pointed out nevertheless that the number of composite latex particles determined using eqn (5) (Table 6) is close to the number of silica aggregates (1.2×10^{14}). This result suggests that the polymerization mainly occurred around these aggregates although TEM clearly proved that encapsulation also involved individual silica particles. This last observation thus demonstrates the importance of using different techniques in order to get a correct description of the morphology of the

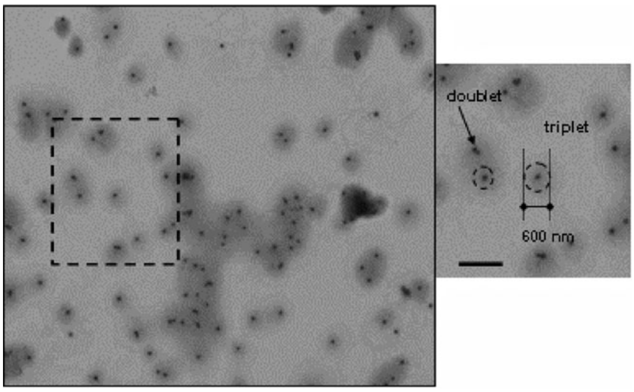


Fig. 2 TEM micrograph of PCL-encapsulated silica particles obtained through dispersion polymerization of CL (run 12 in Table 5). Scale bar: 1000 nm.

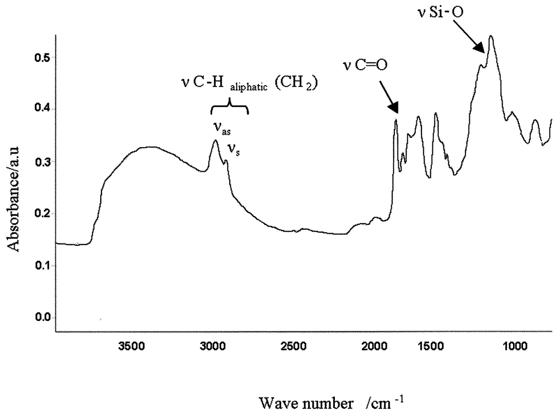


Fig. 3 DRIFT spectra of PCL-encapsulated silica after extraction with toluene (run 13 in Table 5).

Table 7 Composition of the PCL-encapsulated silica nanocomposites particles before and after extraction with toluene

Runs[a]	Weight loss before toluene extraction (%)[b]	Weight loss after toluene extraction (%)[b]	Polymer grafting density/mg m^{-2c}	Grafting efficiency (%)[d]
12	97	30.2	13.6	1.1

[a] [OH-functionalized silica] = 1.6 g L^{-1}. [ε-CL] = 56 g L^{-1}. [Al(O^{i}Pr)$_3$] = 0.63 × 10^{-2} mol L^{-1}. Temperature = room temperature. OH/Al = 0.056. [b] Weight loss between 200 and 1100 °C determined by TGA. [c] Determined using eqn (3). [d] Determined using eqn (4).

composite material. In summary, and in spite of particle coalescence during the drying step, TEM analysis clearly demonstrates that every silica bead is recovered by polymer (there are no isolated silica beads) and that the composite particles contain on average one or two silica beads.

Concerning now the mechanism of formation of the composite particles, we can reasonably assume that only a fraction of the polymer chains is effectively grafted to silica and that the encapsulation process involves both grafted and "free" unbonded polymer chains.

To examine this hypothesis, we carried out Soxhlet extraction experiments of the composite latex particles with toluene. Qualitative evidence of PCL bonding to the silica surface was provided by DRIFT spectroscopy analysis of the recovered silica powder after extraction (vibration band at 1735 cm^{-1}, Fig. 3).

As expected, the PCL content, estimated by TGA, decreased from 97% (before extraction) to around 30% (after dissolution of the free un-grafted polymer chains) (Table 7). This corresponds to around 1% grafting efficiency which is relatively high compared to the efficiency of the "graft from" process reported above and considering the low OH : Al ratio of run 12 (OH : Al = 0.056). This can be due to compartmentalization of the reactive species and differences in polymerization mechanisms between dispersion and solution polymerizations. In particular, equilibria between monomeric active centers and non reactive aggregated species, which are known to exist in solution, may affect the kinetics of the polymerization although it would be purely speculative to conclude on the role of such equilibria in dispersed media in view of the limited number of available experimental data.

In view of these results, we suspect that the coating is promoted by monomer swelling at the vicinity of the silica surface and subsequent growth as described above for conventional dispersion polymerization rather than by entanglements between free and grafted polymer chains. As a matter of fact, the average molecular weight of the recovered free polymer (*e.g.*, M_n = 11 000 g mol^{-1}) is really inferior to the critical entanglement molecular weight of poly(ε-caprolactone). According to this mechanism, monomer molecules are solubilized in the polymer-grafted interface layer giving rise to high local concentration near to the grafted active centers in the vicinity of the silica surface. The grafting of only 1% of polymer thus appears to be sufficient to promote monomer swelling and subsequent encapsulation. Similar observations were made by Bourgeat-Lami and Lang during the encapsulation of silica particles by polystyrene (PS) through dispersion polymerization.[28] They concluded that grafting of only a small amount of PS was sufficient to obtain encapsulation of the silica particles with the entire amount of polymer synthesized.

Conclusion

We have developed two original routes to synthesize poly(ε-caprolactone)–silica based hybrid materials with well-defined morphologies. The "graft from" technique enabled the formation of hairy colloids with polymer contents in the range typically 12 to 34% by mass depending on the OH : Al ratio and on the initial monomer concentration. In agreement with our previous work, decreasing the polymerization rate promoted exchange reactions between the grafted alcohol molecules and the metal alkoxide resulting in higher polymer contents. Although in this system exchange reactions are not favoured which might affect the livingness of the polymerization, the formation of ordered domains of silica particles within the polymer matrix suggests a controlled grafting process. In the second part of this work, silica–poly(ε-caprolactone) colloidal nanocomposites were readily obtained through dispersion polymerization. The grafting of poly(ε-caprolactone) onto silica in the early stages of polymerization was essential for encapsulation to succeed, even if a relatively small amount of polymer, around 1% of the total amount of poly(ε-caprolactone) synthesized, was effectively bonded to the silica surface. In this case, the morphology was of the "core–shell" type with, on average, one or two silica beads per composite particle. We did not observe the formation of free latex particles nor isolated un-coated silica beads which means that nearly all the polymer synthesized was involved in the encapsulation process leading to more than 97% polymer content.

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