Preparation and Application of Double Hydrophilic Block Copolymer Particles

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Summary: The preparation of some unique block copolymers and block copolymer particles via radical heterophase polymerization is described. Special emphasis is placed on double hydrophilic block copolymers such as poly(styrene sulfonic acid)-*b*-poly(methacrylic acid) diblock copolymer and double hydrophilic block copolymer particles consisting of both hydrophilic shells and cross-linked hydrophilic cores. Examples are given for the application of such particles as adsorbents, nano-reactors for chemical synthesis, and as colloidal stabilizers in both heterophase polymerization and biomineralization reactions.

Keywords: block copolymers; double hydrophilic particles; heterophase polymerization

Introduction

During the last decade radical polymerization experienced an outstanding renaissance for the preparation of block copolymers due to the enormous progress made in the development of controlled or living radical polymerization techniques [1, 2]. Also the first block copolymers mentioned in a scientific paper as early as 1939 were prepared by radical polymerization. Bolland and Melville [3], who studied the polymerization of methyl methacrylate in the gaseous phase, observed that the polymer deposited on the sides of the reaction vessel was "active" in that it possessed the ability of causing the continued polymerization of either further methyl methacrylate or chloroprene vapor. The activity remained over a long period of time (several days) so that it was possible to alternate the two monomers and to build up what the authors thought to be "molecular sandwiches" [4]. The kernel of this route of block copolymer preparation is the only little tendency of the adsorbed polymeric radicals to terminate. Another idea to get amphiphilic block copolymers via radical polymerization was published 1952 by Dunn and Melville [5], who utilized aqueous heterophase copolymerization of styrene and acrylic or methacrylic acid

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with aqueous phase photonitiation. Block copolymer formation took place when growing radicals passed the phase boundary and continued to grow. Obviously, this method leads to the formation of block copolymers made of copolymer blocks as both the monomeric acids are soluble in styrene and the styrene is soluble in water.

Recently a first report was published combining both of Sir Harry Melville's ideas, that is the use of polymeric radicals and aqueous heterophase polymerization, to prepare block copolymers [6]. The aim of this contribution is to describe the synthesis and the properties as well as applications of unique block copolymers and double hydrophilic block copolymer particles which are easily accessible only by this route. Some of the block copolymers described might also be accessible by controlled radical polymerization techniques but with much more efforts. After a brief description of the principle of this route examples are given for the preparation, properties, and application of poly(styrene sulfonic acid)-*b*-poly(methacrylic acid) (PSS-PMAA) diblock copolymer, poly(ethylene glycol)-*b*-poly(N-isopropylacrylamide)-b-poly(methyl methacrylate) triblock copolymer particles (PEG-PNIPAM-PMMA), and poly(diethylaminoethyl methacrylate)-*b*- poly(N-isopropylacrylamide)-*b*-poly(methacrylic acid) (PDEAEMA-PNIPAM-PMAA) double hydrophilic triblock copolymer particles via hydrolysis of poly(diethylaminoethyl methacrylate)-*b*- poly(N-isopropylacryl-amide)-*b*-poly(t-butyl methacrylate) (PDEAEMA-PNIPAM-PtBMA) precursor particles. To avoid dissolution of the double hydrophilic particles at temperatures below the critical solution temperature of the PNIPAM – block 1,3-diisopropenylbenzene was employed as cross - linker during the t-butyl methacrylate polymerization.

Experimental Information

Chemicals. If not otherwise stated all chemicals except the monomers were used as received. In order to remove inhibitors the monomers were either carefully distilled under reduced pressure, or passed over neutral alumina (Sigma Aldrich) according to a procedure described in [7], or at least two times recrystallized from an appropriate solvent prior to use. 2,2-azobis(2-methyl-N-(2-hydroxyethyl)propionamide) (VA-086) and 2,2-azobisiso-butyronitrile (AIBN) from Wako) were employed as thermal initiators whereas VA-086 was used to prepare polymers with hydroxymethyl terminal groups used as reductant. Cerium ammonium nitrate (CAN) from (Fluka) was used as ceric ion source (oxidant) and

PEG-monomethylether with an average molecular weight of 5000 g mol^{-1} (Fluka) as a particular reductant. The water was taken from a Seral purification system (PURELAB PlusTM) with a conductivity of 0,06 µS cm^{-1} and de-aerated prior to use for the polymerizations.

Polymerizations. The polymerizations were carried out at elevated temperatures either in all glass reactors equipped with stirrer, reflux condenser, nitrogen inlet and outlet, heating jacket to control the temperature, and a valve on the bottom to remove the latex or in reaction calorimeter CPA200 with a cylindrical reactor made of glass wall and stainless steel bottom and lid. All recipe components except the initiator or the ceric ions were placed in the reactor during the thermal equilibration method and the reaction was started by injecting an aqueous solution of the initiator or ceric ions. All polymerizations were allowed to run until complete conversion. For the detailed polymerization recipes see the corresponding caption of the Figures and the text. The reaction products were ultrafiltrated through a regenerated cellulose membrane with a cut-off of 10 kD (Millipore, Bedford, USA) with at least the 10-fold amount of distilled water in order to remove unreacted monomers and inorganic salts before the polymers were isolated by freeze – drying. Further details of the polymerizations can be found elsewhere [6].

Characterization methods. Homopolymer (PEG precursor polymers) and latex characterizations were carried out by standard procedures such as gel permeation chromatography (Thermo Separation Products set-up being equipped with UV (TSP UV1000) and RI (Shodex RI-71) detectors in THF at 30 °C with a flow rate of 1 ml per minute, elemental analysis (vario EL elemental analyzer, Analysensysteme GmbH, Hanau, Germany), dynamic light scattering with a NICOMP particle sizer (model 370, NICOMP particle sizing systems, Santa Barbara, California, USA), scanning electron microscopy (SEM, LEO Electron Microscopy Ltd., UK), and transmission electron microscopy (TEM) Zeiss EM 912 Omega operating at 100 kV. FT-IR spectra were recorded either with a Nicolet Impact 400 or a BioRad FTS6000 spectrometer. For selected samples dynamic and static light scattering investigations were carried out simultaneously with a goniometer ALV/SP-86#057 (ALV, Langen, Germany) in order to determine the radius of gyration (R_g) and the hydrodynamic radius (R_h) from static and dynamic ZIMM plots, respectively. Ultracentrifugation was carried out with a Beckmann Coulter Optima XLI centrifuge. A TG 209 from Netzsch, Germany was used for thermogravimetry.

Results and Discussions

The simplest way to take advantage of the ideas of Sir Harry Melville is the use of polymeric hydrophilic radicals to start the polymerization of a second preferably hydrophobic monomer. Such combination leads in the course of the polymerization to phase separation that is the formation of block copolymer particles or block copolymer micelles. Exemplary, by the redox reaction between monohydroxy terminated poly(ethylene glycol) and ceric ions a single hydrophilic polymeric radical is generated at the terminal carbon atom that is a $PEG-C^{\bullet}H-OH$ radical capable of starting radical polymerization [8, 9]. If N-isopropylacrylamide is used as monomer at elevated temperatures the observation was made that phase separation does not lead to substantial termination between aggregating amphiphilic polymeric radicals. Radical formation that is the redox reaction is very fast and ceases after about 5 minutes whereas newly added batches of monomer can be repeatedly polymerized inside the particles even hours after starting the polymerization with almost unchanged rate as proven by reaction calorimetry [10, 11]. It was possible to realize 5 NIPAM additions over 20 hours with absolutely no indication of decreasing rate of polymerization [10]. This result suggests that after particle formation the radical termination obviously almost vanishes. A seemingly daring conclusion which however might be understand taking into account firstly, that the amphiphilic radicals are practically fixed in place as they are both polymeric and surface active and secondly, that homopolymeric and low molecular weight radicals via side oxidation reaction between Ce^{4+} and NIPAM practically are not formed [6].

The solubility behavior and hence, the temperature and the length of the PNIPAM block causing phase separation depends on the block copolymer composition. For PEG-PNIPAM block copolymers with PEG and PNIPAM block lengths between 114 – 274 and 60 – 1200, respectively, the lower critical solution temperature (LCST) varies only between 29.5 and 30.9 °C [11]. For pure PNIPAM (hydrogen end groups) the LCST behavior can already be observed at an average degree of polymerization of 3 [12]. This is in accordance with the experimental observation that within the first two minutes after starting the redox polymerization the reaction system becomes turbid [11]. Furthermore, the nucleation or phase transition period is rather short as the size distribution determined for cross-linked particles is narrow [11] which means that most of the NIPAM monomer is polymerized inside the block copolymer particles. If at the end of the NIPAM

polymerization another hydrophobic monomer is added triblock copolymer particles should be accessible. Indeed, this protocol as schematically depicted in Figure 1 was successfully employed to prepare a variety of different triblock copolymers [6, 13]. In principle, this route can also be utilized to prepare either double hydrophilic or amphiphilic diblock copolymers [6]. In any case the block copolymer particles are built up from the periphery to the core. The use of NIPAM as middle block monomer is advantageous for comparing different kinds of hydrophobic monomers as only in that case the reactive intermediate state is identical. In the absence of NIPAM diblock copolymer particles are eventually obtained as well but the transition from homogeneous to heterogeneous reaction conditions might be quite different depending particularly on the solubility behavior of the hydrophobic monomer block.

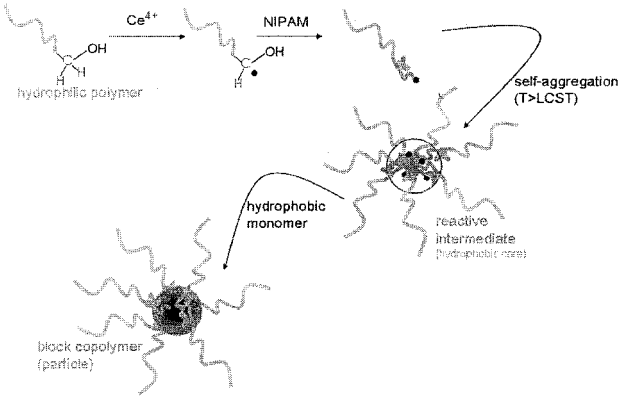

Figure 1. Schematic illustration of the block copolymer formation protocol via aqueous heterophase polymerization started with hydrophilic polymeric radicals; not to scale.

The first example describes the preparation and properties of two kinds of diblock copolymers starting from methylol terminated poly(styrene sulfonate) which was prepared by radical polymerization of styrene sulfonate in water initiated with VA-086. Compared to the protocol given in Figure 1 NIPAM is omitted and directly either methyl methacrylate (MMA) or t-butyl methacrylate (tBMA) as second block monomer is polymerized. The resulting particles are electrosterically stabilized by the initiating PSS chains but both second stage monomers behave extremely differently during the polymerization. For tBMA the block copolymer yield is with about 40 % relative to the mass of tBMA extremely low. However, for MMA as monomer the block copolymer yield

is above 90 % relative to the mass of MMA as proven by thin layer chromatography [13]. The reason for the high content of homo-PtBMA in the reaction mixture is very likely a side oxidative reaction of the Ce^{4+} leading in that case to the formation of free radical intermediates which are capable of starting tBMA homopolymerization [9, 14, 15]. The amount of homo-PtBMA increases with increasing Ce^{4+} concentration. This side reaction can take place under participation of either the tBMA or the methacrylic acid as under the acidic aqueous reaction condition partial hydrolysis of the tBMA-monomer as parallel reaction to the polymerization takes place (proven by FT-IR spectroscopy). In this sense it is to note that also for MMA and vinyl acetate hydrolysis has been observed in distilled water at 70 °C even in the absence of any acid or base [16].

Only the PSS-PtBMA block copolymer particles were subjected to hydrolysis. Larger amounts of homo PtBMA form coagulum during the polymerization and were easily removed by filtration. After ultrafiltration of the remaining latex and lyophilization further removing of the homopolymer was achieved by extraction with tetrahydrofuran, which is a nonsolvent for the block copolymer. The scheme for the whole reaction path is detailed in Figure 2. The double hydrophilic poly(styrene sulfonate)-b-poly(methacrylic acid) (PSS-PMAA) block copolymer is due to the combination of blocks of a strong and a week acid a very unique double hydrophilic block copolymer.

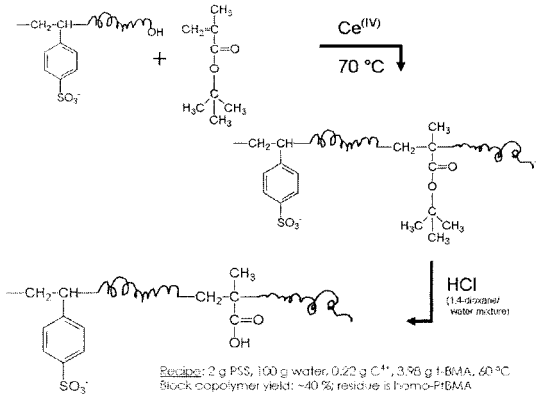

Figure 2. Illustration of the reaction pathway for the preparation of PSS-PMAA double hydrophilic block copolymers.

Both the PSS-PMMA and the PSS-PtBMA particles behave like electrosterically stabilized colloids as the thickness of the PSS corona decreases with increasing ionic

strength; cf. [6] and discussion therein. One might expect that after hydrolysis the double hydrophilic PSS-PMAA block copolymer forms homogeneous aqueous solutions at least at pH values above 7 where the methacrylic acid block is completely ionized. However, this is not the case as proven by SLS measurements at pH 7 in 0.1 M Na_2HPO_4 buffer at 25 °C revealing an apparent molecular weight of about $8 \cdot 10^6$ g mol^{-1} and a negative second virial coefficient. Both the extremely high apparent molecular weight and the negative second virial coefficient prove that there is net attraction between the PSS-PMAA molecules, cf. [17]. Furthermore, the dependence of the hydrodynamic radius (R_h) of this double hydrophilic block copolymer in aqueous solutions of varying pH as shown in Figure 3 reveals attraction, obviously of different origin, over the whole pH range.

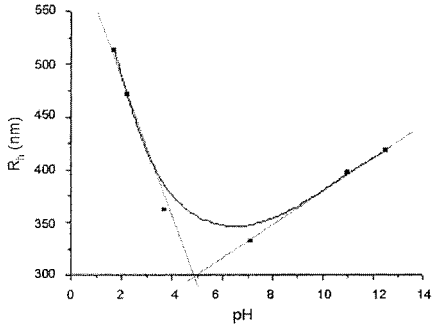

Figure 3. Dependence of the hydrodynamic radius of the PSS-PMAA double hydrophilic block copolymer on the pH-value of an aqueous solution at 25 °C; the pH was adjusted with a H_3PO_4 / Na_3PO_4 buffer at constant ionic strength of 0.1 M; block copolymer concentration 0.1 mg per ml water.

The two subsidiary lines in Figure 3 might indicate the limits of these different interactions mainly governed by the PMAA block. The intercept of both subsidiary lines with the X – axis is in a pH – range of about 5 which is close to the apparent pK – value of PMAA homopolymer (5.65) [18]. An interpretation of the curve as shown in Figure 3 is possible considering that in the case of block copolymers the local segment concentration is much higher than the overall concentration per unit solvent. Under theses conditions phase separation occurs, compared with a mixture of the two homopolymers, at lower overall concentrations. It is fair to assume that at pH-values below 5 where the methacrylic acid groups are protonated the PMAA blocks aggregate and the PSS blocks electrosterically stabilize the particles. Contrary, at higher pH-values where both blocks are in an ionized

state domain formation might be driven due to the incompatibility between both polyacid blocks. At pH 7 the ratio R_g / R_h is about 0.54. Assuming spherical morphology this low value indicates core - shell morphology where the shell is largely extended, cf. model calculations of R_g / R_h values in [6] and references therein.

The second example shows the application of PEG-PNIPAM-PMMA triblock copolymer particles, prepared according to the protocol given in Figure 1, as hosts for inorganic colloidal nanoparticles. In principle, both shell blocks, i. e. PEG and PNIPAM, are able to contribute to complexing.

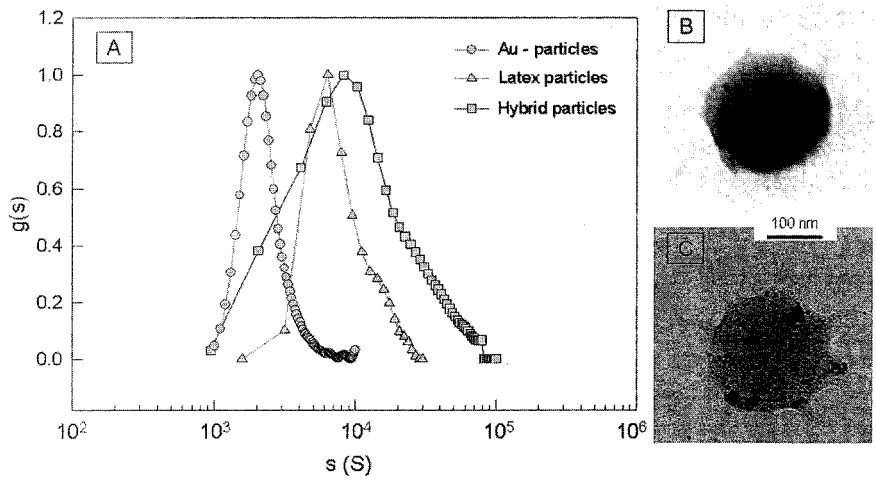

Figure 4. A: Sedimentation coefficient distribution of the composite hybrid particles (squares), the PEG-PNIPAM-PMMA host particles (triangles), and the gold guest particles (circles); B and C: TEM picture of the host (B) and the hybrid composite particles (C); the gold nanoparticles were stabilized with 4-dimethylaminopyridine.

The TEM pictures and the distribution of the sedimentation coefficients as depicted in Figure 4 clearly prove the complex formation. The broad distribution of the sedimentation coefficient of the hybrid particles indicates a broad distribution of the loading of the host triblock particles with the guest gold nanoparticles. The peculiarity of the appearance of the PEG-PNIPAM-PMMA particles on the TEM grids, i.e. the polymer ropes of the particles is discussed in [6, 19].

PEG-PNIPAM-PMAA(x-linked) particles are an example of double hydrophilic triblock copolymer particles useful to incorporate guest material inside the core via specific

interactions. These particles are prepared via PEG-PNIPAM-PtBMA(x-linked) precursor particles (cf. Figure 1) whereby during the polymerization of the t-BMA 1,3-diisopropenyl-benzene as cross-linker is employed and subsequent almost complete hydrolysis of the tBMA groups [13] (cf. Figure 2). Exemplary, such particles have been used to prepare hybrid composite particles with iron oxide (Goethite) according to standard procedures as described in [20]. The composite particles in a stable dispersion can contain up to about 60 weight-% of iron oxide (cf. Figure 5 B) and TEM images (cf. Figure 5 A) reveal a change in the morphology of the iron oxide due to the interaction with the double hydrophilic particles as pure Goethite precipitates under the condition employed with needle – like morphology [20].

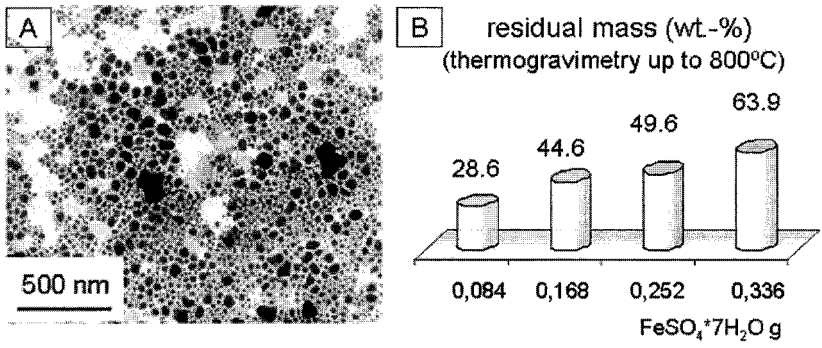

Figure 5. TEM picture of PEG-PNIPAM-PtBMA(x-linked) – Goethite composite particles (A) and residual mass after thermolysis at 800 °C in dependence on the amount of $FeSO_4$; recipe: 0.1 g of PEG-PNIPAM-PtBMA(x-linked) particles, 0.252 g of $NaHCO_3$, various amounts of $FeSO_4 \cdot 7H_2O$ as given in Figure 5 B, 25 °C cf. [20].

For the sake of completeness another type of double hydrophilic particles should be mentioned, namely PEG-PNIPAM-PSS(x-linked) particles, which were prepared by selective sulfonation of the polystyrene core of PEG-PNIPAM-PS(x-linked) precursor particles [21]. These particles can interact electrostatically with cationic surfactants resulting in particles with again hydrophobic but now anisotropic cores as the surfactant tails arrange in lamellar regions as elaborated in detail in [21].

To illustrate the various possibilities to apply double hydrophilic particles two more examples are given describing the use of PDEAEMA-PNIPAM-PMAA(x-linked) particles as stabilizers in different preparation processes of colloidal particles. It is known since more than 100 years that colloidal particles itself can act as stabilizers in colloidal systems. These so called Pickering stabilizers were mainly inorganic colloidal particles. However,

recently also the use of polystyrene particles to stabilize successfully oil in water emulsions has been described [22-24]. Contrary to these results, the PDEAEMA-PNIPAM-PMAA(x-linked) double hydrophilic particles, which are in fact hydrophilic microgel particles, were employed as stabilizers in reacting systems such as aqueous heterophase polymerizations and precipitation of calcium carbonate. To check whether or not PDEAEMA-PNIPAM-PMAA(x-linked) really acts as stabilizer in heterophase polymerization AIBN was used as initiator as it does not contribute to the stability of hydrophobic latex particles. The average particle diameter of the stabilizing microgel particles as determined by dynamic light scattering is about 1000 nm. The comparison with the size of the dried particles as obtained by TEM (cf. Figure 6), which is only between 170 and 220 nm in diameter, reveals the enormous ability of these double hydrophilic particles to swell with water.

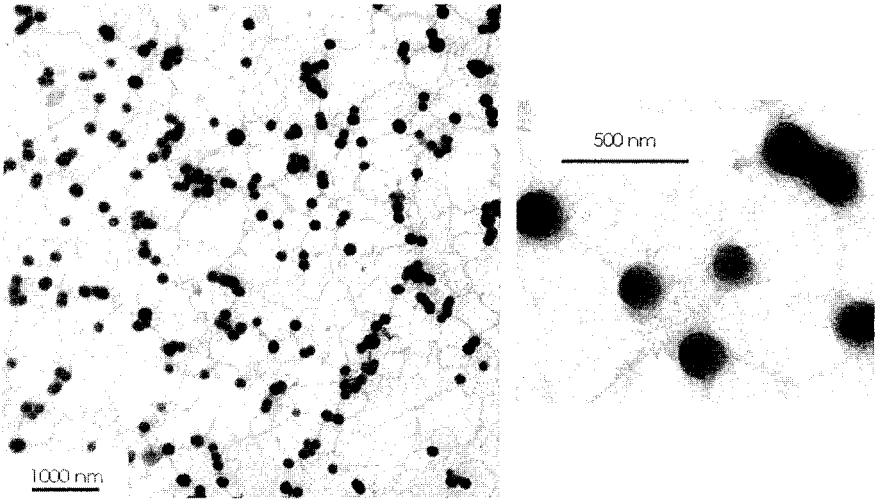

Figure 6. TEM images of PDEAEMA-PNIPAM-PMAA(x-linked) double hydrophilic particles obtained from aqueous dispersions which were easily obtained by dispersing the lyophilized triblock copolymer in distilled water.

The TEM images of Figure 6 show spherical particles with narrow size distribution, which is typical for this kind of polymerization procedure as the precipitation during the addition of the NIPAM - block (cf. Figure 1) is governed by the thermodynamics of phase separation. In the magnified image of Figure 6 a core – shell structure of the particles with a darker outer layer is clearly to see. Contrary, the polystyrene latex particles possess a

much broader particle size between about 150 and 600 nm (cf. Figure 7). Furthermore, the TEM images reveal a nonspherical shape predominantly of the larger particles, which might be the result of flocculation and not – completed coalescence processes between mainly duplets and triplets of particles. The TEM pictures in Fig. 7 suggest that the stabilizer particles are obviously almost completely inserted into the polystyrene particles as no raspberry-like structures are to recognize. Despite the limited flocculation and the nonspherical shape of the particles the polymerization result clearly proves that the double hydrophilic particles act as stabilizer as surfactant-free heterophase polymerization of styrene initiated with AIBN leads to complete coagulation. Note, the polymerizations as described in the captions of Figs. 7 and 8 were carried out at neutral pH and allowed to run to complete conversion. Also particles of other composition such as PDEAEMA-PNIPAM-PS(x-linked) or PDEAEMA-PNIPAM-PMMA(x-linked) have been tested successfully as stabilizers in heterophase polymerization of styrene, t-butyl styrene, and MMA.

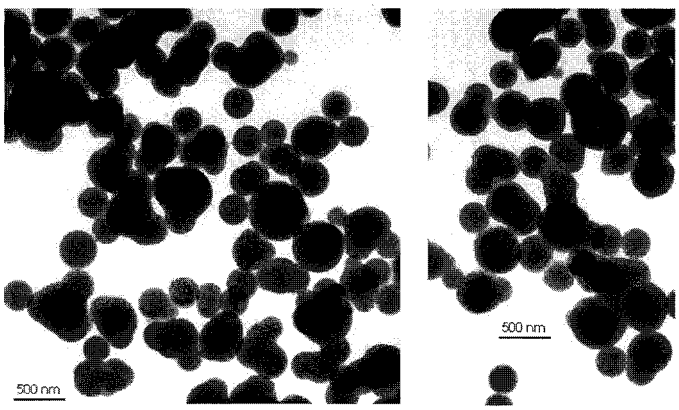

Figure 7. TEM images of polystyrene particles prepared with PDEAEMA-PNIPAM-PMAA(x-linked) double hydrophilic particles as stabilizers; polymerization recipe: 50 g of water; 5 g of styrene; 0.025 g AIBN; 0.04 g of stabilizer particles; 50 °C.

However, if instead of the above triblock particles the PDEAEMA-PMAA(x-linked) diblock particles are employed as stabilizer the amount of coagulum drastically increases and the appearance of the particles in the TEM pictures changes considerably (cf. Figure 8). The particles are spherical in shape and exhibit a clear core – shell morphology. The lighter corona made of the double hydrophilic polymers surrounding the much darker polystyrene core is clearly to see.

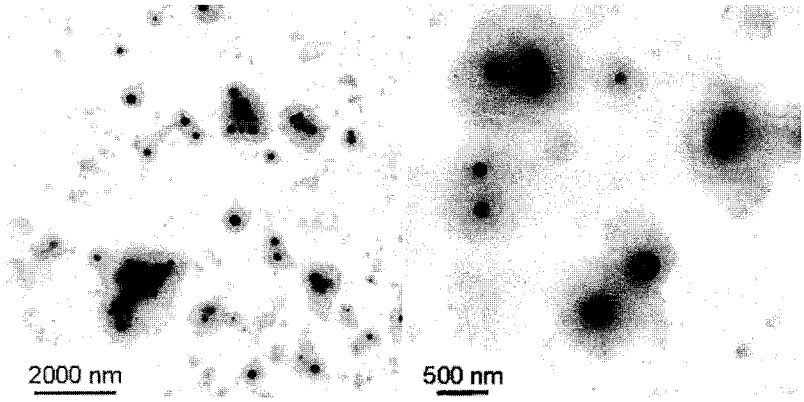

Figure 8. TEM images of polystyrene particles prepared with PDEAEMA-PMAA(x-linked) double hydrophilic particles as stabilizers; polymerization recipe: 50 g of water; 5 g of styrene; 0.025 g AIBN; 0.04 g of stabilizer particles; 50 °C.

This different behavior between the di- and triblock stabilizer particles might be attributed to the PNIPAM block which makes the triblock particle stabilizers hydrophobic at polymerization temperature and hence it favors not only adsorption but very likely also partial burying in the particles cores. The results as described in Figs. 7 and 8 are to the best of the authors' knowledge the first experimental data regarding the application of polymeric microgel particles as stabilizers in aqueous heterophase polymerization. Hence, several issues remain to investigate such as the particle nucleation mechanism (whether it takes place inside the monomer droplets or via aggregative nucleation [25] or do the microgel particles act as seed as it was concluded for block copolymer micelles as stabilizers [26]), the particular type of stabilization (whether steric or Pickering – like, or a combination of both), the role of the nature of the initiator (compare AIBN with water-soluble initiators), the limits regarding minimum stabilizer amount and maximum solids content or particle morphology just to mention a few.

A completely different field where double hydrophilic particles might be useful is the crystallization of inorganic solids in which the beneficial application of double hydrophilic polymers is known since several years [27, 28].

Double hydrophilic PDEAEMA-PNIPAM-PMAA(x-linked) particles have a distinct influence on the morphology of the $CaCO_3$ crystals formed during mineralization

experiments with $CaCl_2$ according to the so-called vapor method [29] with $(NH_4)_2CO_3$ as CO_2 source. Under these conditions, i.e. in the absence of any additives, calcium carbonate precipitates in the form of well-shaped calcite rhombohedra as proven by the SEM pictures in Figure 9 A. However, in the presence of the double hydrophilic triblock copolymer particles besides calcite rhombohedra also particles with a different morphology are formed. These particles are made of the aragonite polymorph of $CaCO_3$ as proven with FT-IR spectroscopy by absorption bands at 851 and 1081 cm^{-1} [30]. The magnification on the right hand side in Figure 9 B evidently demonstrates the enormous influence of the block copolymer particles on calcium carbonate crystallization.

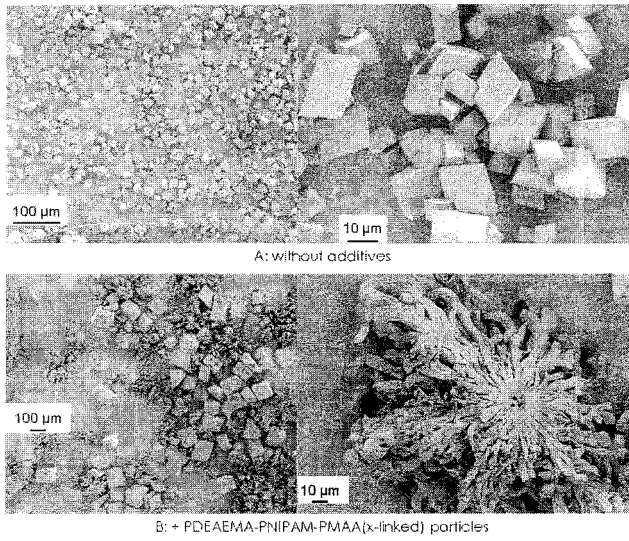

Figure 9. SEM pictures of calcium carbonate crystals prepared with the $(NH_4)_2CO_3$ vapor method in the absence of any additives (A) and in the presence of PDEAEMA-PNIPAM-PMAA(x-linked) particles (B); mineralization conditions: vapor method with $(NH_4)_2CO_3$, 0.001mg / ml water block copolymer particles; 1.47 mg / ml water $CaCl_2 \cdot 2H_2O$.

Conclusions and Summary

Radical heterophase polymerization started with polymeric radicals is a versatile technique to easily produce various types of unique both block copolymers and block copolymer particles, which are only hardly accessable by other polymerization methods. Although the detailed composition of the particles regarding block length distribution and block copolymer morphology (di-, tri- or multiblocks) is not known such particles are useful in

many respects. Exemplary, PSS-PMAA block copolymers combining strong and week acid groups in one molecule have been prepared. Furthermore, double hydrophilic di- and triblock copolymer particles are accessible, which can be used to make colloidal composite particles with either inorganic colloidal particles or low molecular weight organic molecules whereby the block copolymer particles can act as adsorbents or nano-reactors depending on the particular task. Such particles can be applied as colloidal stabilizers in heterophase polymerizations and also mineralization reactions causing the formation of peculiar morphologies.

Work in progress focuses on the characterization of molecular parameters of the polymers and block copolymers after each step mainly by analytical ultracentrifugation techniques. Also further investigations are necessary regarding the application of double hydrophilic microgel particles as stabilizers in aqueous heterophase polymerizations.

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