Amino-Functionalized Nanoparticles via Copolymerization with 2-Aminoethyl methacrylate in Miniemulsion

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Summary: The copolymerization of 2-aminoethyl methacrylate hydrochloride (AEMA) with styrene (St), butyl acrylate (BuA) or butyl methacrylate (BuMA) in miniemulsion leads to amino-functionalized nanoparticles. The influences of different pH values and different monomer/water ratios onto the incorporation of AEMA into the particles were studied. In order to prevent the rearrangement of AEMA into the 2-hydroxy-ethyl methacrylamide (HEMAA), a pH value below 4 has to be used. AEMA and HEMAA were studied regarding the copolymerization behavior. The monomer/water ratio has an influence on the stability of the resulting latices. The surface area of the according amino-particles was analysed with conductometric titration.

Keywords: amino-functionalized; conductometric titration; miniemulsion; nanoparticles; radical copolymerization

Introduction

Polymer latices are currently enjoying numerous applications in many fields. The main focus of the studies lies on the preparation of nanoparticles having functional groups able to build up a covalent bond to biomolecules or polymers.[1–6] Thus they can provide unique properties to the resulting material by varying the type and the concentration of the functional group or the base monomer inside the particles. The main object for most applications is to get controlled particle sizes with narrow size distributions. Therefore miniemulsions are widely used to synthesise nanoparticles with a monomodal size distribution.[7–10]

Conventional emulsion and miniemulsion polymerization are divergent in the particle nucleation step. Whereas macroemulsions consist of many monomer-swollen micelles and micron-sized monomer droplets, miniemulsions contain only monomer droplets in the size range of 5–500 nm. In macroemulsions the surface area of the monomer droplets is much smaller than the surface area of the micelles. Hence the particle nucleation inside the monomer droplets can be neglected. Micellar and homogeneous nucleation can take place, whereas most of the particles are formed in micelles if the amount of surfactant is above the critical micelle concentration (cmc). Below the cmc homogeneous nucleation will become more significant.

In miniemulsions usually the amount of surfactant is lower than in macroemulsion. Therefore there are no micelles but only monomer droplets in a miniemulsion. High shear rates are used for emulsification which leads to monomodal droplet size distributions. It is assumed that diffusion does not take place in a miniemulsion. Starting the polymerization with a water- or an oil-soluble initiator produces a polymeric copy of the droplet.[7–8,11–14] Homogeneous nucleation leads to secondary nucleation and is often observed when a water-soluble initiator or a highly water

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soluble comonomer is used.[5,7–8] In this case droplet nucleation can be enhanced by using an oil-soluble initiator.

When a copolymerization with functional monomers is carried out in a miniemulsion, nanoparticles with functional groups and a narrow particle size distribution can be received. 2-aminoethyl methacrylate hydrochloride (AEMA) is one of the few primary amino-group containing monomers which are commercially available. Amino-functionalized particles are often synthesized for biomedical applications.[1,2,15] A primary amino-group is a versatile reaction partner to form covalent bonds which have many advantages compared to the physical absorption of atom groups. Most of these particles with primary amino-groups are polystyrene-based.[15–19] Other applications are conceivable when styrene is replaced by another monomer, like butyl acrylate or butyl methacrylate as base monomer to produce soft particles.[23] Regarding this aspect, no studies are known. Commonly, for the synthesis of polystyrene based particles a water soluble initiator was used in literature in the presence of several surfactants: cationic,[20] anionic[19] or no emulsifier at all.[16] However, to eliminate polymerization in the aqueous phase an oil-soluble initiator is required.[12,15,18]

In this paper AEMA was used as comonomer for three different base monomers, styrene, butyl acrylate and butyl methacrylate in a miniemulsion process. In the current paper the effect of the amount of functional comonomer on the particle size, the copolymer composition and the functional group density on the surface for every base monomer is shown. The copolymerization behavior for the three different copolymerizations can be derived from these results. It is discussed that AEMA undergoes a quick rearrangement due to an acyl migration at $\mathrm{pH} > 4$.[21] To compare the rearranged species with the aminoethyl methacrylate relating to the copolymerization behavior, first the water-soluble initiator potassium persulfate (KPS) and then the oil-soluble initiator 2,2′-azobisisobutyronitrile (AIBN) were used at different pH values. In addition, to enhance the stability of the resulting emulsions, two different monomer/water ratios were carried out for the AIBN-initiated latices.

Experimental Part

Materials

Styrene (Aldrich), butyl methacrylate (Aldrich) and butyl acrylate (Aldrich) were distilled under reduced pressure and stored at 2 °C before use. Potassium peroxo disulfate (KPS) (Fluka) and α,α'-azobisisobutyronitrile (AIBN) (Fluka, 98%) were recristallized with ethanole respectively ether. Other reagents were used as received: 2-aminoethyl methacrylate hydrochloride (AEMA) (Polysciences, 98%), sodium hydrogencarbonate (Merck), sodium hydroxide (Fluka), the hydrophobe hexadecane (Merck), the surfactants sodium dodecyl sulfate (SDS) (Roth) and cetyltrimethylammonium bromide (CTMA-Br) (Merck). Deionized water was used during all experiments.

Miniemulsion Polymerization with Water-Soluble Initiator

Amino-functionalized nanoparticles were prepared by the miniemulsion copolymerization of AEMA with styrene, butyl methacrylate and butyl acrylate to produce hard as well as soft particles. The recipe for these copolymerizations is listed in Table 1. The given amount of AEMA, sodium hydrogencarbonate and the surfactant SDS were dissolved in 100 ml of deionized

Table 1.
Miniemulsion recipe for the copolymerizations with KPS.

Ingredients	amount, g	comments
Butyl acrylate	25–30	
Butyl methacrylate	25–30	
Styrene	25–30	
$NaHCO_3$	5	
AEMA	0–10	0–23 mol-%
Water	105	
KPS	0.09	

water. The pH value was raised with a sodium hydroxide solution (1N) to 10.5. The amount of base monomer was then added to the aqueous phase. The miniemulsion was prepared by ultrasonification for 90s at 90% intensity (Sonics Vibracell). The temperature was increased to 75 °C and a solution of 90 mg KPS in 5 ml deionized water was added to start polymerization.

Miniemulsion Polymerization with Oil-Soluble Initiator and Different Monomer/Water Ratios

The recipe for the copolymerization of AEMA with styrene, butyl methacrylate and butyl acrylate is given in Table 2 (monomer/water ratio 1:4 and 1:8). AEMA and CTMA-Br were dissolved in deionized water. 100mg of AIBN was dissolved in the given amount of comonomer and 250mg of hexadecane were added. Both solutions were combined and cooled to 0 °C before ultrasonification for 90s at 90% intensity to prevent polymerization. For polymerization, the temperature was increased to 75 °C.

Characterization of Latex Particles

The total solid contents of the latices were determined gravimetrically. The latex samples with oil-soluble initiator were cleaned by repetitive centrifugation/redispersion in deionized water. The particle sizes were measured by dynamic light scattering (DLS) using the photon crosscorrelation spectroscopy (PCCS) (Nanophox, Sympatec).

For morphological observations, transmission electron microscopy (TEM) was carried out with a JEOL JEM-2100 at 100 kV. The diluted latices (to about 0,09 wt.-% solid content) were placed on a 400-mesh formvar-coated copper grid (Plano) and left to dry. No additional contrasting was applied.

Conductometric titration was used to determine the accessible amino-groups on the surface. After cleaning, the titration of the latices was carried out with 0,01N NaOH aqueous solution after addition of 0,01N HCl aqueous solution to be sure that all amino-groups are protonated. The titrations were performed until the conductivity reached nearly the initial value. The amount of amino-groups per gramm polymer was calculated from the conductivity curve as a function of consumed NaOH solution:

$$[groups/_{g_{Polymer}}] = \frac{V \times M \times N_A}{m_{Polymer}}$$

where V is the volume of consumed NaOH in liters, M is the molar concentration of the NaOH solution, N_A is the Avogadro‘s constant ($6.022 \cdot 10^{23}$ mol^{-1}).

From the elemental analysis results of the produced copolymers, the copolymer composition and the total amount of amino-groups in a particle can be calculated. Therefore the percentage of amino-groups which are on the particle surface can be expressed with this equation:

$$\%_{on\ the\ surface} = \frac{[groups/_{g_{polymer}}] \times M_{AEMH} \times 100}{wt. - \%_{AEMA\ in\ copolymer} \times N_A} \times 100$$

With the total conversions and the results of the elemental analysis a relative conversion x of the amino-monomer can be

Table 2.
Miniemulsion recipe for the copolymerizations with AIBN.

Ingredients	Amount, g	comments
Butyl acrylate	4–6	
Butyl methacrylate	4–6	
Styrene	4–6	
Hexadecane	0.16	
AEMA	0–2	0–20 mol-% based on total monomer amount (6 g)
Water	24, 48	m/w-ratio 1:4, 1:8
AIBN	0.1	

calculated:

$$x_{AEMA} = \frac{m_{total\ solid\ content} \times wt.\!-\!\%_{AEMA\ in\ copolymer}}{m_{AEMA\ feed}}$$

Results and Discussion

Polymerization with Water-Soluble Initiator

Landfester et. al [15] and Van Es et al. [21] had published that if the AEMA is neutralized, a quick rearrangement of the monomer takes place which leads to a hydroxy functionalized acrylamide (HEMAA = 2-hydroxy-ethyl methacrylamide) (Figure 1). Pichot et. al. showed that the isoelectric point of AEMA is about 10.5, accordingly all amino-groups should be deprotonated afterwards.[22] That is why AEMA was first rearranged to HEMAA by adding a sodium hydroxide solution to get a pH-value above 10. The acrylamide species should be more located inside the droplets than the charged AEMA and therefore a water soluble initiator could be used with an anionic surfactant. The goal was to compare the incorporation of the neutralized and rearranged species with the charged AEMA monomer which was used later with an oil-soluble initiator under a pH-value <4.

Figure 2a) shows the particle average diameter of the copolymers with the rearranged HEMAA. The particles grow with increasing comonomer-content in the feed mixture. Furthermore the size increases from styrene and butyl methacrylate to butyl acrylate. The copolymer composition for these particles can be seen in Figure 2b). The incorporation of the neutralized comonomer is higher with the acrylates than with styrene. Combined with the results for the particle size we preserved that the higher the HEMAA-content in the copolymer is the larger are the particle sizes.

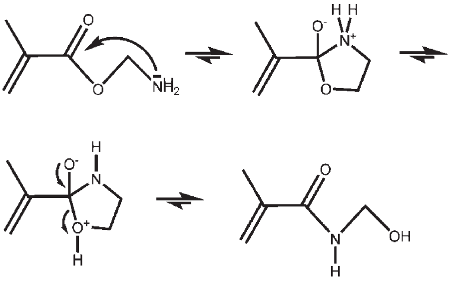

Figure 1.
Acyl migration of 2-amino-ethyl methacrylate (AEMA).

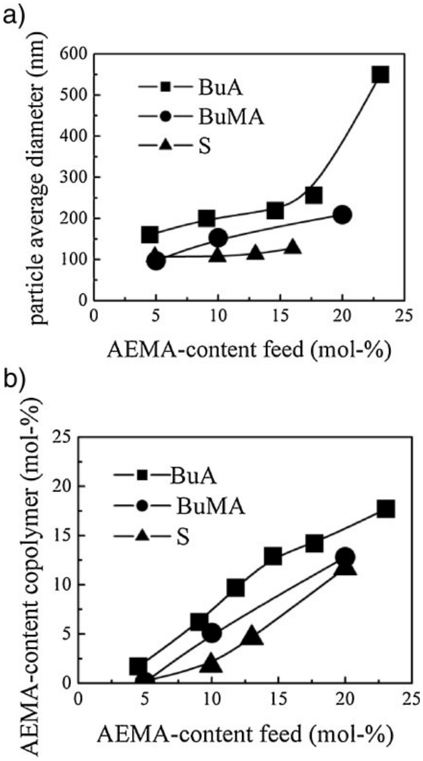

Figure 2.
a) Particle average diameter as a function of the AEMA-content in the feed mixture for the three different monomers b) AEMA-content in the copolymers versus the AEMA-content in the feed mixture.

This can be explained by the fact that the comonomer has still a polar end group which may lead to an expansion of the particles if the comonomer content increases or due to the polar group the particles may swell with water. Moreover HEMAA seems to copolymerize better with acrylates or methacrylates because of its structural similarity.

Polymerization with Oil-Soluble Initiator

For the preparation of the particles with AEMA pH-values <4 with the oil-soluble initiator AIBN were used to prevent the rearrangement as well as polymerization in the water phase. In addition, the anionic surfactant SDS which was used with the rearranged species was replaced by the cationic surfactant CTMA because tests showed that otherwise the cationic AEMA-monomer was not able to enter a particle to polymerize and so only homopolymers were obtained. The first experimental series was carried out with a monomer/water ratio of 1:4 which leads to the desired amino-functionalized particles but also to coagulation at higher AEMA-contents particularly with butyl acrylate. Therefore a second series was conducted with a monomer/water ratio of 1:8. Unfortunately this causes a lower solid content (from 20% to 10%) but no coagulation was observed in all experiments.

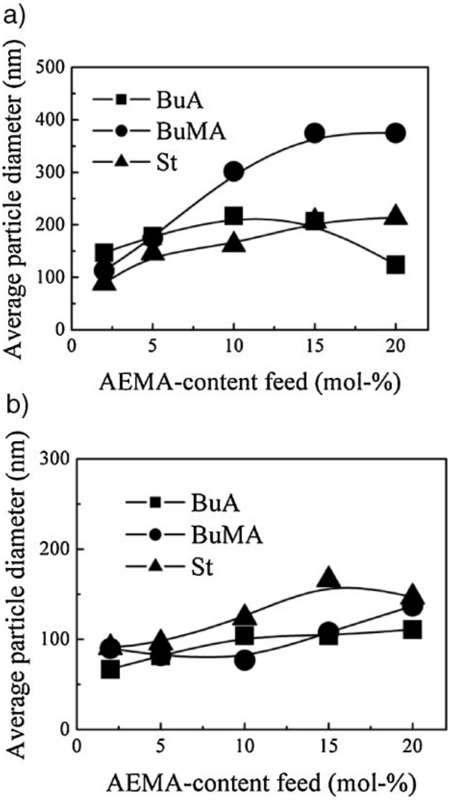

Figure 3.
Number average particle diameter (determined by DLS) as a function of the comonomer-content in the feed mixture for the monomer/water ratios a) 1:4 and b). 1:8.

The resulting average particle diameters are shown in Figure 3 for both monomer/water ratios. Compared to the results for the HEMAA copolymers it is obvious that the particle sizes also increases first but then stagnate or even decrease with more AEMA in the feed mixture. Because of its protonated amino-group and the methacrylic residual, AEMA has amphiphilic qualities that enable the comonomer to act as a co-surfactant. Therefore AEMA has the ability to stabilize the particles as well which results in smaller particle sizes with increasing amount of AEMA. This effect occurs in all copolymerization but is very important in the copolymerization with BuA in which a decrease of the particle size was received. The comparison of both monomer/water ratios points that the particles are all much smaller when more water is used and the particle sizes vary in a range of 50 nm.

The copolymer compositions for both monomer/water ratios are shown in Figure 4. It seems that also with low comonomer contents in the feed mixture an incorporation of AEMA takes place whereas with HEMAA (Figure 2b) the comonomer could only copolymerize from a content of about 5 mol-% in the feed mixture. Anyway, with HEMAA higher comonomer contents were received than with AEMA. This is due to the higher water solubility of the charged AEMA which causes a loss of comonomer into the water phase. As expected both comonomers copolymerize better with the acrylates or methacrylates than with styrene, furthermore the results show that HEMAA copolymerizes better with styrene compared to AEMA. Increasing the amount of water at the copolymerizations with AEMA has almost no effect on the copolymer compositions. This may be due to the fact that AEMA is acting as a co-surfactant and is therefore nearly independent of the amount of water but dependent

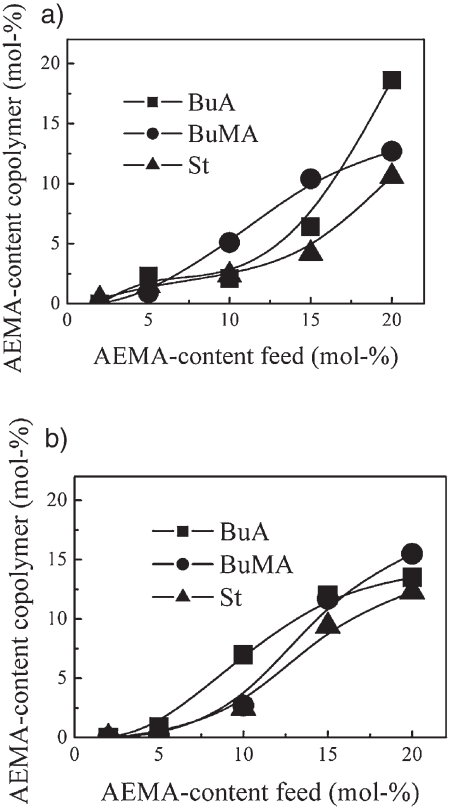

Figure 4.
a) Comonomer content in the copolymer versus the content in the feed mixture for the monomer/water ratio 1:4 and b) for the monomer/water ratio 1:8.

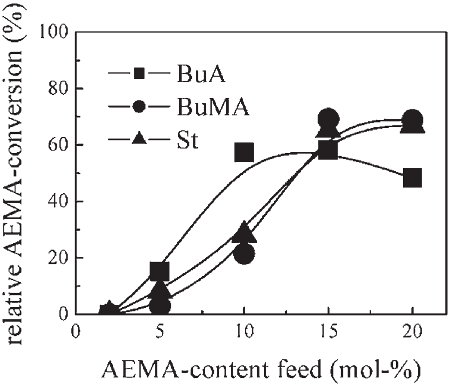

Figure 5.
Relative conversion of AEMA for the different copolymers and a monomer/water ratio of 1:8.

of the amount of monomer which stays the same. In addition, the surface area of the droplets which can be stabilized by surfactants is enhanced because of the smaller particle sizes which may compensate the increased loss of AEMA into the water phase.

The total conversions of the copolymerizations with a monomer/water ratio of 1:8 vary between 78% and 85%. The relative conversion of AEMA can be calculated with the results of the elemental analysis. Figure 5 shows the results of the calculation.

It appears, that the highest relative conversion and therewith the best option for almost all copolymerizations is achieved when the AEMA-content in the feed mixture is about 15 mol-%. The relative conversion of AEMA with BuA is the highest, which follows the discussed results for the incorporation of AEMA (Figure 4b). BuA has the highest water solubility of the investigated monomers, therefore AEMA which is located in the waterphase or as co-surfactant in the water-oil interface, can react best with BuA. Even with lower AEMA-contents in the feed mixture of about 10 mol-%, good conversions above 50% can be obtained. It is observable that it is not an alternative to use a preferably high comonomer-content in the feed mixture, because a maximum content in the copolymers which is limited by the co-surfactant qualities of AEMA and its water solubility will be achieved. If the amount of AEMA is above this maximum value, only the comonomer content in the water phase will be increased which does not lead to a higher content in the copolymers. The amount of AEMA, which is able to act as a co-surfactant, can therefore be incoporated to a limited extent.

Transmission Electron Microscopy (TEM)

The TEM-pictures show that the particle sizes measured with TEM are 20–50 nm smaller than those measured with DLS. Because of the great amount of ammonium-groups on the surface the particles can swell a lot with water. With DLS only the

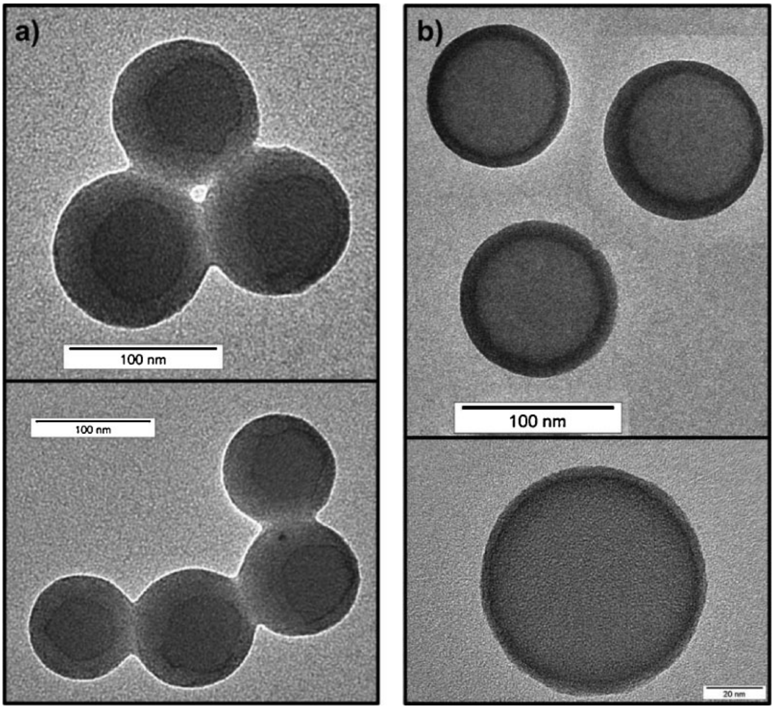

Figure 6.
TEM pictures of the P(St-*co*-AEMA) particles with a) 20 mol-% and b) 5 mol-% AEMA in the feed mixture.

hydrodynamic radius of the swollen particles is measured which will be bigger than the real particle size. In the TEM-pictures, it can also be seen that the particles are all spherical and the particle size distribution is narrow.

It can be discovered that there is a sharp border between the light outside and the dark interior of the particles. It seems that the particle morphology is a core/shell-like structure. To proof if it is a core/shell-like structure or just an artefact of measuring spherical particles, TEM pictures of styrene particles of the copolymerizations with 5 mol-% and 20 mol-% AEMA in the feed mixture were done. Comparing the pictures it can be seen that the ‘‘shell’’ is much smaller when only 5 mol% AEMA was used in the feed. The approximated thickness for both ‘‘shells’’ are about 4 nm for 5 mol-% AEMA and about 16 nm for 20 mol-% AEMA in the feed. This shows that the AEMA content in the particles follows the thickness of the ‘‘shell’’. Therefore it is assumed that there is a core/shell-like structure. To be sure of that more studies regarding this aspect will follow.

Titration of Surface Groups

The results of the elemental analysis yield the total number of amino-groups/g polymer. The number of amino-groups per gram polymer can be calculated from the results of the conductometric titrations and the solid content of the washed latices. Therefore the percentage of amino-groups which are located on the surface can be derived, too. The results are shown in Figure 7. The number of amino-groups per gram polymer increases for all copolymers with increasing AEMA-content in the feed mixture. That indicates that AEMA is well incorporated on the surface of the particles no matter which monomer is used as reaction partner, but BuA and BuMA show also

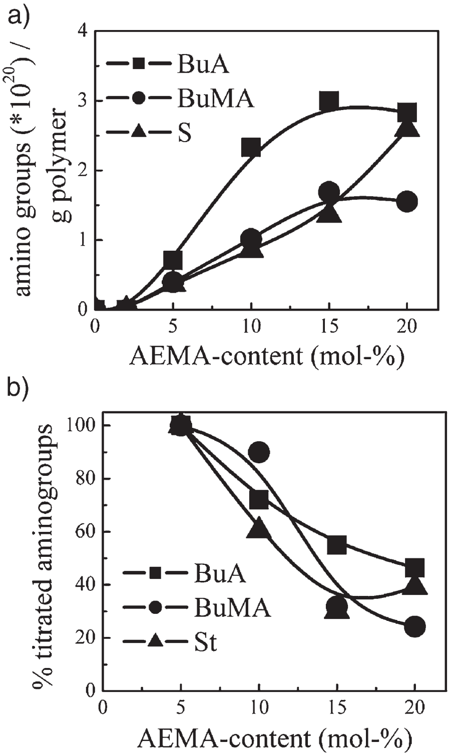

Figure 7.
a) Amino-groups/g polymer versus the AEMA-content in the feed mixture and b) the percentage of the amino-groups which were titrated versus the AEMA-content in the feed mixture.

a maximum number of amino-groups. Thus it appears that with an AEMA-content in the feed of 15 mol-% the surface areas of the particles seem to be fully crowded for both monomers. That is why the relative AEMA conversion shows a maximum, too (Figure 5). The percentage of the amino-groups which are located on the surface is first very high, decreases then and increases slightly in the end for styrene.

This shows that AEMA is first incorporated on the particle surface because there is enough space on the surface for all amino-groups. But the surface area grows not to the same extent with increasing AEMA-content, because the average particle sizes increase only slightly (see Figure 3b). From this it follows, that with increasing number of amino-groups they are forced to go further into the droplets and therefore the percentage on the particle surface decreases. If the number of amino-groups is still increased some of them may insert between the existing amino-groups during the incorporation which leads to the small increase of the percentage at high AEMA-contents for styrene. Moreover it can be seen, that BuA has the highest comonomer content in the particles and so the highest number of amino-groups on the surface, too, but percentage of amino-groups on the surface is relatively low. Because butyl acrylate has the highest water solubility, AEMA will be best soluble in BuA and additionally will swell most with water which enables the amino-monomer to insert well in the water-oil-interface and the inside of the particles, too.

Conclusion

Amino-functionalized nanoparticles could be synthesized by copolymerization of AEMA with styrene, butyl acrylate and butyl methacrylate. The copolymerization behavior was affected by the pH value, where even two completely different comonomers were obtained, and the monomer/water ratio of the miniemulsions. Under acid conditions, real amino particles could be obtained by using the oil-soluble initiator AIBN and the cationic surfactant CTMA bromide. The resulting particles were analysed regarding the total comonomer content in the copolymers and the particle sizes. The comonomer content was increased when using an acrylate or methacrylate instead of styrene. Moreover AEMA is able to react as a co-surfactant which leads to smaller particle sizes. After using the best miniemulsion recipe, the relative conversion of the AEMA comonomer was calculated from the elemental analysis and the total conversions. It was shown that a maximum relative AEMA-conversion was obtained with a comonomer content of about 15 mol-%. TEM-pictures of the polystyrene particles with a low and a high amount of amino-groups suggest a core/shell-like structure. The surface areas of the particles were studied regarding the amino-groups per g polymer and the percentage of the total number of aminogroups which are located on surface. The number of aminogroups increases and shows a maximum for butyl acrylate and butyl methacrylate from an AEMA content of 15 mol-%. The percentage decreases with increasing AEMA-content in the feed mixture for all monomers.

Acknowledgements: The authors acknowledge the Deutsche Forschungsgemeinschaft for financial support within the European Graduate School ''Microstructural Control in Free-Radical Polymerization''.

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