e-Polymers **2006**, no. 030

http://www.e-polymers.org
ISSN 1618-7229

Emulsion copolymerization of hydrophobic and hydrophilic monomers: an experimental study with styrene and 2-hydroxyethyl methacrylate

Hasan Ahmad,[1] A.H.M. T. Islam,[1] M. Amran Hossain,[1] M.A. Jalil Miah,[1] Klaus Tauer*[2]*

[1] Department of Chemistry, Rajshahi University, Rajshahi 6205, Bangladesh; e-mail: samarhass@yahoo.co
[2] MPI of Colloid and Interfaces, Am Mühlenberg, D 14476 Golm, Germany; e-mail: klaus.tauer@mpikg.mpg.de

(Received: 29 November, 2005; published: 16 June, 2006)

Abstract: Ab initio emulsion copolymerization of styrene with 2-hydroxyethyl methacrylate (HEMA) at weight ratios of the hydrophilic monomer of 1 and greater was investigated at various temperatures in dependence on the concentration of sodium dodecylsulfate (SDS) and potassium peroxodisulfate as emulsifier and initiator, respectively. Both the course of the polymerization and the latex properties are strongly influenced by the hydrophilic monomer. For instance, transparent or highly translucent latexes are obtained resembling the appearance of microemulsion latexes with polymer contents as high as 10 weight-% but at much lower surfactant concentration. Moreover, polymerization rate, average particle size, and particle morphology depend on the surfactant and initiator concentration, monomer feed composition, and polymerization temperature.

Introduction

Emulsions are heterogeneous, colloidal systems of oil, water, and surfactants. Among this class of colloids microemulsions are thermodynamically stable as they form spontaneously if oil, water, and surfactants are mixed [1]. In contrast, emulsions formed by comminution are only kinetically stabilized. Both emulsions and microemulsions can be subjected to polymerization if monomers are involved. These so-called heterophase polymerizations are industrially important processes for the manufacture of polymers [2]. In general, the emulsifier concentration employed for the preparation of microemulsions is much higher than that used in emulsions. In fact, the emulsifier content in latexes prepared from microemulsions is higher than the polymer content which is a compelling drawback in many latex applications [3, 4]. The advantage of microemulsion based latexes is their small particle size and their translucent or even transparent appearance to the eye.

Copolymerization is the most powerful method for effecting systematic changes of polymer properties [5]. The incorporation of two different monomers, having different physical and chemical properties in the same polymer particle in varying proportions is of great scientific and commercial importance [6, 7]. For any kind of heterophase copolymerization the ratio of the lyophilicity and lyophobicity of the participating monomers is of crucial importance. The combination of extremely hydrophilic with extremely hydrophobic monomers in water based systems is on the one hand a

special challenge but on the other hand also an advantage of heterophase polymerization techniques. Of course, the incorporation of hydrophilic monomers influences the particle nucleation [8], the composition of the particle surface [9], the final particle size [10] and hence, the polymerization kinetics [11, 12].

The combination of monomers with extremely different water solubility leads to products with different chemical composition distribution in any type of aqueous heterophase polymerization as hydrophobic monomers possess a certain solubility in water and vice versa. Interfacial crossing of a growing chain from one phase to the other leads to gradient copolymers as for the first time described in reference [13]. Also in styrene emulsion copolymerization with methyl acrylate with respect to the reactivity ratios, anomalous chemical composition distributions were observed thus reflecting the various comonomer concentrations at the different reaction loci [14].

Such studies are of fundamental interest as the partitioning of monomers in different phases is challenging for modeling. Already slight differences in the hydrophilicity / hydrophobicity of the comonomers or changes in the type of heterophase polymerization technique might have a strong influence on the copolymerization kinetics as well as on the polymer properties. For instance, the higher copolymerization rate of styrene with methacrylic than with acrylic acid under emulsion polymerization conditions reflects the higher solubility of the methacrylic acid in the organic phase [9]. The copolymerization of styrene and acrylonitrile under emulsion and microemulsion polymerization conditions with either potassium peroxodisulfate (KPS) or 2,2'-azobis(isobutyronitrile) (AIBN) as initiator and dodecyltrimethylammonium bromide (DTAB) or sodium dodecylbenzenesulfonate (SDBS) as surfactants is compared in [15]. The results reveal that the polymerization in DTAB microemulsion initiated with AIBN is faster than that initiated with KPS, whereas the opposite effect is observed for emulsion polymerization. Under both conditions the copolymers are richer in styrene than the initial monomer composition. As expected the particles made by microemulsion polymerization are much smaller than those prepared by emulsion polymerization.

Investigations in the open literature concentrate mainly on acrylic or methacrylic acid as hydrophilic comonomers due to their commercial importance as these monomers are frequently used in industrial heterophase polymerizations to increase the latex stability [16-19]. Ionic comonomers other than carboxylic acids can be applied to control particle properties as well. Examples are sodium 2-acrylamido-2-methylpropane sulfonate [20] and vinyl sulfonate [21]. In microemulsion polymerizations hydrophilic ionic comonomers have also been used to modify particle properties [22, 23]. Frequently mixtures of hydrophilic monomers are also employed; such as carboxylic acids and acrylonitrile [24, 25].

The number of reports available in the open literature on investigations of emulsion copolymerization of hydrophobic monomers with nonionic hydrophilic monomers is much less. As nonionic water-soluble polymers can also contribute to the colloidal stability of latex particles, investigations in this field are not only a matter of scientific curiosity but also of some technical importance. Recently, the polymerization at emulsion droplet interfaces has been successfully carried out with dibutyl maleate as hydrophobic and a poly(ethylene glycol) divinyl ether as hydrophilic monomer initiated with 2,2'-azobis(N-octyl-2-methyl-propionamidine)dihydrochloride as surface active initiator [26].

This contribution focuses on emulsion copolymerization of styrene with the water soluble comonomer 2-hydroxyethyl methacrylate (HEMA). Polymeric particles

containing HEMA surface groups are potentially useful for immobilizing biomolecules in order to design biosensors, kits for diagnosis, soft contact lenses and chromatographic columns [27-31]. There are a few reports describing the use of HEMA as hydrophilic comonomer in emulsion polymerization in order to control surface property and to improve latex stability [32-38]. In [38] the authors developed a mathematical model to describe the conversion - time curves during emulsion copolymerization of styrene and HEMA at 70 °C with KPS as initiator and sodium dodecyl sulfate as emulsifier. Unfortunately, no latex properties are reported but the authors were able with some overall copolymerization parameters of r_{HEMA} = 2.34 and $r_{styrene}$ = 0.605 to describe the conversion time curves obtained for different initiator concentrations and monomer to water ratios quite well. However, there is a lack of experimental data regarding the influence of polymerization parameters such as surfactant and initiator concentration and polymerization temperature on both the overall rate of polymerization and the colloidal properties of the latexes (average particle size, particle number). In this paper experimental results are reported how changes of the emulsifier and the initiator concentration, the composition of the monomer mixture, and the reaction temperature influence the overall rate of polymerization, the particle size, and the appearance of the latexes.

Results and discussion

Conversion – time curves and rate of polymerization

The conversion – time curves depicted in Figure1 show the strong influence of the emulsifier concentration on the overall polymerization kinetics. The shape is similar for all the runs containing SDS (A2-A4) as in only exemplary shown in Figure 1 for the highest SDS concentration (A4) in order to avoid overloading of the graphs. It is straightforward to assume that HEMA as water soluble monomer determines strongly the very initial polymerization behavior because the reaction starts with the decomposition of peroxodisulfate in the aqueous phase. The initial conversion rate seems to be a good measure to compare the polymerizations with different recipes and to quantify the influence of changes in the reaction conditions.

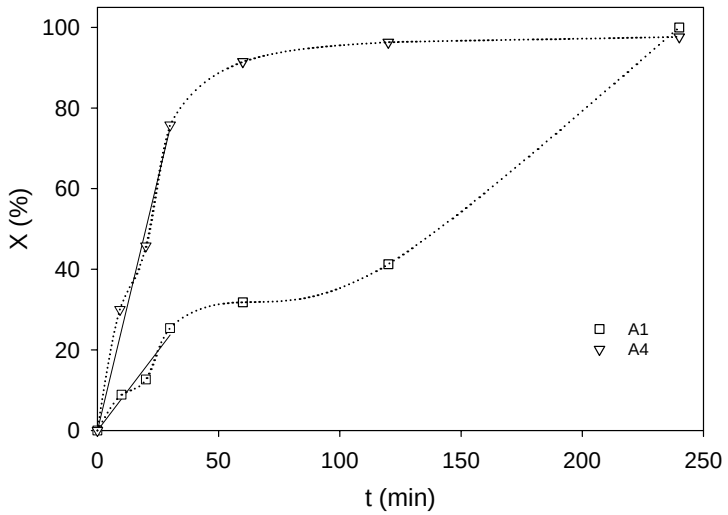

Fig. 1. Conversion – time curves for copolymerizations A1 (surfactant-free) and A4 (SDS concentration of 52 mM); the dotted lines are just for guiding the eye; the solid lines are linear regressions forced through the origin to determine the initial conversion rates; C_{KPS} = 0.37 mM, T = 70 °C.

Compared with the emulsifier-free polymerization, the presence of SDS facilitates the participation of the hydrophobic styrene in the reaction already at lower conversion and leads consequently to higher polymerization rate with increasing concentration. Moreover, the presence of SDS allows the stabilization of a higher particle surface area, which means at given conversion smaller particles and higher particle numbers. According to the general rate equation for heterophase polymerizations (1) the observed increase in the conversion rate with increasing SDS concentration (cf. also Figure 2A) is fully explainable [39]. R_P is the average rate of polymerization as obtained from the linear part of the conversion – time curves and corresponds to the experiments considered here to the initial conversion rate, k_p is the propagation rate constant, $\bar{n}$ is average number of radicals per particle, N is the particle concentration per unit volume of continuous phase, and C_{mp} is the monomer concentration per particle.

$$R_P = k_p \cdot \bar{n} \cdot N \cdot C_{mp} \qquad (1)$$

The dependence of the initial conversion rate on the emulsifier concentration is shown in Figure 2A.

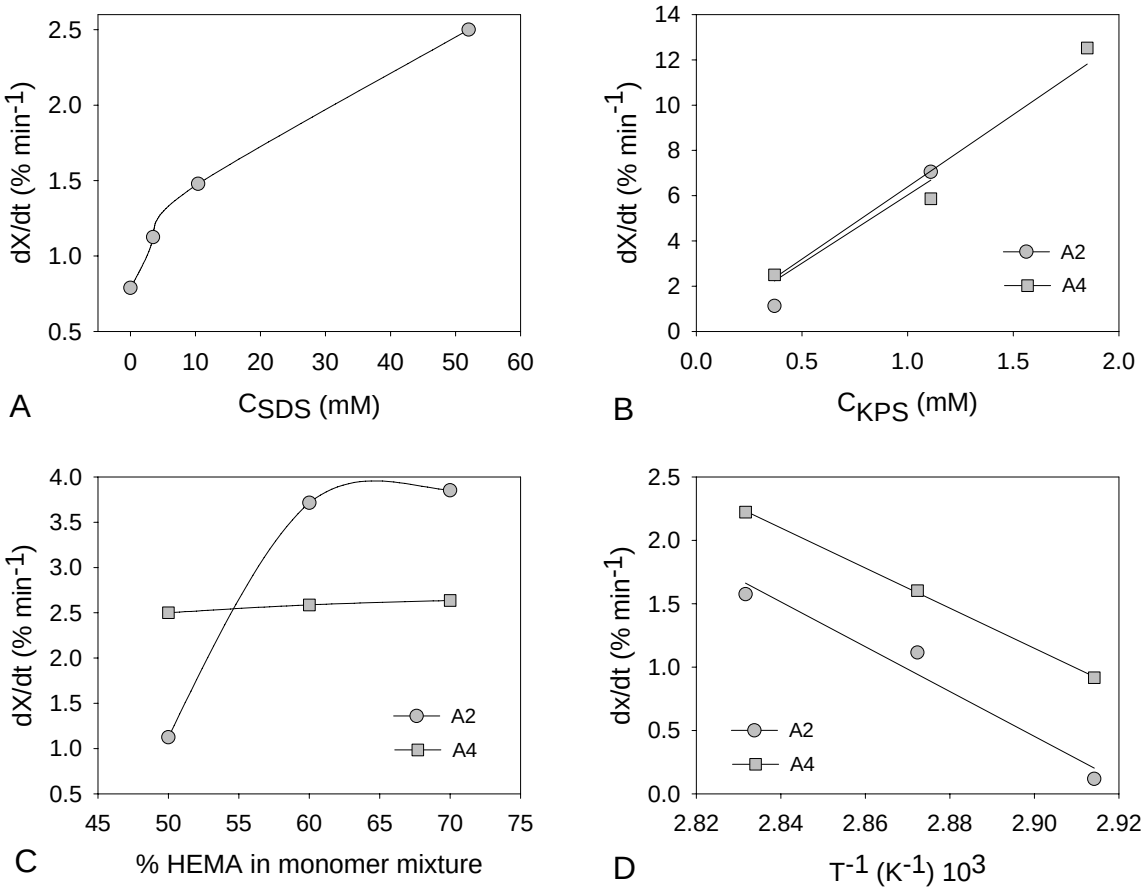

Fig. 2. Conversion rate in dependence on polymerization parameters; cf. experimental part and Figure 1 for the determination of the conversion rate; for the data in A, B, and C the temperature was 70 °C; for the data in A, C, and D the KPS concentration was 0.37 mM; A2 and A4 refer to SDS concentrations of 3.47 and 52 mM, respectively; the lines in A and C are just for guiding the eyes, the lines in B and D represent linear regressions forced for B through the origin.

The increase in the rate of polymerization with increasing amount of stabilizer is the

very typical behavior as observed for emulsion polymerizations as long as the rate of initiation is high enough to deliver sufficient radicals for the increasing number of particles [39].

As expected the rate of polymerization also depends on the initiator concentration as shown for two emulsifier concentrations in Figure 2B. The conversion rate scales almost linearly with the KPS concentration which is rather unusual even for emulsion polymerization where exponents between 0.5 and 0.6 have been found for monomers of different water solubility such as styrene and vinyl acetate [40-44]. A possible explanation might be that the bimolecular radical termination is hindered as HEMA has a tendency to gel formation due to cross-linking, cf. [31] and references therein. That HEMA plays a key role in the kinetics at lower SDS concentrations is underlined by the increase in the conversion rate by a factor of about 4 if the HEMA weight fraction in the monomer mixture increases by a factor of 1.2 (cf. run A2 of Figure 2C). At SDS concentration well above the critical micelle concentration (A4 of Figure 2C) the initial rate is entirely controlled by the emulsifier concentration and depends only slightly on the HEMA fraction in the monomer mixture. This might be explained according to equation (1) with the higher particle number that can be stabilized with this high emulsifier concentration. This condition favors polymerization inside the particles on expense of the polymerization in the continuous phase.

Arrhenius plots for the initial conversion rates as shown in Figure 2D lead to energies of activation of 147 and 132 kJ mol^{-1} for the runs with 3.47 (A2) and 52 mM (A4) SDS, respectively. These values are in the same order as the energy of activation for the KPS decomposition [45].

Average hydrodynamic particle size

The average particle size in ab-initio, that is, non - seeded heterophase polymerizations is mainly determined by the ability of the reaction system to what extent the polymer – water interface can be stabilized. Hydrophilic polymer end groups stemming from the initiator, hydrophilic comonomers, and emulsifier molecules contribute to that ability. A larger stabilizing ability of a polymerization recipe means that at given solids content latexes with smaller particles result. Sulfate ions as polymer end groups and SDS molecules contribute to electrostatic stabilization whereas HEMA – rich region in the polymer molecules contribute to steric stabilization of the copolymer latex particles. On the other hand, KPS contributes mainly to the ionic strength in the continuous phase and thus, increasing its concentration beyond a critical value resulting in larger particles.

The experimental results show that the average particle sizes of the copolymer latexes are mainly determined by the emulsifier concentration (cf. data in Figure 3 and TEM pictures in Figure 6) and by the composition of the monomer mixture (cf. data in Figure 4).

The dependence of the average particle size on the SDS concentration follows the typical rules for emulsion polymerizations as it decreases with increasing emulsifier concentration [39]. The decreasing average particle size changes also the optical appearance of the dispersions. The latexes prepared in the absence of SDS or with the lowest SDS concentration of 3.47 mM (systems A1, A2 in Table 1) appear opaque with average particle sizes of about 200 and 53 nm, respectively.

Increasing the SDS concentration to 10.5 mM and to 52 mM (systems A3, A4 in Table 1) reduces the average hydrodynamic particle size to about 30 and 20 nm, respectively, and changes the appearance of the latexes to translucent and almost

completely transparent.

The more or less transparent dispersions as obtained with the highest emulsifier concentration resembles the appearance of so-called microemulsion latexes obtained usually at much higher surfactant to monomer mass ratio. In this study the highest amount of emulsifier, which was only 15 weight-% relative to the overall monomer mass (1.5 g of SDS to 10 g of monomers) compared to more than 100 weight-% for typical microemulsion polymerizations [3, 4] allows to mimic the optical look as obtained for microemulsion latexes however at much higher polymer content. Note that, the starting system, that is the reaction mixture before adding the initiator solution, is an opaque emulsion and does not at all resemble the transparent appearance of microemulsions. This is an interesting result as it is thought that nanoscopic transparent latexes might be of potential importance in biotechnology especially if the particle surface is made of biocompatible polymers such as poly-HEMA [27, 28].

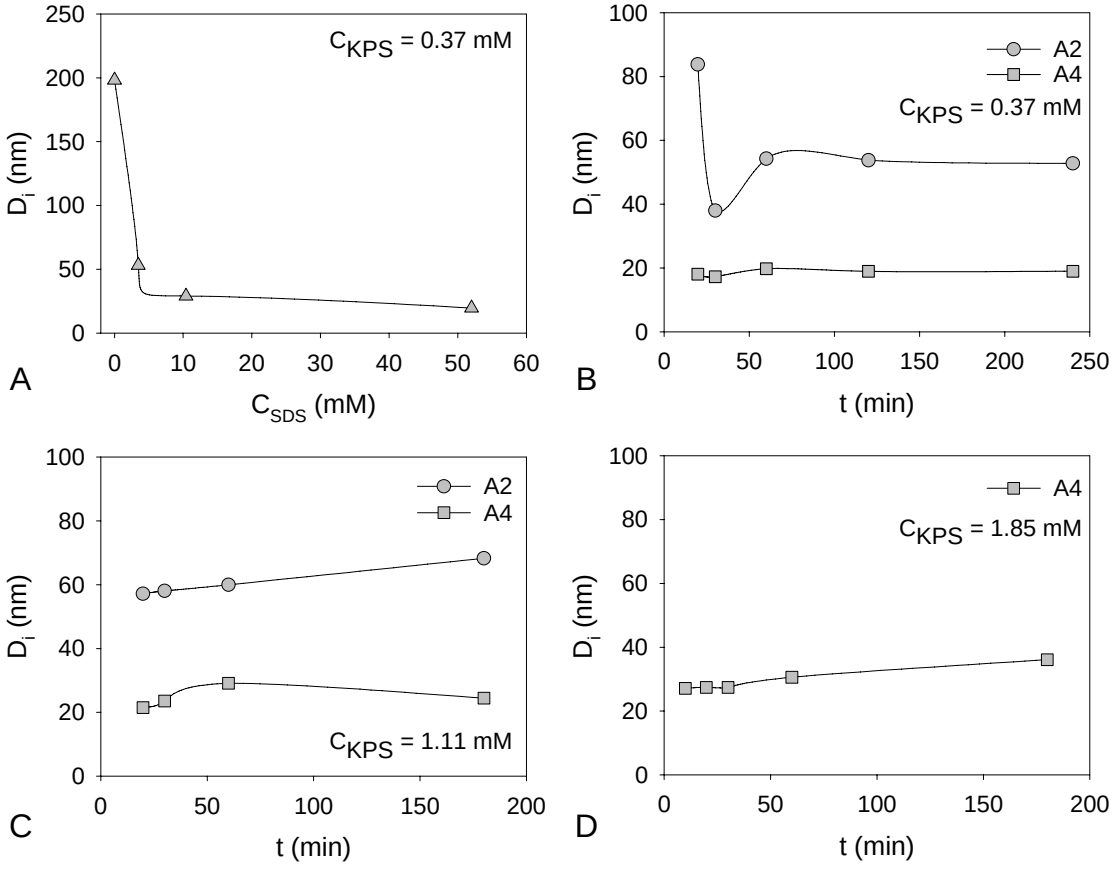

Fig. 3. Change of the average particle size in dependence on the SDS concentration (A, final particle size), and during the course of the polymerization in dependence on SDS and KPS concentration (B – D) for 50 weight-% HEMA in the monomer mixture; polymerization temperature 70 °C, A2 and A4 refer to SDS concentrations of 3.47 and 52 mM, respectively.

The data of Figure 3B show the influence of the SDS concentration on the development of the average particle size in the course of the polymerization. During run A2 where the emulsifier concentration is still below the cmc the average particle size decreases initially before it levels. This behavior reflects the fact that mainly HEMA reacts during the first minutes of the reaction before more and more styrene

participates and more and more particles are generated. For the surfactant – free polymerization (A1, data not shown) an increase in the average particle size is observed over the whole duration of the polymerization starting from about 80 nm and ending with about 200 nm. As the final particles are quite monodisperse (cf. Figure 5A) one can conclude that in this case only a single, quite short nucleation period occurred.

Moreover, comparing the data in Figures 3 B – D reveals that the hydrodynamic particle diameter D_i increases with increasing KPS concentration for all SDS concentrations. Obviously, with increasing initiator concentration the partial destabilization of the latex particles due to the increasing ionic strength dominates instead of a possible stabilization due to a higher surface charge density. This destabilization is for the lower SDS concentration (A2, C_{SDS} = 0.37 mM) so strong that the highest KPS concentration of C_{KPS} = 1.85 mM causes complete coagulation of the latex in the course of the polymerization.

Changing the temperature is another possibility to change the radical flux without changing the ionic strength so drastically. The data of the temperature variation as depicted in Figures 4A and B reveal indeed that the radical flux is only of minor importance for the average particle size.

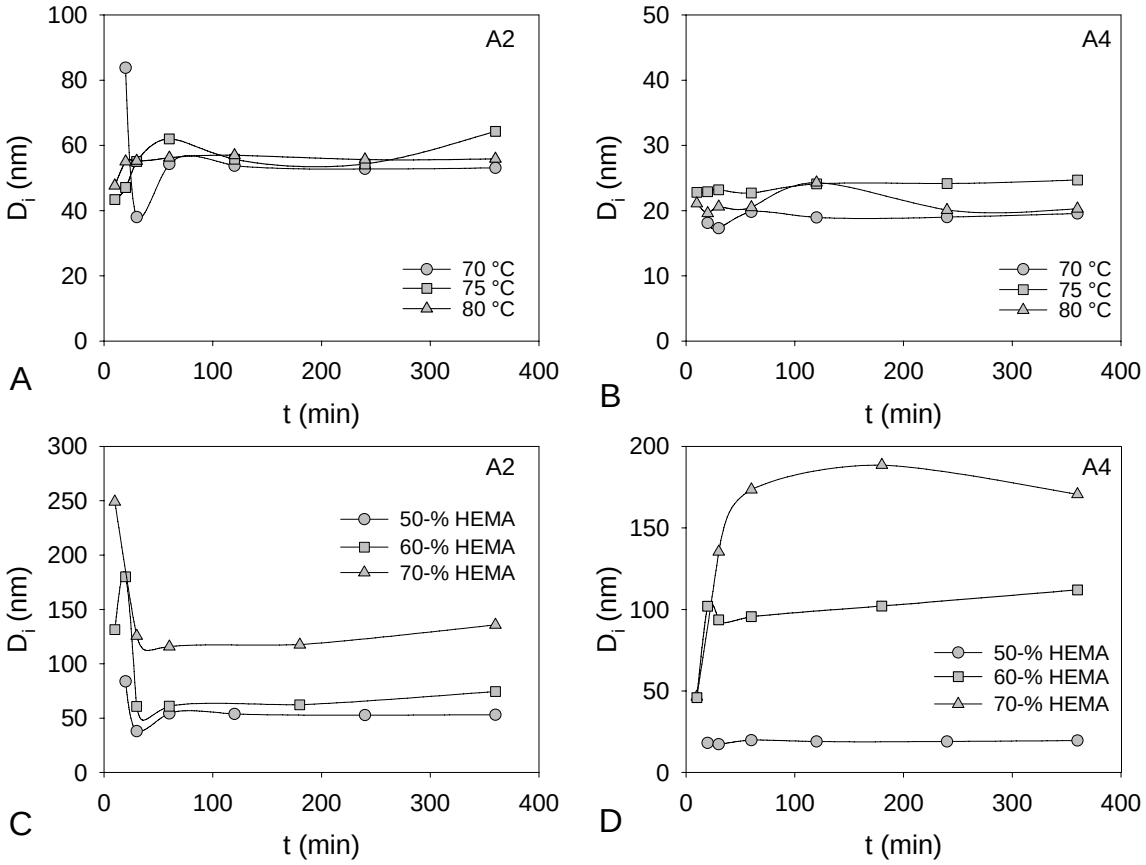

Fig. 4. Change of the average particle size during the course of the polymerization in dependence on the polymerization temperature (A, B) and in dependence on the weight-% of HEMA in the monomer mixture (C, D); A2 and A4 refer to SDS concentrations of 3.47 and 52 mM, respectively; C, D – T = 70°C.

Also the composition of the monomer mixture has a strong influence on the hydrodynamic particle size. Increasing the HEMA content from 50 to 70 weight-%

causes an increase of the average hydrodynamic particle size. The relative increase is extremely high for the polymerizations with the highest SDS concentration (cf. Figure 4D). In this case D_i increases by more than a factor of 7 if the HEMA content rises in the monomer mixture from 50 to 70 weight-%. Obviously, with increasing HEMA content in the monomer mixture the main locus of the polymerization is shifted more and more towards the aqueous phase and the kinetics becomes increasingly controlled by the peculiarities of HEMA as described in [31]. Briefly, the nucleation of particles during HEMA polymerization in aqueous media requires hydrophobic groups stemming either from the initiator or comonomers. Thus, in homopolymerization poly-HEMA latex particles are only formed with initiators containing hydrophobic groups. Oil – soluble or surface active initiators lead to latexes in high yields whereas with the hydrophilic KPS the latex yield is less than 10 % and most of the polymer is obtained in form of coagulum even at high emulsifier concentrations. This means for the polymerizations considered here that the aggregation of styrene units present in the copolymer molecules determines the particle nucleation. These copolymers are formed after initiation in the aqueous phase and their composition is rich in HEMA governed by both the reactivity ratios (cf. above and [38]) and the concentration ratio of the monomers in water. Compared to styrene heterophase homopolymerization the styrene concentration in the continuous phase is enhanced as the HEMA - in - water solution has a higher solvency for styrene than pure water. According to this scenario the hydrodynamic particles size increases with decreasing styrene content in the monomer mixture (cf. Figure 4D). Another peculiarity of poly - HEMA particles is the weak emulsifier adsorption [31]. The same is true for the HEMA - styrene copolymer particles as the shell of the particles is rich in HEMA. Consequently, during fortification of the dispersions as it takes place during sample preparation for electron microscopy (cf. below) SDS molecules easily desorbs and fusion of particles is facilitated.

Transmission electron microscopy images

The TEM images in Figure 5 confirm the strong influence of the SDS concentration on the size of the particles as it was also observed with dynamic light scattering (cf. Figures 3 and 4). An estimation of the size of the particles from the TEM pictures yields values of about 150-160, 45-55, 25-30, and 10-15 nm for the samples A, B, C, and D, respectively, as displayed in Figure 5. Except for the particles prepared in the absence of surfactant (Figure 5A) an estimation of the hydrodynamic layer thickness by comparison with the D_i values from dynamic light scattering is not possible as for the other samples as there is not enough individual particles on the TEM pictures which can be clearly identified and enumerated for the calculation of average values. Moreover, the particles of Figure 5A are, despite their non-spherical shape, quite monodisperse, which is again a common behavior known from emulsion polymerizations in the absence of surfactants or with emulsifier concentrations below the critical micelle concentration [46]. For this sample, the difference between the diameter of the particles in the dispersed state (from dynamic light scattering) and in the dried state (from TEM) allows to approximate the hydrodynamic layer to be at least between 20 and 25 nm. This rather high value points to a polymeric shell composed of water soluble copolymers with a high HEMA content.

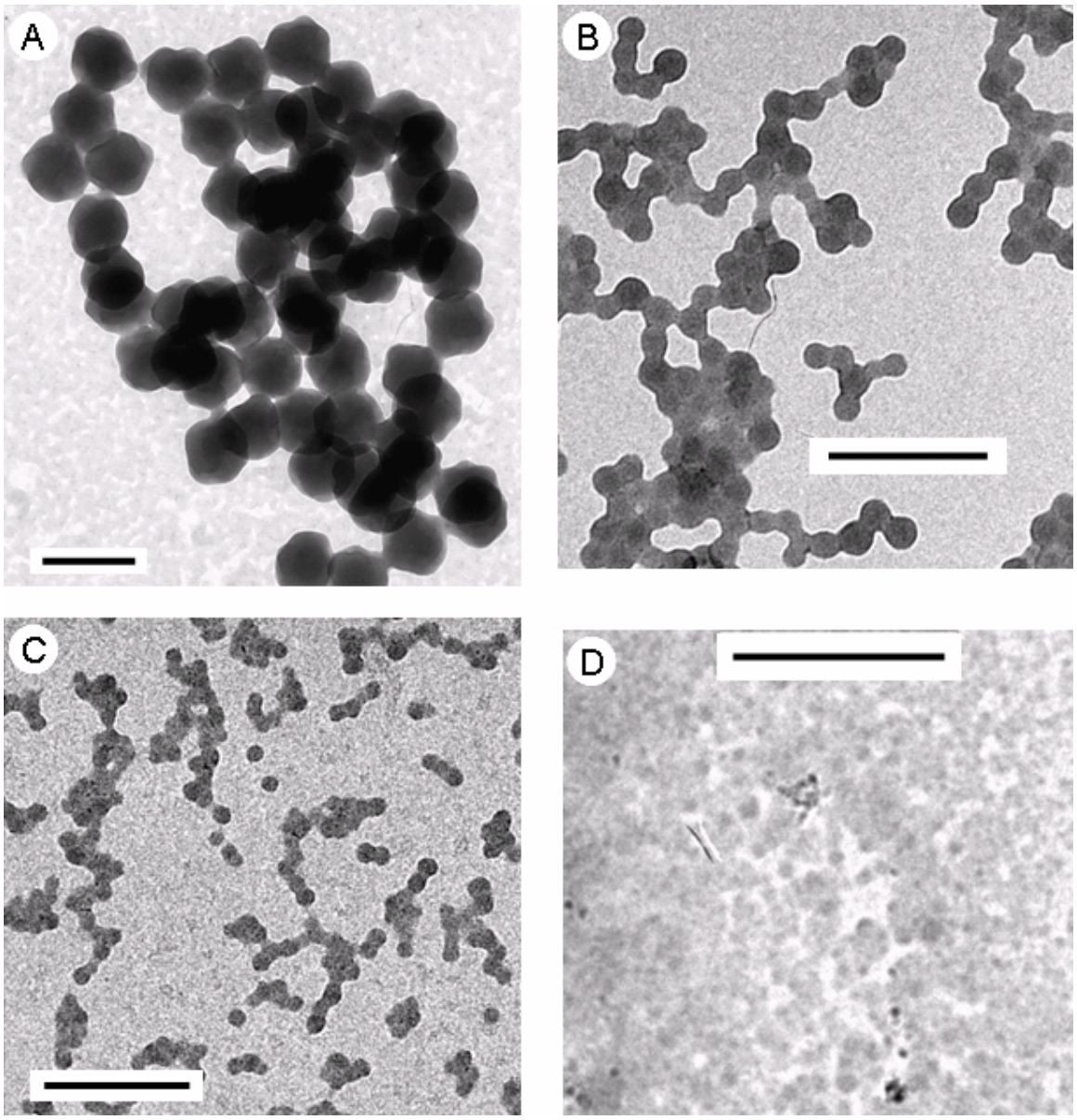

Fig. 5. TEM images of styrene – HEMA (1:1 weight content) copolymer latex particles prepared with varying amounts of SDS emulsifier, the bars indicate in any case 250 nm, A – emulsifier – free, B – 3.47 mM SDS, C – 10.5 mM SDS, D – 52 mM SDS ; C_{KPS} = 0.37 mM; T = 70 °C.

The existence of a HEMA – rich shell around the particles is supported by the non-spherical shape reflected in the TEM images (Figure 5A and Figure 6A). This creasing or shriveling appearance of the particles might be the consequence that during fortification syneresis in HEMA – rich portions of the particle shell may take place as it is typical for poly-HEMA [47]. The composition of the shell copolymer regarding HEMA – content and cross-linking density is not uniform at each surface spot, and so is the shrinkage of the shell. Besides the size also the shape of the dried particles is strongly influenced by the presence of surfactant (Figure 6). SDS present at concentrations even below the critical micelle concentration leads to spherical particles and syneresis around a single particle is obviously suppressed. The particles depicted in Figure 6 clearly elucidate the different shape of the dried copolymer particles in the absence and presence of SDS.

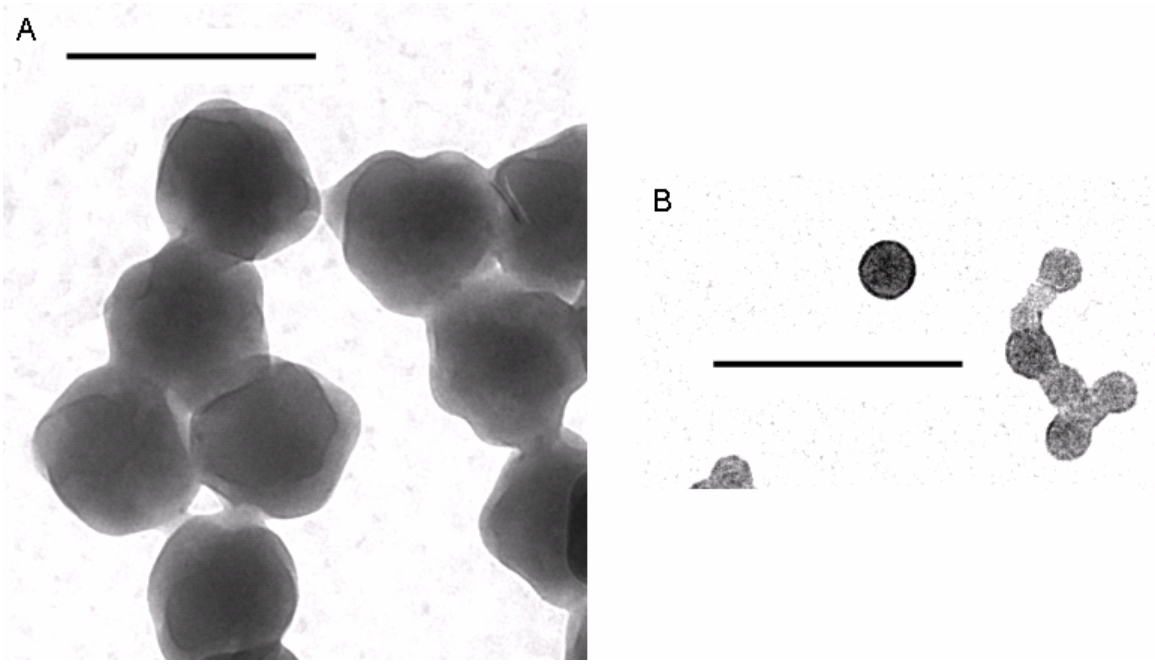

Fig. 6. TEM pictures illustrating the shape of styrene – HEMA copolymer particles (weight ratio styrene : HEMA 1:1) prepared in absence (A) and in the presence of 3.47 mM SDS (B), the bars indicate in any case 250 nm; C_{KPS} = 0.37 mM; T = 70 °C

The shape of the particles prepared in the absence of SDS (Figure 6A) is for both the shell and the core and the non-centrosymmetric shell appears clearly brighter than the core. Contrary, the particles made in the presence of SDS exhibit a spherical shape and the particle shell appears much darker (Figure 6B), which is normal for particles with ionic surface groups as discussed in [48].

The syneresis of poly-HEMA also causes a change in the state of the particles when they are either in the dispersion or dried on any substrate. In the aqueous dispersion the particles are separated from each other and they diffuse independently as indicated by the low diameters obtained by dynamic light scattering. Contrary, on the TEM grid the particles are agglomerated and even partly fused together as illustrated by the images put together in Figure 7. These pictures reveal that the extent of agglomeration and fusion depends on the amount of HEMA in the monomer mixture.

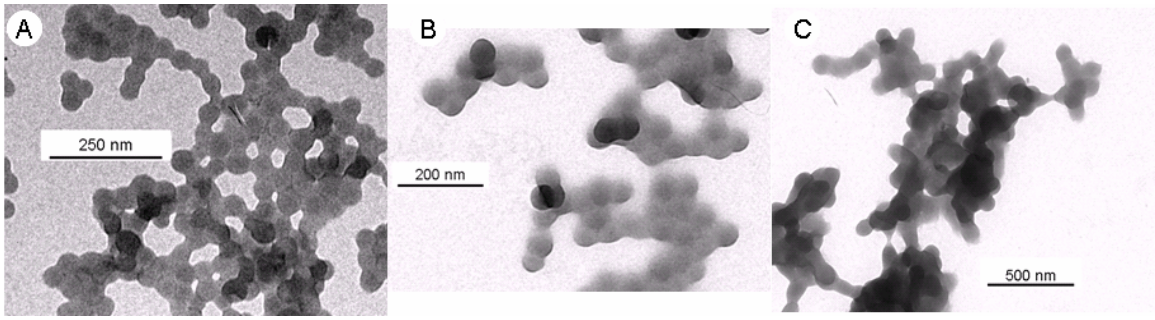

Fig. 7. TEM images of styrene – HEMA copolymer particles showing growing agglomeration and fusion with increasing portion of HEMA in the monomer mixture, A – 50 %, B – 60 %, C – 70 %; C_{KPS} = 0.37 mM; T = 70 °C.

An explanation of this observation might be possible in the following way. At some stage in the fortification of the dispersion, which takes place during electron microscopy sample preparation (so-called suspension preparation), water is expulsed out of the HEMA – rich shell of the particles. As the P-HEMA interface is extremely polar, the surfactant molecules are only weakly adsorbed and they may easily desorb and accumulate in water rich regions. The particles attraction is now stronger and the still partly swollen and soft poly-HEMA shells penetrate each other. The fusion is hindered and more water is evaporated when the glassy polystyrene – rich cores are reached.

Conclusions

The application of HEMA as hydrophilic comonomer in styrene emulsion polymerization in the presence of SDS allows the preparation of special gradient latex particles. The particles possess a hydrophobic core and a hydrophilic shell and have at higher SDS concentration such a small size that the latexes appear transparent. For example, latex with a polymer content of about 10 weight - % prepared with 15 weight - % of SDS relative to the amount of monomer in a styrene – HEMA mixture containing equal mass of both monomers appears transparent.

The colloidal stability of the reaction system is quite sensitive to the KPS concentration. Increasing the KPS concentration to 1.11 mM leads to larger particles for quite high SDS concentrations (10.4 and 52 mM) but causes complete coagulation if the stabilizer concentration is zero or 3.47 mM.

Moreover, the experimental data show that the polymerization kinetics as well as the particle properties is governed by the peculiarities of HEMA, especially if it is present in higher portions.

Experimental part

Materials and experimental techniques

Styrene and HEMA of monomer grade, purchased from Fluka, Chemika, Switzerland were distilled under reduced pressure. Potassium peroxodisulfate (KPS) from LOBA Chem, India, was recrystallized from water at low temperature and preserved in the refrigerator.

Tab. 1. Polymerization recipes for the standard conditions, polymerization temperature 70°C, all concentrations relative to water.

Code	Styrene (g/mM)	HEMA (g/mM)	C_{SDS} (mM)	C_{KPS} (mM)	Water (g)
A1	5 / 480	5 / 384	0	0.37	100
A2	5 / 480	5 / 384	3.47	0.37	100
A3	5 / 480	5 / 384	10.40	0.37	100
A4	5 / 480	5 / 384	52.00	0.37	100

SDS of Fluka, Chemika, Switzerland was used without purification. Deionized water was distilled using a glass (Pyrex) distillation apparatus.

Intensity weighted average particle diameters (D_i) of the latex particles were measured with a NICOMP 380 particles sizer (Santa Barbara, California, USA). The reproducibility of the size measurements is less than ± 10 % for the intensity weighted average diameter. For transmission electron microscopy (TEM) investigations the latex samples were diluted to about 0.1% solid by distilled water and a drop was placed on the carbon coated copper grid. The sample were dried at ambient temperature and observed at an accelerating voltage of 100 kV by a Zeiss EM 912 Omega micro-scope.

Copolymerization reactions

The emulsion copolymerizations were carried out in three necked round bottom glass reactors immersed in a thermo stated water bath with a total monomer weight content of 10 % relative to the amount of water with varying amount of SDS in a nitrogen atmosphere under mild stirring (about 100 revolutions per minute). The particular recipes and the polymerization codes are detailed in Table 1 for the standard conditions regarding polymerization temperature of 70 °C and KPS concentration of 0.37 mM in water.

In order to study the influence of changes in the reaction conditions, additional polymerizations were carried out with SDS concentrations clearly below (3.47 mM) and well above (52 mM) the critical micelle concentration. Note that, under the particular experimental conditions regarding polymerization temperature and ionic strength in the reaction mixture the critical micelle concentration of SDS is between 5 and 8 mM [49]. In comparison to the standard conditions as given in Table 1 polymerizations were also carried out at both higher KPS concentration (1.11 mM and 1.85 mM) and temperature (75 °C and 80 °C). Moreover, the HEMA content in the monomer mixture was increased from 50 weight-% at standard conditions to 60 and 70 weight-%.

Overall monomer conversion and rate of polymerization

Polymer samples were withdrawn from the reactor at defined times and instilled in a pre-weighed dried ceramic Petri dish. To prevent further polymerization the ceramic dish contained a known amount of 1% hydroquinone solution and was additionally rapidly dipped in an ice water bath. Samples were kept in an oven at around 80°C until a constant weight was reached. Then the percentage of overall monomer conversion (X) was calculated from the solids content by correcting for the amounts of auxiliary materials. In order to check the reproducibility of the polymerization runs A2 and A3 were repeated. The procedure as applied was quite reproducible as the conversion data could be reproduced with an accuracy of ± (1-2) %. The initial overall rate of polymerization was expressed by the initial conversion rate, which is the slope (dX/dt) of the linearized initial part of the conversion – time (t) curve as exemplary illustrated in Figure 1.

Acknowledgements

The authors thank Mrs. Rona Pitschke and Mrs. Heike Runge for taking the transmission electron microscopy images.

References

[1] Hoar, T. P.; Schulman, J. H.; *Nature* **1943,** *152*, 102.
[2] Urban, D.; Takamura, K.; *Polymer Dispersions and Their Industrial Apllications*. (eds) ed.; Wiley-VCH: Weinheim, **2002**; 408.
[3] Candau, F.; *J. Chim. Phys. Physico-Chim. Biol.* **1987,** *84*, 1095.
[4] Candau, F.; Polymerization in microemulsions. In: *Polymerization in Organic Media*; Paleos, C. M. (ed.); Gordon and Breach: Philadelphia, **1992**; 215.
[5] Tirrell, D. A.; Copolymerization. In: *Encyclopedia Polymer Science and Engineering*; Mark, H.; Bikales, N. M.; Overberger, C. G.; Menges, G. (eds.); Wiley: New York, **1985**; Vol. 4, 192.
[6] Delair, T.; Pichot, C.; Mandrand, B.; *Coll. Polym. Sci.* **1994,** *272*, 72.
[7] Sugiyama, K.; Ohga, K.; Aoki, H.; Amaya, N.; *Macromol. Chem. Phys.* **1995,** *196*, 1907.
[8] Ceska, G. W.; *J. Appl. Polym. Sci.* **1974,** *18*, 427.
[9] Wang, P. H.; Pan, C. Y.; *Coll. Polym. Sci.* **2001,** *279*, 98.
[10] Kang, K.; Kan, C. Y.; Du, Y.; Liu, D. S.; *J. Appl. Polym. Sci.* **2004,** *92*, 433.
[11] Yang, B.-Z.; Chen, L.-W.; Chiu, W.-Y.; *Polym. J.* **1997,** *29*, 744.
[12] Yang, B.-Z.; Chen, L.-W.; Chiu, W.-Y.; *Polym. J.* **1997,** *29*, 737.
[13] Dunn, A. S.; Melville, H. W.; *Nature* **1952,** *169*, 699.
[14] Van Doremaele, G. H. J.; Van Herk, A. M.; Ammerdorffer, J. L.; German, A. L.; *Polym. Comm.* **1988,** *29*, 299.
[15] Mendizabal, E.; Rodriguez-Ruvalcaba, R.; Rabelero, V.; Puig, J. E.; Velazquez, R.; Castano, V.; *Int. J. Polym. Mat.* **1995,** *30*, 167.
[16] Reynhout, X. E. E.; Meuldijk, J.; Drinkenburg, B. A. H.; *Progr. Coll. Polym. Sci.* **2004,** *124*, 64.
[17] Skarpa, I.; Hamersak, Z.; Slogar, I.; Skarpa, D.; *Polimeri* **1990,** *11*, 181.
[18] Urban, D.; Distler, D.; Introduction. In: *Polymer Dispersions and Their Industrial Apllications*; Urban, D.; Takamura, K. (eds.); Wiley-VCH: Weinheim, **2002**; pp 1.
[19] Wesslau, H.; *Makromol. Chem* **1963,** *69*, 220.
[20] Yin, W.; Kong, Z.; Zhu, K.; Xuan, N.; He, Q.; Zhang, B.; *Tul. Gong.* **2002,** *32*, 1.
[21] Casagrande, M.; Heldmann, C.; Pawelzik, U.; Meier, G.; Stamm, M.; *Progr. Coll. Polym. Sci.* **2000,** *115*, 128.
[22] Puig, J. E.; Corona-Galvan, S.; Maldonado, A.; Schulz, P. C.; *J. Coll. Interf. Sci.* **1990,** *137*, 308.
[23] Xin, Y.; Hu, Y.; Zeldin, M.; Fife, W. K.; *Macromolecules* **1993,** *26*, 4670.
[24] Askarov, M. A.; Tadzhieva, M. A.; Rakhmanberdyev, R. I.; *Uzb. Khim. Zh.* **1963,** *7*, 65.
[25] Kozhevnikov, N. V.; Teryokhina, N. V.; Goldfein, M. D.; *Izv. Vyss. Uch. Zav. Khim. Khim. Tekhn.* **1998,** *41*, 83.
[26] Scott, C.; Wu, D.; Ho, C.-C.; Co, C. C.; *J. Am. Chem. Soc.* **2005,** *127*, 4160.
[27] Elvira, C.; Gallardo, A.; Lacroix, N.; Schacht, E.; San Roman, J.; *J. Mater. Sci.: Mater. in Med.* **2001,** *12*, 535.
[28] Stol, M.; *J. Bioactive Comp. Polym.* **1991,** *6*, 308.
[29] Ahmad, H.; Miah, M. A. J.; Rahman, M. M.; *Coll. Polym. Sci.* **2003,** *281*, 988.
[30] Okubo, M.; Hattori, H.; *Coll. Polym. Sci.* **1993,** *271*, 1157.
[31] Tauer, K.; Ali, A. M. I.; Sedlak, M.; *Coll. Polym. Sci.* **2005,** *283*, 351.
[32] Guo, T.; Song, M.; Hao, G.; Zhao, F.; Zhang, B.; *Chin. J. React. Polym.* **1999,** *8*, 38.

[33] Kamei, S.; Okubo, M.; Matsumoto, T.; *J. Polym. Sci., A: Polym. Chem.* **1986,** *24*, 3109.
[34] Klocke, M.; Maltzahn, J.; Moritz, H.-U.; *Dechema Monographs* **1992,** *127*, 389.
[35] Okubo, M.; Yamamoto, Y.; Kamei, S.; *Coll. Polym. Sci.* **1989,** *267*, 861.
[36] Okubo, M.; Yamamoto, Y.; Uno, M.; Kamei, S.; Matsumoto, T.; *Coll. Polym. Sci.* **1987,** *265*, 1061.
[37] Schoonbrood, H. A. S.; Aerdts, A. M.; German, A. L.; van der Velden, G. P. M.; *Macromolecules* **1995,** *28*, 5518.
[38] Chen, Z.; Pruess, J.; Flechtner, U.; Warnecke, H.-J.; *Chem. Eng. Technol.* **2002,** *25*, 1115.
[39] Tauer, K.; The role of emulsifiers in the kinetics and mechanisms of emulsion polymerization. In: *Applied Surfactant Series*; Karsa, D. R. (eds.); Blackwell Publishing, CRC Press: Oxford, UK, **2003**; Vol. vol 1, 32.
[40] Chang, K. H. S.; Litt, M. H.; Nomura, M.; The reinvestigation of vinyl acetate emulsion polymerization. I. The rate of polymerization. In: *Emulsion Polymerization of Vinyl Acetate*; El-Aasser, M. S.; Vanderhoff, J. W. (eds.); Applied Science: London, **1981**; 89.
[41] Chatterjee, S. P.; Banerjee, M.; Konar, R. S.; *J. Polym. Sci., Polym. Chem. Ed.* **1978,** *16*, 1517.
[42] Friis, N.; Nyhagen, L.; *J. Appl. Polym. Sci.* **1973,** *17*, 2311.
[43] Kolthoff, I. M.; Dale, W. J.; *J. Am. Chem. Soc.* **1945,** *67*, 1672.
[44] Ryabova, M. S.; Beresnev, V. N.; Smirnov, N. I.; *Zh. Priklad. Khim.* **1973,** *46*, 2663.
[45] Behrman, E. J.; Edwards, J. O.; *Rev. Inorg. Chem.* **1980,** *2*, 179.
[46] Tauer, K.; Latex particles. In: *Colloids and Colloid Assemblies*; Caruso, F. (eds.); Wiley VCH: Weinheim, **2004**; pp 1.
[47] Dusek, K.; Sedlacek, B.; *Eur. Polym. J.* **1971,** *7*, 1275.
[48] Schellenberg, C.; Tauer, K.; Antonietti, M.; *J. Disp. Sci. Technol.* **1999,** *20*, 177.
[49] Mukerjee, P.; Mysels, K. J. Critical Micelle Concentrations of Aqueous Surfactant Systems; National Bureau of Standards: Washington, DC, **1971**; Vol. 36.