Macromolecules **2002,** *35,* 2538−2544

Linear and Star-Shaped Polystyrene-*block*-poly(sodium glutamate)s as Emulsifiers in the Heterophase Polymerization of Styrene

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Received September 10, 2001; Revised Manuscript Received December 13, 2001

ABSTRACT: Linear and hetero multiarm polystyrene-*block*-poly(sodium DL-glutamate) copolymers were used as emulsifiers in the radical emulsion polymerization of styrene in order to investigate the impact of the stabilizer topology on the main latex properties, namely average particle size, polydispersity, electrolyte stability, and electrophoretic mobility of particles, in dependence of the electrolyte concentration and pH. Compared to the linear analogues ($d_H = 100-220$ nm, PDI < 1.04), the star-shaped stabilizers yield smaller latexes particles ($d_H = 70-130$ nm) with broad or even bimodal distributions (PDI > 1.13), which indicates a higher stabilizing efficiency and the ability to stabilize a second generation of particles. The topology of the stabilizer affects as well the critical coagulation concentration of the latex, which is 1.0 M NaCl for linear and 0.2 M for branched copolymers. The observed stability of the latexes against electrolytes and the mobility of particles support an electrosteric stabilization of the particles.

Introduction

Heterophase polymerization is one of the oldest polymerization techniques which enables the facile preparation of aqueous dispersions, so-called latices, with a high polymer content but low viscosity. For this and other reasons, it plays a very important role in industrial-scale syntheses of for example dispersion colors, adhesives, or clues.[1] However, the ease of operation opposes the complexity of the mechanism of heterophase polymerizations, which is still a subject of current investigations.[2]

In a typical procedure, hydrophobic monomers like styrenes or acrylates are polymerized in a free-radical process in aqueous media in the presence of an emulsifier, usually a low-molecular-weight surfactant (tenside) or amphiphilic block copolymer. Commonly used tensides like sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) will prevent the latex from coagulation via electrostatic repulsion between polymer particles; nonionic surfactants and block copolymers with for example hydrophilic poly(ethylene glycol) segments instead will stabilize particles by steric repulsion (formation of hairy particles; cf. Chart 1). Block copolymers with a polyelectrolyte stabilizing moiety combine the best properties of both stabilization modes, namely the long-range electrostatic repulsion between polymer colloids and the good stability against ionic additives. In addition, strong polyelectrolytes like sulfonates will exhibit a stabilizing ability which is insensitive to changes of pH and temperature.[1] As a matter of their extraordinary properties, polyelectrolyte block copolymers are a promising class of new surfactants for aqueous heterophase polymerization systems.

Chart 1. Schematic Representation of a Hairy Latex Particle with a Stabilizing Corona of Polymer Chains

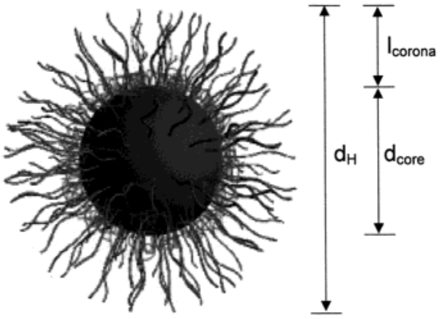
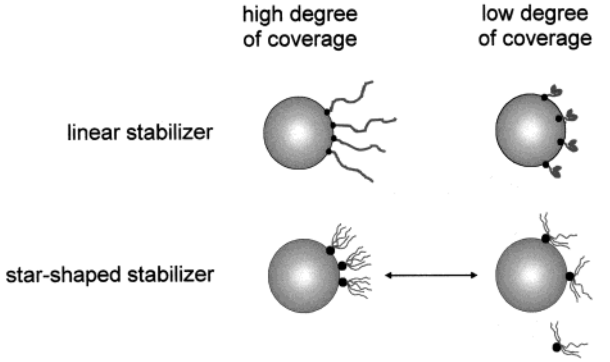


Chart 2. Schematic Drawing of the Adsorption of Linear and Star-Shaped Stabilizers onto the Particle Surface



Well-defined amphiphilic polyelectrolyte block copolymers are available in a large variety via living/controlled polymerization techniques and subsequent modification reactions.[3] Nevertheless, only a very few studies have been reported yet that investigate the stabilization abilities of linear polymeric surfactants with polyelectrolyte sequences (either as block or statistically distributed along the chain) such as poly([2-hydroxy-1-sulfonyl]ethyl methacrylate),[4] poly(styrenesulfonate),[5] poly(acrylic acid),[6] and poly(vinylbenzyltrialkylammonium halide).[6,7] However, none of these studies refer to any effects of branching on the stabilization ability of copolymers, although one might expect multiarm polyelectrolyte star block polymers to exhibit a higher stabilization efficiency than their linear analogues due to the increased bulkiness of the headgroup (cf. Chart 2).

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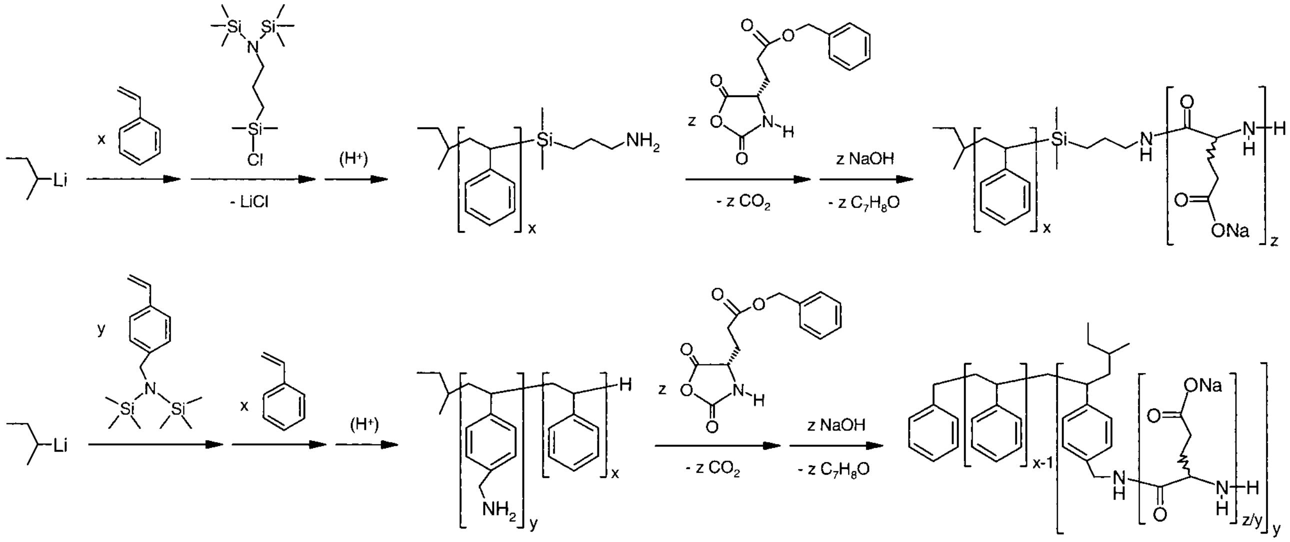
10.1021/ma011606q CCC: $22.00

Scheme 1. General Reaction Scheme of the Anionic Synthesis of Linear and Star-Shaped Polystyrene-*block*-poly(sodium DL-glutamate) Copolymers



In another project we are investigating linear and star-shaped diblock copolymers with polystyrene and poly(γ-benzyl-L-glutamate) segments, among others, in view of their lyotropic phase behavior and solid-state morphologies.[8] These copolymers yield, after removal of the benzyl protecting groups, water-soluble polyelectrolytes with anionic poly(sodium DL-glutamate) segments, which should afford electrosterically stabilized latices—such particles with a polypeptide surface coating might be, for instance, of certain interest in the field of medicinal chemistry as drug carrier systems.

Here, we report on the emulsifying properties of linear and star-shaped polystyrene-*block*-poly(sodium DL-glutamate) copolymers in the heterophase polymerization of styrene. The major aim of this work is to elucidate the impact of topology of these polymeric surfactants on their stabilizing properties in aqueous emulsion polymerization. Charts 1 and 2 illustrate the types of particles which can be expected: Chart 1 shows the sketch of a hairy particle with its characteristic sizes, as there are the hydrodynamic diameter (d_H), the hard core diameter (d_{core}), and the thickness of the corona (l_{corona}), and Chart 2 illustrates the tentative impact of the topology of the stabilizer on the coverage of the particle surface.

Experimental Section

Chemicals. Chemicals with a purity grade greater than 96% were purchased from Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany) and were used as received, except for styrene, dimethylformamide (DMF), cyclohexane, and tetrahydrofuran (THF), which were fractionally distilled and purified following standard procedures. 2,2′-Azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (radical initiator VA-086) was purchased from Wako Chemicals GmbH (Neuss, Germany) and used as received. Argon as the inert gas was purified by passing successively over an 1 m column containing P_2O_5 on silica and an Oxysorb catalyst (Messer Griesheim GmbH, Berlin, Germany). 1-(Chlorodimethylsilyl)-3-[*N*,*N*-bis(trimethylsilyl)amino]propane was obtained from the hydrosilylation of 3-[*N*,*N*-bis(trimethylsilyl)amino]-1-propene with dimethylchlorosilane;[9] the first reactant was synthesized from potassium *N*,*N*-bis(trimethylsilyl) amide and allyl bromide.[10] 4-[*N*,*N*-bis(trimethylsilyl)aminomethyl]styrene was prepared from potassium *N*,*N*-bis(trimethylsilyl) amide and 4-(chloromethyl)styrene. γ-Benzyl-L-glutamate-*N*-carboxyanhydride was prepared by the Fuchs—Farthing method using triphosgene.[11]

Block Copolymer Synthesis and Characterization. All polymerization reactions were carried out under a dry argon atmosphere employing standard high-vacuum techniques. A detailed description of synthetic procedures and characterization methods will be provided elsewhere.[12]

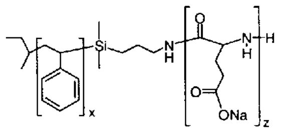
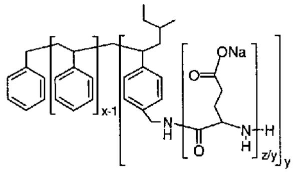
Briefly, polystyrene-*block*-poly(γ-benzyl-L-glutamate) copolymers were prepared by the ω-amino-functional polystyrene initiated ring-opening polymerization of γ-benzyl-L-glutamate-*N*-carboxyanhydride in DMF at +40 °C.[13] Depending on the functionality of the macroinitiator, either linear or hetero multiarm star block copolymers were obtained (see Scheme 1). All polymer samples exhibited monomodal molecular weight distributions (SEC)[14] after polystyrene residuals have been removed by repeated extraction with cyclohexane. Molecular weights were determined from the molecular weight of the macroinitiator (SEC) and the chemical composition of the block copolymer (NMR).[15] The number of polypeptide arms of the star-shaped block copolymers could not be determined yet and is therefore assumed to be equal to the amino functionality of the macroinitiator. The γ-benzyl ester groups were hydrolyzed with aqueous NaOH at room temperature, yielding the polystyrene-*block*-poly(sodium DL-glutamate) copolymers; the molecular characteristics of the copolymer samples are listed in Table 1.

Monofunctional macroinitiators with molecular weights of ~5500 g/mol (SEC) were prepared by quenching a solution of polystyrene lithium in cyclohexane with 1-(chlorodimethylsilyl)-3-[*N*,*N*-bis(trimethylsilyl)amino]propane; the amino protecting group was removed by HCl-catalyzed hydrolysis at room temperature. According to NMR and SEC analyses, polymers exhibited high chain end functionalities ($f_{amino} > 0.9$) and narrow molecular weight distributions (PDI < 1.04).

Polyfunctional macroinitiators were synthesized by stepwise anionic polymerization of 4-[*N*,*N*-bis(trimethylsilyl)aminomethyl]styrene and styrene with *sec*-butyllithium as the initiator in THF at −78 °C and subsequent deprotection of the amino-functional block segment.[16] MALDI-TOF mass spectrometric analysis[17] on the poly[4-(aminomethyl)styrene] precursor provided an average of eight amino groups per polymer chain. The molecular weight of the polystyrene segment was calculated from the copolymer composition (NMR) to be ~6500 g/mol. According to SEC, the apparent PDI of the polyfunctional macroinitiator is less than 1.15.

Heterophase Polymerizations. Heterophase polymerization reactions were carried out in sealed test tubes under an argon atmosphere in a rotational thermostat VLM20 (VLM GmbH, Leopoldshöhe, Germany) at 80 °C using the following recipe: 1.0 g of styrene, 2.0 g of deionized water, 10−50 mg of block copolymer dissolved in 2 g of 0.1 N NaOH, and 32 mg of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]. Poly-

Table 1. Structures and Molecular Characteristics of the Investigated Linear (Samples 1 and 2) and Star-Shaped (Samples 3 and 4) Polystyrene-*block*-poly(sodium DL-glutamate) Copolymers[a]

copolymer sample		M_n [g/mol]	w_G	x	z	y	z/y
	**1**	21300	0.74	52	104	1	104
	2	47500	0.87	57	274	1	274
	**3**	34300	0.78	63	176	8	22
	4	51900	0.85	63	293	8	37

[a] M_n = number-average molecular weight; w_G = weight fraction of sodium glutamate in the copolymer; x, z = number of styrene and glutamate repeat units, respectively; y = number of glutamate segments per polymer molecule (≡ amino functionality of the polystyrene macroinitiator); z/y = number of glutamate repeat units per segment.

merizations were run for at least 15 h to ensure complete monomer conversion. To investigate the influence of the block copolymers on the reaction rate profile, polymerizations have been carried out in a reaction calorimeter RM-2S (ChemiSens AB, Lund, Sweden) as described in detail elsewhere.[18] For these investigations, the above recipe was enlarged by a factor of 21.5. A comparison latex was prepared with sodium dodecyl sulfate (SDS) also in the presence of NaOH in order to keep the electrolyte concentration comparable.

Measurements. All samples were filtered prior to further characterizations. Hydrodynamic diameters of particles (d_H which corresponds to the intensity-weighted average particle size) in aqueous solution were determined from dynamic light scattering (DLS) measurements with a Particle Sizer Nicomp 370 (Santa Barbara, CA) operating with a He–Ne laser light source (λ = 632.8 nm) at a fixed scattering angle of 90°. Transmission electron microscopic (TEM) analyses on latexes yielding the core diameter of particles (d_{core}) were performed with a Zeiss EM 912 Omega operating at 120 kV. Samples were prepared by suspension preparation; i.e., a drop of the diluted latex was placed onto a carbon-coated copper grid, and the water was allowed slowly to evaporate. Particle size distributions were obtained by enumerating TEM pictures with a Opton TGZ 3 considering at least 500 particles. These data were used to calculate number- and weight-average particle diameters, d_n and d_{core}, respectively. The width of the particle size distributions was evaluated with the polydispersity index d_{core}/d_n. Solid contents of latexes were determined with an HR 73 halogen moisture analyzer (Mettler-Toledo, Giessen, Germany) operating at 150 °C.

To quantify the stabilizing ability of the stabilizers, efficiencies were calculated according to

$$E_{stab} = \frac{w}{s}\,\frac{sc}{100 - sc}\,\frac{6 \times 10^7}{\rho_p d_{core}}$$

where w and s are the amount of water and stabilizer (in grams), respectively, sc is the solids content, and ρ_p is the polymer density (=1.04 g/cm^3).[5] This quantity characterizes the total polystyrene particle surface area per mass unit stabilizer and is estimated from the solids content and the particle size of the final latexes. E_{stab} reflects the whole history of the polymerization including particle formation as well as possible instabilities occurring in the further course of the process such as due to the action of shear forces as the solids content increases. Note that the so-calculated efficiency is not a material constant but a good measure to characterize the performance of the stabilizer for a particular procedure, and hence one can only compare data which were obtained under identical reaction conditions.

The electrolyte stability of the latexes was determined by DLS of latex samples which were diluted with NaCl solutions of different concentrations. About 1 μL of the latex was diluted with 10 mL of a NaCl solution to get the necessary count rate for the DLS measurements. The salt concentration at which the particle size started to increase was considered as the critical coagulation concentration (ccc). By this procedure the first sign of a coagulation is detected including already the formation of dimers or trimers. Note, these measurements are much more sensitive than the visual inspection on a spotting plate whether or not a latex coagulates upon the addition of electrolytes.

Electrophoretic mobilities of the latexes were measured with a Malvern Zetasizer 3000 HS (Malvern Instruments Ltd., England) in dependence on the electrolyte concentration (10^{-5}–10^{-2} M KCl) and the pH (3–10) according to standard procedures. Before the measurements, the latexes were carefully dialyzed against distilled water to remove NaOH and residual monomer.

Results and Discussion

The molecular characteristics of amphiphilic polystyrene-*block*-poly(sodium DL-glutamate) copolymers, which we used as stabilizers in the heterophase polymerization of styrene, are listed in Table 1. Apart from two linear copolymers (**1** and **2**), we prepared two hetero multiarm star block copolymers (**3** and **4**) of similar composition with one polystyrene arm and eight poly(sodium DL-glutamate) arms in order to examine the impact of the polymer topology on latex properties. The polymer samples, which are all soluble in water due to their high polypeptide content (>70 wt %), exhibit virtually the same length of the polystyrene chain but differ in copolymer composition and thereby in the length of the polypeptide segments.

It was shown in former investigations[5a,b] that the stabilizing efficiency of polyelectrolyte block and statistical copolymers depends strongly on the ionic strength in the reaction medium. It turned out that water-soluble nonionic initiators result in a higher stabilizer efficiency compared to that of persulfates, for instance. In this study, the radical initiator of choice was the 2,2′-azobis-[2-methyl-*N*-(2-hydroxyethyl)propionamide], which is nonionic in nature and does not contribute to the stabilization of particles by initiator fragments.[19] The amount of added stabilizer was in the range of 1–5 wt % with respect to the monomer; the targeted solids content of the latex at full monomer conversion was 20%.

Table 2 summarizes the main characteristics of the obtained polystyrene latexes, namely solids content, average particle sizes, and polydispersity indices of particle size distributions. All polymerization runs

Table 2. Characteristics of the Latexes Obtained from the Aqueous Heterophase Polymerization of Styrene at 80 °C in the Presence of Different Amounts of Linear and Star-Shaped Polystyrene-*block*-poly(sodium DL-glutamate) Emulsifiers[a]

run	stabilizer	c_{stab} [%]	sc [%]	d_{H} [nm]	d_{core} [nm]	l_{corona} [nm]	PDI	E_{stab} [10^7 cm^2 g^{-1}]	N [10^{14} cm^{-3}]
1/1	**1**	1.1	17.5	153	144	5	1.01	3.061	1.08
1/2	**1**	3.1	20.3	116	79	19	1.03	2.377	2.97
1/3	**1**	4.7	21.8	99	76	12	1.03	1.784	5.23
2/1	**2**	1.0	14.8	214	194	10	1.01	2.047	0.32
2/2	**2**	3.1	21.3	141	121	10	1.02	1.649	1.76
2/3	**2**	4.9	19.7	132	107	13	1.02	1.070	1.94
3/1	**3**	1.0	18.6	131	125	3	1.16	4.178	1.85
3/2	**3**	3.9	22.2	76	62	4	1.22	2.697	11.8
3/3	**3**	4.9	21.7	74	68	3	1.23	1.901	12.4
4/1	**4**	1.0	19.3	130	123	4	1.14	4.444	1.98
4/2	**4**	3.0	18.2	91	61	(15)	1.18	2.779	5.37
4/3	**4**	5.0	18.5	88	92	(−4)	1.15	1.128	6.06

[a] c_{stab} = stabilizer concentration relative to the amount of monomer; sc = solids content; d_{H} = hydrodynamic diameter of dispersed latex particles (DLS); d_{core} = weight-average diameter of dried particles with a collapsed corona (TEM); $l_{\text{corona}} = (d_{\text{H}} - d_{\text{core}})/2$ = thickness of the polypeptide corona; PDI = polydispersity index (TEM); N = particle number calculated with d_{H}.

yielded stable latexes with a polymer content of ~20% and particles of 70−220 nm in diameter. As expected,[1] the hydrodynamic diameter of the particles decreases with increasing amount of the stabilizer; this is true for both the linear and branched stabilizers. However, a clear difference between both types of stabilizers exists with respect to the average particle size, the width of the particle size distribution, and the thickness of the corona. In general, the linear block copolymers lead to significantly larger particles (d_{H} = 100−220 nm) than the branched ones (70−130 nm), and this holds for both the hydrodynamic and the hard core diameter. Furthermore, the thickness of the stabilizer corona (l_{corona}) of linear and branched polypeptide chains is clearly different with 10−20 and 3−4 nm, respectively. Another striking difference between the linear and branched stabilizers is the particle size distribution of the latexes (see Figure 1). The linear copolymers result in virtually monodisperse particle size distributions (PDI < 1.04) whereas the star-shaped ones lead to considerably broadened or even bimodal particle size distributions (PDI > 1.1). Note that the PDI increases with increasing stabilizer concentration.

The broad particle size distributions of the latexes prepared with the branched stabilizers put the calculation of the corona thickness—which is based on the assumption of a monodisperse particle size distribution—in question, and thus such very low l_{corona} values might not reflect the real situation. This is in particular obvious for run 4/3 for which DLS and TEM data suggest a negative value of l_{corona}; i.e., either DLS or TEM (or both techniques) does not yield reasonable results. Note that a difference in the particle sizes determined with DLS and TEM of a few nanometers is typical for purely electrostatically stabilized systems.[20] Despite these shortcomings of the sizing techniques to calculate the corona thickness, the data are able to differentiate clearly between both types of surfactants. The linear hydrophilic blocks are stretched out into the aqueous phase whereas the branched hydrophilic blocks form a much more thinner but more compact corona.

The impact of the stabilizer shape on the particle size distribution might be due to a different stabilizing ability of the two types of amphiphilic polystyrene-*block*-poly(sodium DL-glutamate) copolymers. As illustrated in Chart 2, branched copolymers should be able to stabilize a larger particle surface than their linear analogues, especially at lower degrees of surface coverage. Note that the dependence of the average distance between two adsorbed chains scales for linear polymers with the inverse square root of the adsorbed amount;[21] this dependence might be much stronger for the branched copolymers due to an enhanced repulsion between the branched hydrophilic blocks. Indeed, this expectation is proved by the experimentally obtained stabilizer efficiencies which are summarized in Table 2. These data show that the efficiencies for the star-shaped stabilizers are higher than those for the linear copolymers and are, on a weight base, only by a factor of 2 lower compared to that of SDS (~6 × 10^7 cm^2 g^{-1} at 1 wt % stabilizer based on monomer). This means that, in this particular case, single molecules of **1**−**4** were able to stabilize hypothetical particles with diameters of about 5, 7, 8, and 10 nm, respectively, whereas a single SDS molecule would stabilize a particle with a diameter of just ~1 nm.

The very broad or even bimodal particle size distributions found for the branched stabilizers indicate either a second nucleation step to occur in the course of the polymerization or a much longer nucleation period compared to the linear stabilizers. Because of the same radical flux in all experiments (same temperature and initiator concentration), the most likely reason for the difference in the particle size distribution is the occurrence of a secondary nucleation step. It has to be pointed out that the new particle generation manifests in the final latex only if the stabilizer is efficient enough to stabilize both the newly formed particles and those of the older generation. If this stabilization is not possible, both generations will coalesce and form a "mixed" generation, which has a monomodal or even narrow, almost monodisperse size distribution. Again, compared to the linear copolymer stabilizers, the branched molecules are able to stabilize a larger particle surface due to the variable expanse of their hydrophilic groups in dependence on the degree of coverage (see Chart 2). This idea is proven by the fact that branched molecules can stabilize a larger surface area than linear stabilizer molecules. For instance, 353 molecules of the linear **2** stabilize an interface of 4.6 × 10^4 nm^2 (run 2/2) while 124 branched copolymer molecules **4** can stabilize almost the same area (4.8 × 10^4 nm^2, run 4/1). In addition, the higher stabilizer efficiency of the branched stabilizers finds its expression in a higher number of particles (N, see Table 2).

The impact of a hairy layer of linear stabilizer molecules on polymerization kinetics due to the influence of exchange processes between the continuous phase and the particles (radical exit and entry as well as monomer uptake) has been investigated,[22] but the

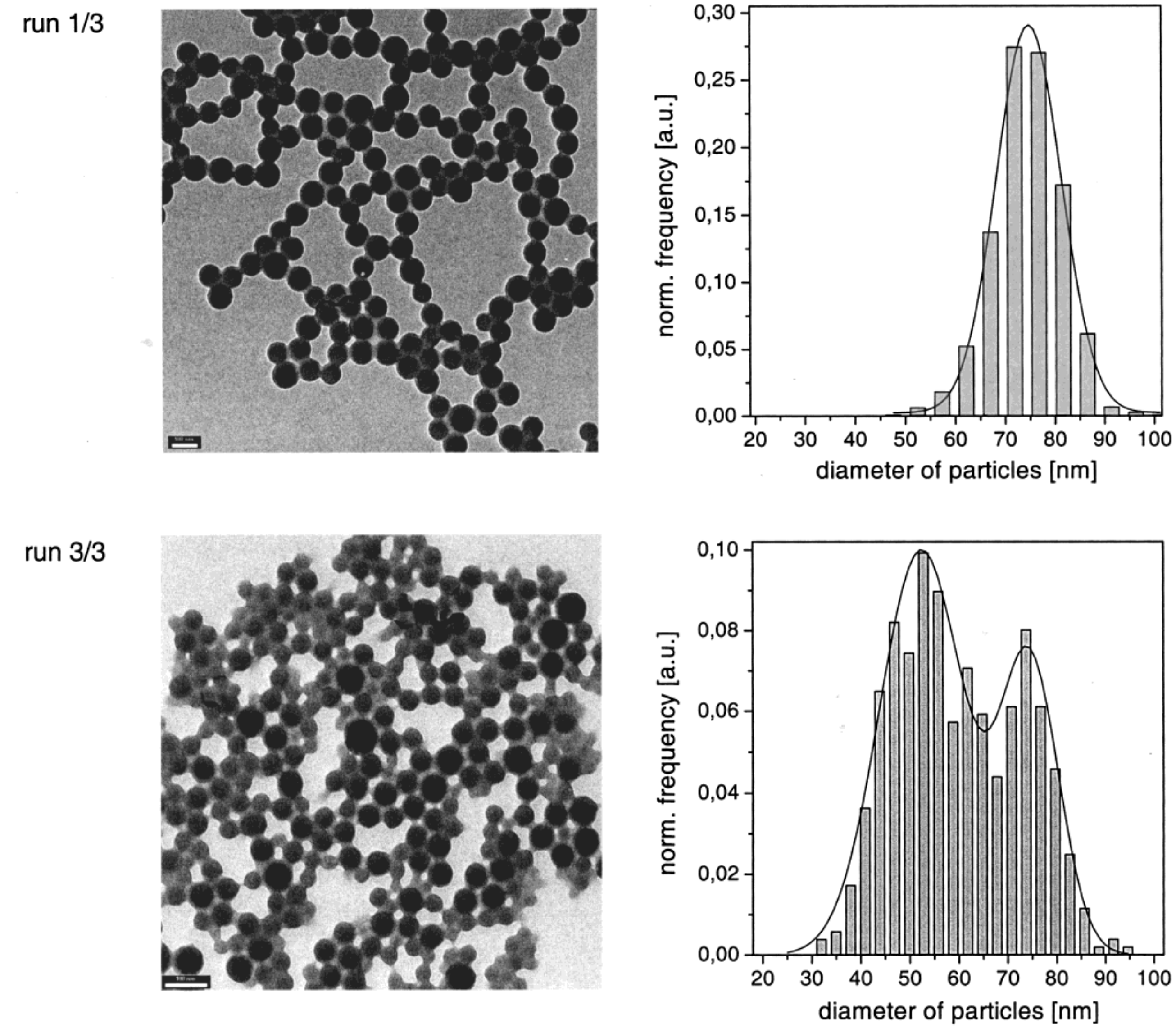


Figure 1. Typical TEM pictures (scale bar = 100 nm) and particle size distributions of latexes obtained in the presence of linear (above; run 1/3) and star-shaped polystyrene-*block*-poly(sodium DL-glutamate) stabilizers (below; run 3/3).

question arises: how does a more dense but thinner stabilizer layer (as verified for the branched copolymers) behave in comparison to the standard SDS system? A very useful and effective tool to answer this question is the on-line monitoring of the rate of polymerization by reaction calorimetry. Indeed, the heat flow curves (which are a direct measure of the heat developed during the polymerization and thus correspond directly to the rate of polymerization) depicted in Figure 2 reveal a huge difference between both stabilizer types. In the presence of SDS (curve A), the overall reaction is faster and the maximum reaction rate is higher than with the star-shaped stabilizer **3** (curve B). Moreover, the rate profiles are vastly different, and the most striking difference is the occurrence of a second rate maximum in the presence of **3** which can be assigned to a gel effect. In this context, a comparison with the reaction rate profiles obtained for linear poly(ethyl ethylene)-*block*-poly(styrenesulfonate) stabilizers[5a] (under otherwise identical conditions) is of special interest. A sample with 215 ethyl ethylene and 233 styrenesulfonate units (448 styrene units with degree of sulfonation of 52%), which forms a corona of 9 nm around particles, yields virtually the same profile as SDS; only the position of the rate maximum is slightly shifted from 7 to 15 min. A block copolymer with 44 ethyl ethylene and 448 styrenesulfonate units instead, which produces a much thicker corona of 60 nm, affords a drastic change in the rate profile (curve C in Figure 2), and the rate maximum occurs at about 90 min, i.e., when the polymerizations with the other stabilizers are already finished. However, the rate profile for **3** is just between these extreme cases which is attributed to the intermediate sized but more dense corona. These results demonstrate the drastic effect of the particular arrangement of the stabilizer layer on polymerization kinetics which is supposed to be mainly caused by influencing radical and monomer diffusion processes into the latex particles.

Another behavior of latexes which is strongly affected by the nature of the stabilizer and its arrangement is the stability against electrolytes. It is known that latexes stabilized with low molecular weight ionic surfactants like SDS are prone to coagulate if the ionic strength of the continuous phase is increased.[1] In contrast, latex particles stabilized with polyelectrolyte chains show an extraordinary stability against salt additives. It was both theoretically predicted[23] and experimentally verified[5b] that the critical coagulation

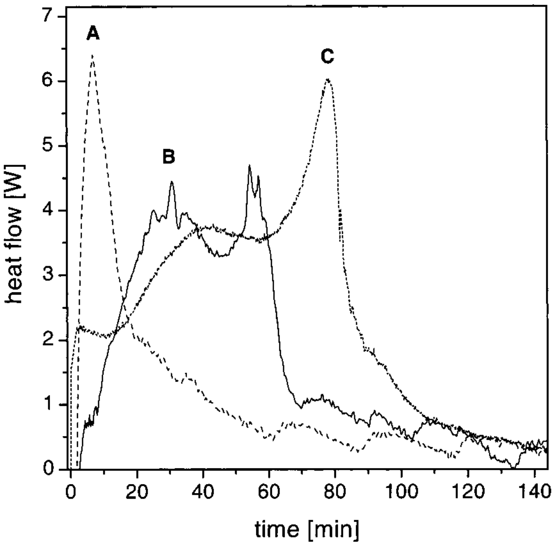


Figure 2. Reaction profiles of styrene emulsion polymerizations in the presence of SDS (A), the star-shaped polystyrene-*block*-poly(sodium DL-glutamate) stabilizer **3** (B), and a linear poly(ethyl ethylene)$_{44}$-*block*-poly(styrenesulfonate)$_{448}$ (C).

concentration, ccc, depends strongly on the thickness of the corona. For instance, polystyrene particles prepared with poly(ethyl ethylene)$_{44}$-*block*-poly(styrenesulfonate)$_{448}$ possess a ccc of about 6.0 M whereas a SDS–stabilized latex already coagulates at 0.03 M NaCl. Latex particles prepared with the stabilizers **1**–**4** show an intermediate ccc as it is revealed by the data depicted in Figure 3. In particular, latexes prepared with the linear and the star-shaped stabilizers coagulate at NaCl concentrations of about 1.0 and 0.2 M, respectively. These data indicate that at least the linear amphiphilic copolymers act as electrosteric stabilizers. It is interesting to note that the branched stabilizers lead to a ccc which is about one order of magnitude higher than that of SDS although the corona thickness is almost the same—this can be considered as a consequence of the more dense and compact stabilizer layer compared to SDS. However, in both cases, the ccc against NaCl is higher than the normal saline (0.155 M), which makes these latexes with a biocompatible shell interesting for potential therapeutic or diagnostic applications.

Besides polymerization kinetics and colloidal stability, the stabilizer determines as well the electrophoretic mobility of the colloidal particles. The mobility of charged colloidal particles in an electric field mainly depends on the charge density ($\rho_\pm$), the effective particle size (d_eff), and the electrolyte concentration in the continuous phase. Depending on the concentration of the electrolyte, the electropohoretic mobility of electrostatically stabilized polystyrene particles was shown to go through a maximum before the expected decrease occurs at higher electrolyte concentrations.[24] A maximum was also observed for particles whose surface charges were surrounded by a hydrophilic polymer layer of glycidyl methacrylate that enlarges the distance of the shear plane from the hard core surface and thus d_eff. However, in the case of the electrosterically stabilized particles with poly(ethyl ethylene)$_{44}$-*block*-poly(styrenesulfonate)$_{448}$, the electrophoretic mobility hardly showed a maximum and decreased at salt concentrations above 0.1 M KCl.[25] Moreover, the mobility of these particles (d_H = 294 nm, $\rho_\pm$ = 159 μC cm^{-2}) remained at a rather low level of ~3.5 μm s^{-1} cm V^{-1} in the examined KCl concentration range compared to purely electrostatically stabilized particles (d_H = 31 nm, $\rho_\pm$ = 6.1 μC cm^{-2}) with a maximum mobility of ~6.5 μm s^{-1} cm V^{-1}. As can be seen in Figure 4, the mobility of particles with a poly(sodium DL-glutamate) stabilizing layer **3** exhibits the characteristics of a electrosterically stabilized particle. Note, the mobility is only slightly decreasing at KCl concentrations below 0.01 M, but the decrease is much steeper for higher electrolyte concentrations.

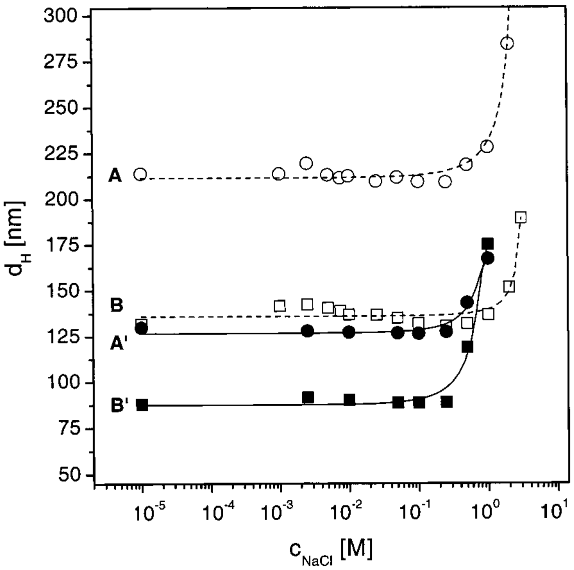


Figure 3. Influence of NaCl on the hydrodynamic size of particles (d_H) being stabilized with the linear copolymer **2** (A, 1 wt %; A′, 5 wt %) and the star-shaped copolymer **4** (B, 1 wt %; B′, 5 wt %) (lines are just for guiding the eye).

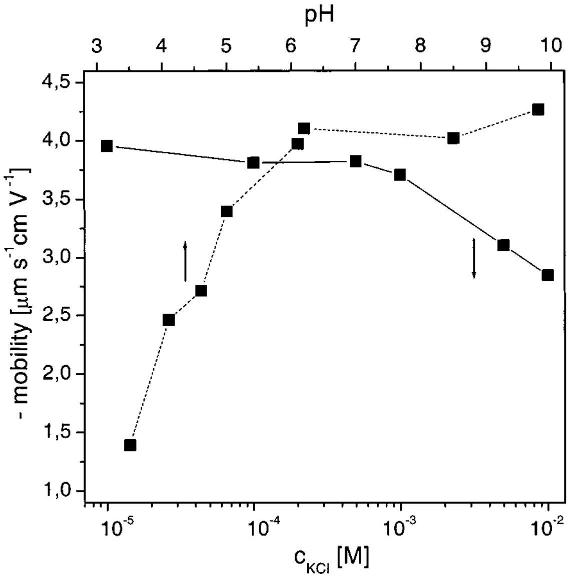


Figure 4. Dependence of the electrophoretic mobility of polystyrene particles stabilized with the star-shaped polystyrene-*block*-poly(DL-glutamate) copolymer **3** on KCl concentration and pH (lines are just for guiding the eye).

In the particular case of the particles stabilized with **1**–**4**, the mobility is also expected to change with the pH, which goes back to the pH-dependent degree of ionization of the polyglutamate segment and thus the changing charge density of the particles. Indeed, the data shown in Figure 4 prove a strong dependence of the electrophoretic mobility on the pH. (The behavior is exemplary shown for the branched stabilizer **3**, but the linear stabilizers behave qualitatively in a very similar way.) Increasing the pH from 3 to 10 causes a strong increase in the electrophoretic mobility up to pH ~6 followed by an almost constant mobility at higher pH values. Since the particle size (d_H) was found to remain constant within experimental errors, the strong increase in the mobility should be caused by an increasing charge density of the particles with increasing pH.

Again, like the results of reaction calorimetry (cf. Figure 2) and of ccc investigations (cf. Figure 3), the electrophoretic mobility data for polyglutamate stabilized latexes indicate that these latexes possess properties in between both purely electrostatically and purely electrosterically stabilized systems.

Conclusions

In conclusion, polymeric particles with polyglutamate stabilizing moieties are accessible by emulsion polymerization with amphiphilic polystyrene-*block*-poly(sodium DL-glutamate)s and nonionic water-soluble azoinitiators. The topology of the polyelectrolyte shell, which can be composed of either linear or branched polyglutamate blocks, was found to affect considerably the properties of the latexes. The particle size and the particle size distribution can be varied over a wide range (d_H = 70−220 nm, PDI = 1.01−1.23) and depends strongly on the topology of the polyglutamate block; linear copolymers usually yield larger particles with a low polydispersity. However, the stabilizing ability of the branched stabilizers during heterophase polymerization is much higher than that of the linear analogues. These stabilizers are able to change the stabilizing area of the hydrophilic block in dependence of the degree of coverage of the surface, and this area is higher at lower stabilizer concentrations. The branched block copolymers are thus able to stabilize a second particle generation which leads to a bimodal particle size distribution at higher concentrations. In contrast, the linear stabilizers support the formation of monodisperse particle size distributions. Furthermore, these latexes possess a ccc of 1.0 M NaCl, which is clearly above that of the branched stabilizers of 0.2 M, thus indicating the onset of the behavior typical for electrosteric stabilization.

Acknowledgment. We thank Markus Antonietti, Ines Below, Marlies Gräwert, Viktor Khrenov, Olaf Niemeyer, and Heidemarie Zastrow for their valuable contributions to this work. Financial support was given by the Max-Planck-Gesellschaft.

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MA011606Q