Polyelectrolyte Block Copolymers as Effective Stabilizers in Emulsion Polymerization

Harmin Müller, Walter Leube, Klaus Tauer,* Stephan Förster, and Markus Antonietti

Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Kantstrasse 55, D-14513 Teltow-Seehof, Germany

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ABSTRACT: Amphiphilic block copolymers consisting of a hydrophobic block of hydrogenated polybutadiene and a partly sulfonated polyelectrolyte block of poly(styrenesulfonate) are effective stabilizers in emulsion polymerization. At low relative amounts of block copolymer (0.4 wt % as a fraction of monomer weight) and salt-free conditions, well-defined and stable latices with particle diameters of ca. 100 nm and solid contents of 20 wt % are obtained. This high stabilization efficiency of optimized block copolymer systems enables the formulation of latex systems with a relatively low remaining polarity in solid films and offers new interesting model systems with exclusively electrosteric stabilization. A comparison of polymerization in high or low ionic strength solution and the variation of the degree of sulfonation of the poly(styrenesulfonate) block shows an optimum stabilization of the latices at low ionic strength during polymerization. Fully sulfonated polymers systems presumably show a molecular orientation perpendicular to the particle surface, whereas 50% sulfonated species take on a traillike conformation along the surface, which is explained by remaining hydrophobic interactions. Due to this multiple surface particle contacts, the application of partly sulfonated polymers leads to more effective stabilization. At higher stabilizer concentrations, aggregates are found, which can be redispersed by ultrasonification or addition of low molecular weight surfactant solution.

Introduction

Emulsion polymerization gains increasing importance, since it enables the formulation of a fluid containing high weight amounts of polymer with low viscosity, based on water as an environmentally friendly dispersion agent. The resulting polymer dispersions are directly used for a number of applications, i.e. water-based coatings, manufacturing of fabrics, or glues.[1] In many of these applications, however, the water-born nature of these products is connected with inherent weaknesses, since polar initiator fragments, comonomers, and the surfactants remain in the formed solid polymer film and result for instance in a relatively high water uptake and a low block resistance. A mechanism which intensifies this negative influence is the migration of low molecular weight components and their enrichment into the interstitial volume between the particles due to capillary pressure of the drying film.[2] For those reasons, so-called surfactant free dispersions are applied, the most of which contain—beside of the standard hydrophobic monomers—noticeable amounts of acrylic acid and highly polar initiators.[3] Another possible way is the application of reactive surfactants.[4]

In the present paper, a somewhat different approach is applied: we want to use polymeric stabilizers in the emulsion polymerization. It is known already for a long time that nonionic di- and triblock copolymers are effective stabilizers in heterophase polymerization.[5,6] Amphiphilic nonionic block copolymers with rather short block lengths consisting of poly(ethylene glycol) as the hydrophilic block play an important role in many technical emulsion polymerizations. In this contribution, block copolymers with one strong ionic block are investigated as stabilizers in emulsion polymerization.

Since the beginning of the 80s experimental and theoretical investigations have been carried out concerning the association behavior of amphiphilic ionic block copolymers in aqueous solutions in dependence on block lengths and ionic strength. Selb and Gallot investigated polystyrene-*b*-poly(4-vinyl-*N*-ethylpyridinium bromide).[7−10] Valint and Bock reported on poly(*tert*-butylstyrene)-b-poly(styrenesulfonate).[11] Eisenberg reported in a series of papers on the micellization behavior of polystyrene-b-poly(sodium acrylate).[12−14] Munk, Webber, and Tuzar et al. looked at the aggregation behavior of block copolymers,[15,16] for example poly(*tert*-butyl acrylate)-*b*-poly(2-vinylpyridine) in acidic water.[17] As the combination of an uncharged hydrophobic block with a charged hydrophilic block in one molecule exhibits some unusual association behavior, these structures are also a matter of intensive theoretical considerations.[18−21]

Looking at all these activities over the last nearly 20 years it is surprising that only one systematic investigation of block copolymers with one strong ionic block as stabilizer in emulsion polymerization exists in the open literature. Leemans et al. used poly(alkyl methacrylate)-*b*-poly(sulfonated glycidyl methacrylate) as stabilizer in the emulsion polymerization of alkyl acrylates.[22]

Examinations of micelles of polyelectrolyte block copolymers have shown that polyelectrolyte block copolymers in comparison to low molecular weight surfactants require at interfaces with high interface energy rather large surface areas.[23] This might be translated into a rather high stabilization efficiency, for instance in emulsion polymerization.

The aim of this contribution is to report on the behavior of poly(ethylethylene)-*b*-poly(styrenesulfonate) as stabilizer for emulsion polymerization. The motivation for these investigations is 4-fold. First, it is possible to prepare exclusively electrosterically stabilized polymer dispersions. Second, the rate of migration of that stabilizers in the final polymer product (film or bulk material) is expected to be much lower than that for common low molecular weight emulsifiers, and it should be possible to overcome technological drawbacks of the latter.[2] Third, one can expect in films or in bulk

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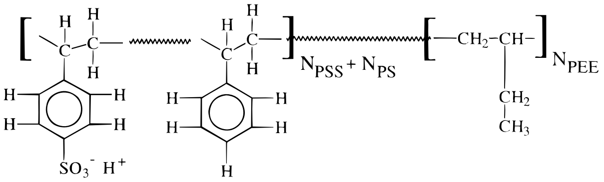


Figure 1. Structure of poly(styrenesulfonate)-*b*-poly(ethylethylene) block copolymer.

materials made of these dispersions that microphase separation would occur which would keep the polar entities even dispersed inside a continuous, nonpolar volume phase. Fourth, if the architecture of the block copolymers is tailored in a proper way, it was argued that the polyelectrolyte blocks are more effective in interface stabilization than common low molecular weight surfactants.

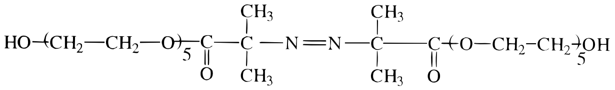
Experimental Section

Materials. Deionized water (18 MΩ cm^{-1}) was received from a REWA HQ 5 system and was degassed. Styrene (Aldrich) was purified by distillation at 60 °C. 1,3-diisopropenyl benzene (Aldrich) and potassium persulfate (Fluka) were used as received.

Block Copolymer Synthesis. The block copolymers were prepared by anionic sequential polymerization of styrene and butadiene (1,2-polymerization) followed by hydrogenation of the remaining double bonds of the butadiene block and subsequent sulfonation of the styrene block. The polydispersity of the precursor polymer polystyrene-*b*-poly(ethylethylene) (M_w/M_n) is less than 1.03. If the degree of sulfonation is less than 100 % the poly(styrenesulfonate) block is a random copolymer of styrene and styrenesulfonate. The completely sulfonated product (1-H100) was synthesized according to a procedure described by Vink.[24] This procedure is very mild and does not lead to a chain scission. The maintenance of the degree of polymerization during the sulfonation of homo polystyrene is confirmed by gel permeation chromatography (GPC) although a slight increase in the breadth of the molecular weight distribution is observed.[25] The aqueous GPC was carried out with HEMABIO columns (Polymer Standard Service, Mainz, Germany) with 40, 100, 300, and 1000 Å pore size. The elution agent was water with 20% methanol and 0.125 M sodium nitrate to ensure the elution of the fully sulfonated polystyrene. Due to the amphiphilic character of the 1-H100 block copolymer the aqueous GPC is in this case more complicated. Adsorption at the column material leads to a delayed elution as well as to a peak broadening. The adsorption of the partly sulfonated block copolymer 1-H52 is so strong that it sticks at the column and is not eluted. The same is true for a partly (57%) sulfonated homopolystyrene (sample S1) with a molecular weight of 10^5 g mol^{-1} before sulfonation. The partly sulfonated products were prepared according to a procedure described by Thaler.[26] A general structure of these block copolymers is shown in Figure 1. The structure and composition is verified by ^{1}H-NMR spectroscopy in D_2O with a Varian Unity 400 spectrometer operating at 400 MHz. In case of the fully sulfonated material only two signals with equal intensity in the range between 6 and 8 ppm are visible. The degree of sulfonation of the other products was estimated from the signal ratios of the polystyrene protons and the poly(styrenesulfonate) protons between 6 ppm and 8 ppm. Table 1 summarizes the composition of the block copolymers used. A more detailed description of the synthesis and the characterization of the block copolymers will be published in a subsequent paper.[27]

Emulsion Polymerization. In order to investigate the stabilizing capability of the block copolymers a symmetrical, nonionic poly(ethylene glycol)−azo initiator PEGA200 with five ethylene glycol units on each side of the azo group (cf. Figure 2) was synthesized and employed.[28,29]

Surfactant free emulsion polymerizations in water with PEGA200 alone do not lead to latices but to complete coagulum formation proving that this initiator does not contribute to latex stability as for instance potassium persulfate (KPS). The reason to use PEGA200 instead of the well-known 2,2′-azobisisobutyronitrile (AIBN) is the fact that much less coagulum is formed with PEGA, as known from standard emulsion polymerizations with surfactant.



$HO{-}(CH_2{-}CH_2{-}O)_5{-}C(=O){-}C(CH_3)_2{-}N{=}N{-}C(CH_3)_2{-}C(=O){-}(O{-}CH_2{-}CH_2)_5{-}OH$

Figure 2. Structure of the initiator PEGA200.

Table 1. Structure and Chemical Composition of Block Copolymers[a]

stabilizer	N_{PS}	N_{PSS}	N_{PEE}	S
1-H52	215	233	42	0.52
1-H100	0	448	42	1.00

[a] Key: N_{PSS}, number of poly(styrenesulfonate) units; N_{PS}, number of polystyrene units; N_{PEE}, number of polyethylethylene units; S, degree of sulfonation of the polystyrene block.

All emulsion polymerizations were carried out batchwise in either a glass reactor or a reaction calorimeter RM2-S (Chemisens, Lund, Sweden) with a stainless steel reaction vessel. The glass reactor has a volume of 100 mL and a heating jacket to control temperature. It is equipped with a baffle stirrer, a reflux-cooler, and a valve on the bottom to remove the latex and is flushed with nitrogen. Polymerizations were performed as follows: a solution of the appropriate amount of block copolymer in 30 mL of water, 10 g of styrene, 0.20 g of 1,3-diisopropenylbenzene as cross-linker, and 0.31 g PEGA200 dispersed in 10 g of water were filled in the reactor and purged with nitrogen gas under stirring for 30 min to emulsify the reaction mixture. Then the emulsion was heated to 82 °C within 2 min.

For polymerizations in the calorimeter the amounts of styrene, water, PEGA200, and cross-linker had to be increased by a factor of 1.5 to ensure proper data acquisition. The block copolymer solution was filled in the calorimeter reactor followed by equilibration at reaction temperature. After calibration the monomer plus cross-linker was added, and when the temperature had reached the reaction temperature again, initiator suspended in 5 mL of water was injected to start the polymerization.

After the polymerization had been finished (6 h in case of the glass reactor and until the end of heat production in case of the calorimeter), the reaction mixture was slowly cooled down to room temperature and the dispersion passed through a glass filter to remove the coagulum. The polymer dispersions were stored in a refrigerator until further use.

Latex Characterization. The latices were characterized with respect to solid content, amount of coagulum, particle size, and stability against electrolytes (cf. Table 2). The amount of coagulum is calculated from the difference between solid content of the final latex and the theoretical solid content. Calorimeter experiments show that the conversion is generally very close to 100%.

The particle size of the final latices were analyzed by dynamic light scattering (DLS, NICOMP particle sizer with a fixed scattering angle of 90°), capillary hydrodynamic chromatography (CHDF, MATEC, eluat: nonionic surfactant solution 1X GR500) and transmission electron microscopy (TEM, either a TESLA BS 500 transmission electron microscope or a Zeiss EM 912 Omega). The filtered latices (Millipore filter) were diluted between 100 and 500 times with either deionized water or with the CHDF eluate to obtain appropriate concentrations for each method.

Results and Discussion

For all following experiments, two different block copolymers having the same chain length, but different degrees of sulfonation, were applied. Both amphiphiles arise from the same parental polystyrene-*b*-polybutadiene block-copolymer, where the polybutadiene chain

Table 2. Results of Latex Synthesis[a]

latex	BS (g)	*T* (%)	SC (%)	CG (%)	D_i (nm)	PD	remark
R01C	0.022	0.147	1.56	98.0	219	0.25	instability
R02C[b]	0.060	0.400	17.9	13.6	94.2	0.18	colloidal
R03C	0.079	0.527	17.0	19.3	116	0.36	stability
R04G	0.100	0.996	19.5	7.4	75.4	0.37	
R05C[b]	0.153	1.02	18.5	11.0	78.5	0.29	
R06C	0.154	1.03	18.4	12.9	85.4	0.42	
R07C	0.379	2.53	17.4	18.9	105	0.36	
R08G	0.506	5.06	21.6	0.0	115	0.47	
R09G[b]	0.507	5.07	21.3	0.0	121	0.47	
R10C[b]	0.750	5.00	20.3	5.0	129	0.53	
R11G	0.830	8.30	21.8	1.5	344	0.63	limited
R12G	0.837	8.40	21.7	2.0	336	0.62	aggregation
R13G	1.013	10.1	22.3	0.5	474	0.57	

[a] Key: BS, block copolymer stabilizer 1-H52; *T*, block copolymer weight as a fraction of monomer weight; SC, solid content of the final latex; CG, coagulum wt % of polymer; D_i, hydrodynamic diameter from DLS without special treatment; PD, polydispersity. In the latex code, C refers to polymerization in the calorimeter (15 g styrene) and G to the glass reactor (10 g styrene). [b] Without cross-linker.

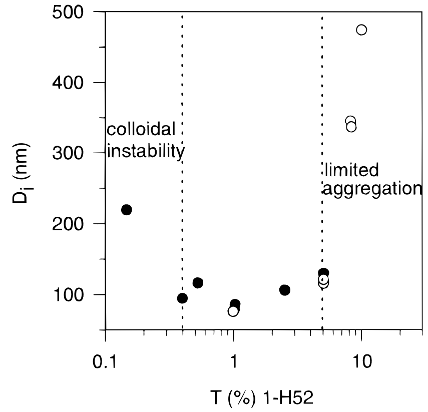


Figure 3. Apparent average latex particle size D_i (DLS) as a function of block copolymer concentration (1-H52) as a fraction of monomer weight *T*, (●) calorimeter (steel reactor); (○) glass reactor experiments.

length is ca. 10 mol % of the whole chain (see Table 1). 1-H52 exhibits a degree of sulfonation of 52%, whereas 1-H100 shows a sulfonation of the styrene units of 100%.

The application of 1-H52 as stabilizer in emulsion polymerization leads to some surprising results. Figure 3 shows the mean hydrodynamic diameter D_i from dynamic light scattering as a function of the amount of block copolymer 1-H52 relative to styrene, *T*.

In a range of about 0.4−5 wt %, the particle size is almost constant or slightly increases with the amount of block copolymer; in this range, the polydispersity constantly increases with amount of amphiphile. At $T > 5$ wt %, the particle size and polydispersity increases rapidly. This is apparently the opposite behavior to the one of common low molecular weight surfactants in a classical emulsion polymerization[30] as well as nonionic block copolymers either with potassium persulfate as initiator[31] or with PEGA200.[32]

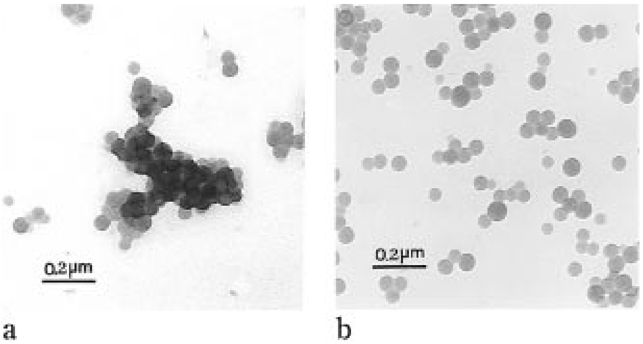


Figure 4. TEM micrographs showing the separate particles of the flocks in the case of latex R13G (a) and latex R04G (b).

On the other hand, coagulum formation during polymerization shows the expected behavior, i.e. the lower the stabilizer concentration the higher the amount of coagulum (Table 2). The lowest 1-H52 concentration ($T = 0.147$ wt %) clearly deviates from the colloidal stable region where 98 wt % of the polymer material coagulates.

The increase of the average particle size with increasing stabilizer concentration is not a result of colloidal instability as the amount of coagulum is decreasing or even vanishing. That this phenomenon is caused by the use of this special kind of stabilizer is revealed by TEM micrographs. Figure 4a shows that a high amount of stabilizer (R13G, $T = 10.1$ wt %) leads to the formation of flocks with a size in the micrometer range which consist of separate small particles. A stabilizer concentration of around 5 wt % (R08G) leads to a much smaller number of flocks of much smaller size, and at 1 wt % there are almost no flocks present. In this case the particles are clearly separated, Figure 4b. The individual particles of all three latices have a similar size.

Looking closer at the flocks it seems that these particles are only stuck together but did not grow together. Although they do not separate after dilution with deionized water, redispersion by ultrasonification of the diluted latex or by dilution with a nonionic surfactant solution (e.g. with the CHDF eluate) even without ultrasonification is successful.

Table 3 summarizes the results of the particle size measurements of latex R13G with different techniques after different pre-treatments. These measurements clearly indicate that the flocks can be redispersed.

All results described so far have been obtained in practically salt-free conditions. (Salt-free means that there was no addition of salt and there were no ionic groups in the system except the sulfonate groups with their counterions.) We expect that the situation completely changes if the polymerization is carried out in an aqueous phase of higher ionic strength. Two possibilities to achieve higher ionic strengths are applied: the addition of an inert salt to the monomer emulsion or the use of potassium persulfate (KPS) as the initiator instead of PEGA200. In the latter case, we have to

Table 3. Particle Size Analysis of Latex R13G with Different Techniques and Pretreatments[a]

method	D_i (nm)/PD	D_w (nm)/PD	D_n (nm)/PD	sample preparation
DLS	474/0.57			diluted with deionized water
DLS	152/0.66			diluted with deionized water & ultrasonification
DLS	158/0.39			diluted with CHDF eluat
CHDF		112/0.56		sample is injected into CHDF eluat stream
TEM			61.3/0.31	diluted with deionized water

[a] Key: D_i, hydrodynamic diameter from DLS, D_w, hydrodynamic diameter from CHDF, D_n, TEM diameter, PD, polydispersity.

Table 4. Influence of Ionic Strength on Latex Properties[a]

latex	T (%) 1-H52	CG (%)	D_i (nm)	D_i^{US} (nm)	electrolyte
R04G	1.0	7.4	75.4	73.0	no additional electrolyte
R04G-K	1.0	10.6	1100	940	initiator: 19.1 mM KPS
R04G-S	1.0	69.0	440	440	100 mM sodium chloride
R13G	10.1	0.5	470	152	no additional electrolyte
R13G-K	10.1	69.5	350	240	initiator: 19.4 mM KPS
R13G-S	10.1	9.7	720	218	100 mM sodium chloride

[a] Key: T, block copolymer/monomer, CG, coagulum, D_i, D_i^{US} hydrodynamic diameter from dynamic light scattering before and after ultrasonification. In the latex code, K refers to KPS as initiator; S refers to polymerization in presence of sodium chloride.

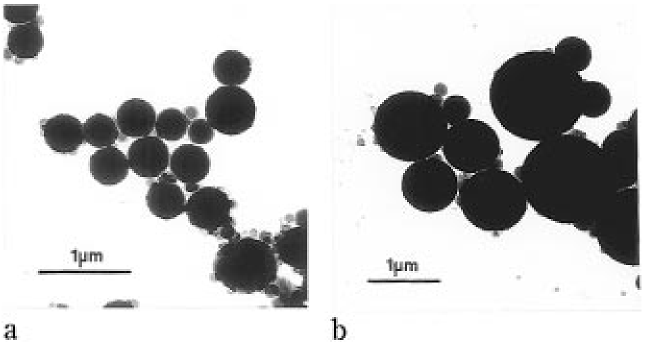


Figure 5. TEM micrographs showing the infuence of electrolyte: (a) R04G-S, 100 mM sodium chloride; (b) R04G-K 19.4 mM potassium persulfate.

expect an additional electrostatic stabilization by sulfate groups from the initiator.

The results of polymerizations with a low stabilizer concentration summarized in Table 4 show that in both cases (R04G-K, R04G-S) a large amount of coagulum and big particles are formed. The resulting particles are depicted in Figure 5; in both samples particles with a diameter of around 1μm together with some small particles are present.

This result has to be expected, since the increase in ionic strength leads to a screening of the electrostatic fields between the protruding polyelectrolyte chains; the density of charged domains is increased, and the stabilization efficiency is lowered. The increase of the amount of coagulum and the mean particle size clearly reflects the sensitivity of the electrosteric stabilization at low grafting densities against salt. It is interesting to note that all latices coagulate if a 1 M sodium chloride solution is added after polymerization.

At higher block copolymer concentrations the dependence of the particle size after ultrasonification D_i^{US} on ionic strength of the solution is less pronounced. Within the framework of electrostatics this reflects the fact that higher amounts of polyelectrolyte block copolymer at constant particle size increase the local charge density in the formed polyelectrolyte shell to such high values that additional salt has only minor influence.

The limited aggregation of the latex particles caused by the block copolymer 1-H52 applied in amounts higher than 5 wt % can be speculatively explained following this route. At low ionic strength of the aqueous phase and at low polyelectrolyte load, the repulsion between the (partially) charged blocks as well as between the latex particles is high. Since the ionic groups of the poly(styrenesulfonate) block (degree of sulfonation is 52%) are distributed statistically, it is very likely that there are some hydrophobic domains present. In this case, we expect the block copolymer to be adsorbed not only with the poly(ethylethylene) block but also with these hydrophobic moieties leading to multiple adsorption points per molecule on a particle and charged loops into the water phase. Increasing the polyelectrolyte block copolymer concentration in the interface results in a screening of the Coulomb interaction until the elctrostatic interaction is less extended than the distance between the different hydrophobic domains of the block copolymers. Exceeding this critical value, each chain can adsorb onto several latex particles leading to limited aggregation through interparticular bridging which depends on the block copolymer as well as on the latex concentration. The formation of flocks at higher block copolymer concentration is also enhanced by hydrophobic interaction of those non-sulfonated domains which are not adsorbed or of the hydrophobic backbone of the polyelectrolyte block. Figure 6 schematically illustrates this stabilization and controlled aggregation mechanism.

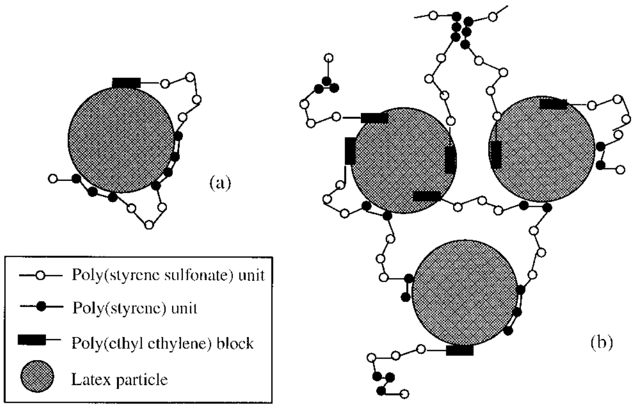


Figure 6. Illustration of the adsorption behavior of the block copolymer 1-H52, (a) block copolymer concentration up to 5 wt %, (b) block copolymer concentration above 5 wt % (limited coagulation).

Table 5. Influence of the Degree of Sulfonation on Latex Properties[a]

latex	stabilizer/T (%)	CG (%)	D_i (nm)/PD	D_i^{US} (nm)/PD	D_n^{EM} (nm)/PD
R04G	1-H52/1.0	7.4	75.5/0.37	73.0/0.36	52.7/0.21
R07C	1-H52/2.5	17.9	105/0.36	103/0.33	67.2/0.26
R08G	1-H52/5.1	4.6	115/0.47	98.3/0.46	55.0/0.21
R13G	1-H52/10.1	0.5	474/0.57	152/0.66	61.3/0.31
R14G	1-H100/2.6	21.2	323/0.29	281/0.22	187/0.19
R15G	1-H100/5.1	19.9	294/0.36	292/0.37	146/0.21
R16G	1-H100/10.1	0.5	491/0.33	341/0.45	111/0.10

[a] Key: T, block copolymer/monomer; CG, coagulum, D_i, hydrodynamic diameter from DLS, before and after ultrasonification; D_n, TEM diameter; PD, polydispersity.

Following this model, a completely sulfonated block copolymer like 1-H100 is expected to be a less effective stabilizer than the block copolymer 1-H52, but should be less afflicted with the problem of partial bridging. The data of the corresponding experiments are listed in Table 5.

Indeed, more coagulum and bigger particles are observed when 2.6 wt % of the block copolymer 1-H100 are used. The resulting particles are however rather monodisperse, as shown in Figure 7. At higher concentrations (T = 5−10 wt %), 1-H100 and 1-H52 behave similar with respect to the amount of formed coagulum, but the particle size taken from TEM is systematically larger for 1-H100 as compared to 1-H52. In addition, 1-H100 shows the normal dependence of the particle size on emulsifier concentration; i.e., the particle size decreases with increasing concentration. All these data

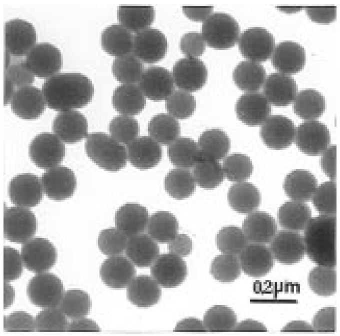


Figure 7. TEM micrograph of R15G with stabilizer 1-H100.

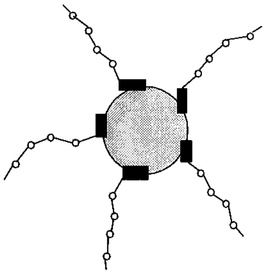


Figure 8. Illustration of the assumed adsorption behavior of the block copolymer 1-H100: hairy layer with nearly stretched ionic blocks.

and relations support the model of a multipodal adsorption of the partly sulfonated chains.

It is seen from Table 5 that there are marked differences between the dynamic light-scattering data (hydrodynamic diameter) and the electron microscopy (hard core diameter). Since the polydispersities of the ultrasonificated latices are comparable low, we can exclude particle aggregation to be responsible for this phenomenon (although a partial influence cannot be excluded). The differences of 43 nm for the latex R08G (stabilizer 1-H52) and 148 nm for the latex R15G (stabilizer 1-H100) are presumably related to the thicknesses of the stabilizer shells which is hydrodynamically active, but not seen in electron microscopy. For 1-H100, we end up with a shell thickness of 74 nm, as compared to the length of the fully extended zigzag shape of the poly(styrenesulfonate) block of 113 nm. This corresponds to a remarkably stretched conformation of these chains perpendicular to the particle surface, sketched in Figure 8. Similar stretching ratios are however well known from block copolymer micelles[23,33,34] and are expected to be even bigger for the polyelectrolyte situation. The thickness of the shell of 1-H52 is calculated to be 21.5 nm, which goes well with the multipodal adsorption depicted in Figure 6.

The difference in particle size of latex R16G before and after ultrasonification shows that a small bridging effect is existing if a very high amount of 1-H100 (10 wt %) is used. This could be caused by the hydrophobic backbone of the block copolymer.

From the hard core diameter and amount of polyelectrolyte block copolymer used, we are able to calculate the area stabilized per gram polymer, A_{BC}, assuming that the polymers are equally distributed and located at the particle−water interface. For better illustration, we also calculate the number of block copolymers per particle, N_P. These data are presented in Table 6.

As expected and related to the electrostatic screening, A_{BC} depends on polyelectrolyte block concentration, but exhibits enormously large values of 10 000 − 520 m^2/g. Transferred to molecular area requirement per block copolymer molecule, each polymer stabilize at the lowest concentration an area of 32 × 32 nm! It also becomes apparent that 1-H52 stabilizes under similar conditions a significantly larger area than 1-H100, which again goes well with the postulated different adsorption mechanism. The partly sulfonated block copolymers with their multipodal adsorption depicted in Figure 6 represent a very efficient stabilizer, as the area that is stabilized per stabilizer molecule is large compared to other stabilizers. Nonionic amphiphilic block copolymers are much less effective stabilizers in emulsion polymerization.[31,32]

Table 6. Stabilizing Properties of 1-H52 and 1-H100 (Values Calculated from D_n^{EM}, All Block Copolymers Assumed To Be Adsorbed at the Interface of Particles)[a]

latex	stabilizer	T (%)	N_P	A_{BC} (m^2 g^{-1})	a_C (nm^2)
R04G	1-H52	1.0	8	10300	1160
R07C	1-H52	2.5	45	2800	310
R08G	1-H52	5.1	43	2000	220
R13G	1-H52	10.1	110	940	110
R14C	1-H100	2.6	820	940	130
R15G	1-H100	5.1	770	620	87
R16G	1-H100	10.1	530	520	73

[a] T, block copolymer/monomer; N_P, number of stabilizer molecules per particle; A_{BC}, particle interface per gram stabilizer; a_C, formal area occupied by one stabilizer chain on a particle.

As the synthesis of block copolymers containing an ionic block is always a time consuming and costly affair the search for alternatives that preserve the advantages seems to be a rewarding task. Indeed, the sequential anionic polymerization can be avoided if instead of the block copolymer (1-H52) an only partly sulfonated polystyrene is used. Such a statistical styrene-styrenesulfonate-copolymer with a degree of sulfonation of 57% (sample S1) leads at $T = 1$ % to a stable latex with an average particle size of $D_i = 81$ nm. This value corresponds exactly to those obtained for the runs R04G, R05C, and R06C, respectively (cf. Table 2). In addition, this result confirms also, however via another way than using other block copolymers with different degrees of sulfonation, the different adsorption modes for completely and partly sulfonated block copolymers shown in Figures 6 and 8, respectively. Furthermore, the GPC results (cf. Experimental Section) give evidence for a stronger adsorption of the partly sulfonated polystyrene samples 1-H52 as well as S1 compared to 1-H100 block copolymer.

Conclusions and Outlook

In this report we investigated the application of block copolymers with one charged block as stabilizers in emulsion polymerization. It turned out that the stabilizing properties of these polyelectrolyte block copolymers strongly depend on the ionic strength and the architecture of the charged block. The lower the ionic strength the better is the ability of the block copolymer to stabilize latex particles. This has to be expected, since the equilibrium surface density of the protruding polyelectrolyte chains depends on the electrostatic screening length. The application of KPS as initiator leads to formation of large amounts of coagulum and very large particles, while the use of the nonionic PEGA200 initiator leads to much less coagulum and small particles of about 100 nm. This is at first glance somewhat unexpected, but simply reflects the high ionic strength of KPS-based recipes.

Contrary to the results described here Leemans et al.[22] found that latices stabilized with a sulfonated poly-

(glycidyl methacrylate) block in emulsion polymerization of acrylic monomers exhibit an electrolyte stability up to 1.2 M potassium chloride. Furthermore, they used KPS (4.6 mM) as initiator and obtained particles with a hard core diameter of about 70 nm. The reason for this difference with respect to the electrolyte stability is the molecular architecture of the stabilizing block. The poly(sulfonated glycidyl methacrylate) block contains two stabilizing groups in equal amounts: the electrolytic sulfonate group and a hydroxyl group. The hydroxyl groups impart stability even if the action of the sulfonate groups is screened in the presence of additional electrolytes. Contrary, the poly(styrenesulfonate) block predominantly acts only as polyelectrolyte and runs the risk of losing its stabilizing properties in the presence of additional electrolyte.

In conclusion, optimized polyelectrolyte copolymers with strong ionic groups possess a high stabilization efficiency in aqueous systems with low ionic strength. Further work related to the investigation of the properties of these purely electrosterically stabilized model systems is currently in progress.

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