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Use of poly(styrene)-block-poly(ethyleneoxide) as emulsifier in emulsion polymerization

Markus Berger, Walter Richtering*, and Rolf Mülhaupt

Institut für Makromolekulare Chemie und Freiburger Materialforschungszentrum
der Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

Summary

Poly(styrene)-block-poly(ethyleneoxide), abbreviated as (PS-b-PEO) were used as emulsifiers in emulsion polymerization of styrene and methyl methacrylate. The block copolymers had a poly(styrene) block with M_n=1000 g/mol and a poly(ethyleneoxide) block with M_n = 1000, 3000 or 5000 g/mol, respectively. Stable dispersions were obtained when the PEO block molecular weight was higher than 1000 g/mol. Also the amphiphilic properties of the copolymers depended on the PEO chain length. Block copolymer micelles with hydrodynamic radii between 11 and 17nm were observed. Emulsion polymerization was performed at different block copolymer concentration at 60 and 80°C. Particle size varied between 50 and 300nm and decreased with increasing copolymer concentration. The particle size was larger at higher temperature, but the size distribution was narrower. Polymerization of methyl methacrylate gave smaller particles when compared to styrene. The dispersions were very stable towards high electrolyte concentration, but flocculation occurred at elevated temperatures. Both observations indicate that the dispersions are sterically stabilized.

Introduction

Polymer dispersions consist of hard, usually spherical particles, which are dispersed in a low molecular weight fluid. In industrial applications, aqueous polymer dispersions with high solid content are synthesized mainly by emulsion polymerization and are used in a vast area of applications such as paper coatings, paints and adhesives.

There are two major routes to stabilized dispersions: firstly, electrostatic stabilization by introducing charged groups on the particle surface, and secondly, steric stabilization involving adsorption of polymers, which are well soluble in the dispersion medium.(1,2) Sterical stabilization of aqueous dispersions provides better colloidal stability with respect to high salt concentration, pH change, freeze-thaw cycles and shear when compared to charge stabilization. Often homopolymers, e.g. poly(vinyl alcohol) or block copolymers like poly(styrene)-b-poly(ethyleneoxide) are used as stabilizers. Preparation of block copolymers, however, is difficult and therefore only a few publications describe polymer dispersions that are exclusively stabilized with block copolymers.(3-5) Today, such block copolymers are available in commercial scale.(6) It is the objective of this contribution to study the influence

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* Corresponding author

of block copolymers on the particle size and size distribution of aqueous polymer dispersions. Macromolecules can be attached to the surface by chemical bonds if polymer initiators are used (7) or simply by adsorption of an insoluble block. According to Piirma and coworkers a block length of 10 styrene units is sufficient to achieve an irreversible anchoring of poly(styrene)-b-poly(ethyleneoxide) block copolymers on particles.(3) Therefore we used three different block copolymers, each of which had a polystyrene block with a molecular weight of M_n=1000 g/mol, and polyethylenoxide molecular weight of M_n=1000, 3000 or 5000 g/mol, respectiveley. The PS-b-PEO block copolymers are named SE1010, SE1030 and SE1050, respectively. By use of these block copolymers one obtains sterically stabilized dispersions that can be flocculated by increasing temperature.

In the following surfactant properties of the block copolymers are characterized, and the influence of block copolymer concentration, PEO block length and reaction temperature on particle size is studied. Finally salt, temperature and freeze-thaw stability of the latices are investigated

Experimental

PS-b-PEO were obtained from Th. Goldschmidt AG and used without further purification. The molecular weight of the block copolymers was determined by vapor pressure osmometry in chloroform on a Perkin Elmer Molecular Weight Apparatus 115. Surface tensions were measured with a Krüss Instrument K10T using the plate method.

Batch emulsion polymerization was carried out at 80 or 60°C using potasium persulfate as initiator. Concentrations of monomer, emulsifier and initiator are given in Table 1. Emulsion polymerization was performed as described by Jialanella et al.(3).

Particle size determination by dynamic light scattering was carried out either by means of a Malvern Zetasizer 3 or an ALV Goniometer connected to an ALV-3000 Correlator. Particle size distributions were determined by inverse Laplace transformation of the time correlation function by the common CONTIN software.

A transmission electron microscope CEM 902 by Carl Zeiss equipped with the KONTON-IBAS software was also used for determination of particle size and size distribution. At least 1200 particles were investigated in order to obtain the size distribution.

In order to study flocculation samples of 1.6% solid content were thermostated at 20,40,60, and 80°C and flocculation was observed visually.

Table 1 Recipe for emulsion polymerization.

Components	Weight (g)
water	140
styrene or methyl methacrylate	20
potasium persulfate	0.26
PS-b-PEO	0.45; 0.9; 1.8; 3.6; 5.4; 14.4

Results and discussion

Characterization of block copolymers

PS-b-PEO were first characterized with respect to their molecular weight by means of vapor pressure osmometry. The results are summarized in Table 2 and show that the measured molecular weights are in good agreement with the expected ones. Quantitative analysis of the ^{1}H-NMR spectra yields the composition of the block copolymer. Again observed and calculated values are in excellent agreement. Polydispersity was determined by GPC in Chloroform and M_w/M_n was found to be 1.12.

Surfactant properties of the block copolymers were studied in dilute aqueous solution. The surface tension was measured as a function of polymer concentration and a critical concentration, $\hat{c}$, was found, above which the surface tension was constant (see Figure 1). Values of $\hat{c}$ and of the surface tension σ at $c > \hat{c}$ are listed in Table 2. $\hat{c}$ decreases with increasing length of the PEO block, but the ultimate surface tension increases. The size of the block copolymer micelles was determined by dynamic light scattering and is also given in Table 2. With SE1030 and SE 1050 the hydrodynamic radii were independent of concentration within the investigated range (0.5 to 15 g/l).

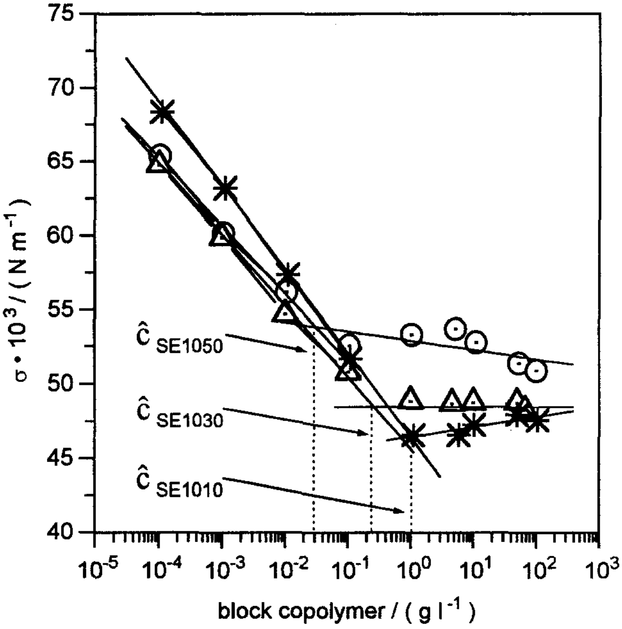

Figure 1 Surface tension of aqueous solutions of PS-b-PEO
—⊙— SE1050, —△— SE1030, —✱— SE1010

Measurements at the smallest concentrations of SE1010 were below the critical concentration $\hat{c}$ and an increase of average hydrodynamic radius was observed with decreasing concentration. Such a behavior was recently described by Winnik and coworkers in a detailed study on block copolymer micelles and was attributed to an equilibrium between micelles and larger aggregates.(8) The hydrodynamic radii decreased at elevated temperature.

Table 2 Properties of PS-b-PEO in $CHCl_3$ and aqueous solution.

	SE1010	SE1030	SE1050
M_n / (g/mol) [a]	1932	3968	6258
$\hat{c}$ / (g/l)	1	0.26	0.03
$\hat{c} \cdot 10^6$/ (mol/l)	500	75	5
$\sigma \cdot 10^{-3}$/ (N/m)	47	49	53
R_h at 20°C /nm	11	19	17
R_h at 55°C /nm	9	13	15

[a] vapor pressure osmometry in $CHCl_3$

Emulsion polymerization

The block copolymers were used as the only emuslifying agent in emulsion polymerization of styrene and methyl methacrylate using potasium persulfate as initiator. The concentration of block copolymers was varied between 2.7 and 88 g/l. The reactions were performed at 80 or 60°C, respectively. Particle size and size distribution of the latices were determined by transmission electron microscopy and dynamic light scattering. Evolution of particle size during polymerization was studied by taking small samples out of the reactor. The particle size was constant after reaction times of approximately three hours.

Figure 2 shows the particle size of the final dispersions obtained at both temperatures as a function of SE1030 concentration. With increasing concentration, the particle size decreases. The results of all emulsion polymerizations are summarized in Table 3. The following observations were made:

i) Stable dispersion were obtained with SE1030 and SE 1050.
ii) There was no significant difference in particle size between samples prepared with SE1030 and SE1050. The small difference in particle size may be associated with the different chain length of the PEO block which results in a different thickness of the stabilizing layer.
iii) Larger particles with a narrower size distribution were found when the emulsion polymerization was performed at an elevated temperature.
iv) Smaller particles with a narrower size distribution were found when methyl methacrylate was used instead of styrene.

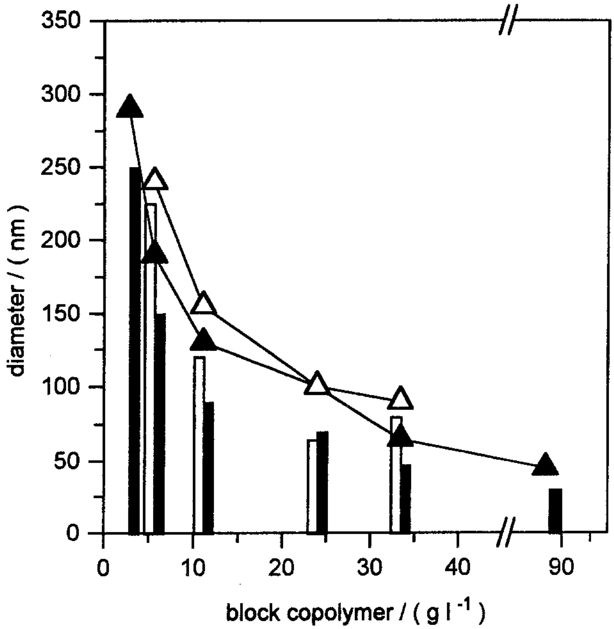

Figure 2 Particle size of latices stabilized with SE1030. Triangles: $D_{(QELS)}$, bars: $D_{(TEM)}$. White symbols: polymerized at 80°C. Black symbols: polymerized at 60°C.

Table 3 Particle size, $D_{(QELS)}$, $D_{(TEM)}$, and relative standard deviation of diameter, St.d. (determined by TEM) of polymer latices.
T: Reaction temperature

SE1030					SE1050				
Conc. [g/l]	T [°C]	$D_{(QELS)}$ [nm]	$D_{(TEM)}$ [nm]	St.d. [%]	Conc. [g(l]	T [°C]	$D_{(QELS)}$ [nm]	$D_{(TEM)}$ [nm]	St.d. [%]
88	60	45	29	31					
33	60	65	47	32	33	60	82	46	26
22	60	90	71	14	22	60	89	52	21
11	60	130	92	12	11	60	141	100	19
5.5	60	190	150	15	5.5	60	224	131	30
2.7	60	290	250	16	2.7	60	306	257	17
33	80	90	81	20	33	80	87	55	22
22	80	100	54	26	22	80	120	70	21
11	80	155	120	15	11	80	171	114	16
5.5	80	240	225	7	5.5	80	237	189	14
88 a)	80	44	19	58					
33 a)	80	64	47	28					
22 a)	80	90	59	12					
11 a)	80	130	71	18					
5.5 a)	80	204	125	18					

a) polymerization of methyl methacrylate

The number of particles present in the final latex was calculated from the particle size and the solid content for latices obtained with SE1030 as stabilizer. The dependence of the number of particles on the block copolymer concentration is shown in a double logarithmic plot in Figure 3. Straight lines are observed with slopes of 1.62 at 60°C and 1.85 at 80°C that are much higher than the exponent 0.6 which was found for sodium dodecylsulfate(9).

Determination of the surface tension of the polymer dispersion showed that the concentration of block copolymer in the aqueous medium was below $\hat{c}$ and block copolymers can not be desorbed by dilution. Therefore one can calculate the surface area per block copolymer on the particle. Values between 2 and 10 nm^2 per molecule were found, indicating a rather dense packing of the block copolymers on the surface.

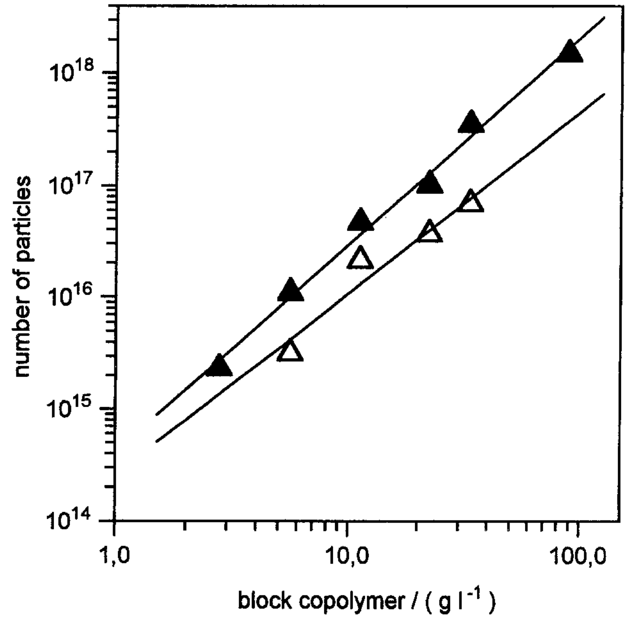

Figure 3 Number of particles as a funktion of SE1030 concentration.
△ polymerized at 80°C, ▲ polymerized at 60°C

Stability of latices

Sterically stabilized dispersions are usually very stable against addition of electrolytes, but flocculation may occur upon heating if the solvent's quality decreases at higher temperatures and the theta point is approached. The theta temperature of PEO in water depends on the salt concentration, therefore salt solutions of different concentrations were added to the latices and heated to elevated temperatures in order to study flocculation. Table 4 displays, time and temperature at which the dispersions started to flocculate. No difference between K^+ and Ca^{2+} ions was observed revealing that electrostatic stabilization is insignificant. Colloidal stability with respect to high electrolyte concentration was expected. However, recently reported results on latices stabilized by diblock macromonomers indicated a low salt stability when ionic initiators were used (10). In our case, however, electrolyte stability was very good, i.e., the latices were effectively stabilized by the poly(ethyleneoxide) chains. Conductometric titration also showed that no ionic groups were present on the particle surface.

Flocculation occurred upon heating and the critical flocculation temperature decreased with increasing salt concentration, increasing particle size and increasing poly(ethyleneoxide) chain length. These findings are typical of sterically stabilized dispersions and reflect the influence of salt concentration and polymer molecular weight on the theta temperature of poly(ethyleneoxide).

Freeze-thaw stability of the dispersions was checked by storing samples at 0 and -16°C for 24 hours. Determination of particle size revealed that no aggregation occurred at 0°C. However, only samples with the highest block copolymer content during emulsion polymerization could be redispersed after storage at -16°C.

Table 5 Flocculation of PEO stabilized latices.

Latex		KCl- and $CaCl_2$-Solutions [mol/l]							
Emulsifier	Diameter [nm]	0,001		0,01		0,1		1	
		[°C]	[h]	[°C]	[h]	[°C]	[h]	[°C]	[h]
SE-1030	240	80	12	40	12	20	24	20	24
SE-1030	155	80	12	80	2	80	2	60	2
SE-1030	100	80	24	80	12	80	12	80	2
SE-1030	90	80	24	80	24	80	12	80	2
SE-1050	306	80	2	40	24	40	24	20	24
SE-1050	224	80	2	60	12	60	12	20	24
SE-1050	141	80	2	60	12	60	24	40	24
SE-1050	89	80	2	60	24	60	24	60	12
SE-1050	82	60	24	60	24	60	24	60	12

Conclusions

PS-b-PEO block copolymers with PS block molecular weight of M_n = 1000 g/mol and PEO block molecular weight of M_n = 3000 or 5000 g/mol are useful as effective stabilizers in emulsion polymerization of styrene and methyl methacrylate. Particle diameters can be variied between 50 and 300nm. If the emulsion polymerization is performed at 80°C instead of 60°C, larger particles with a slightly smaller size distribution are obtained. Polymerization of methyl methacrylate gives narrower particles compared to styrene. The block copolymer are effectively anchored on the particle surface and cannot be desorbed by dilution. The latices show stability towards high electrolyte concentration. Flocculation is observed upon heating. Thus the latices can be used as model systems for sterically stabilized dispersions.

Acknowledgement

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References

1. Napper DH (1983) Polymeric Stabilization of Colloidal Dispersions, Academic Press, New York
2. Lyklema J (1991) Fundamentals of Interface and Colloid Science, Academic Press, London
3. Jialanella GJ, Firer EM, Piirma I (1992) J Polym Sci Part A: Polym Chem 30: 1925
4. Bahadur P, Riess G (1991) Tenside Surf Det 28: 173
5. Riess G (1993) Makromol Chem Macromol Symp 69: 125
6. Fock J Goldschmidt AG Ger Offen DE 4134967
7. Tauer K, Goebel K-H, Kosmella S, Stähler K, Neelson J (1990) Makromol Chem Macromol Symp 31: 107
8. Xu R, Winnik MA, Hallett FR, Riess G, Croucher MD (1991) Macromolecules 24: 87
9. Dunn AS (1992) in: Polymer Latexes, ACS Symp Ser. 492: 45
10. Schechtman LA (1992) in: Polymer Solutions, Blends and Interfaces, Noda I, Rubingh DN (eds), Elsevier, Amsterdam

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