The First Study of the Effect of Surfmer Backbone Structure on the Stability and the Course of Emulsion Polymerization of Methyl Methacrylate and Butyl Acrylate Monomers

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ABSTRACT: This is the first study of the effect of structure of the surfmer on the stability, morphology, and kinetics of the emulsion polymerization of butyl acrylate (BuA) and methyl methacrylate (MMA). Poly(ethylene glycol) behenyl ether methacrylate (PEGBEMA) was used as surfmer in the emulsion polymerization

of BuA and MMA and compared with the same type surfmer with different backbone structure (with four bulky phenyl groups in the backbone of the surfmer) poly(ethylene glycol) 2,4,6-tris (1-phenylethyl) phenyl ether methacrylate.



It was found that the straight chain surfmer produces less stability, lower order reaction less particles size (D_{max}) greater number of polymer particles Nt, worse morphology D_w/D_n , than the bulky surfmer. The order of polymerization reaction of BuA with respect to PEGBEMA was 0.8 compared with 2.6 in case of using PEGTPMA. The surface charge density was dramatically changed when using PEGBEMA from 39.8 to 204 µC in case of PEGTPMA at the same conditions of surfmer concentration, temperature, and other parameters. The D_v was found to be 897 nm for particles prepared in the presence of PEGTPMA surfmer while it was 159 nm for particles prepared in the presence of PEGBEMA at the same surfmer concentrations and other experimental conditions. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1949-1957, 2008

Key words: emulsion polymerization; surfmer; stability; morphology; kinetics; number of polymer particles N_t ; D_v

INTRODUCTION

Economic, human safety, and environmental consideration have driven the substitution of solvent-based formulations with aqueous systems in all industrial sectors. European Union has issued directives limiting the release to the environment of volatile organic compounds from paints and coating formulations. This demands not only a reformulation of existing products but opens opportunities for developing novel surface active agents for example in the field of emulsion polymerization polymers; the reactive (or copolymerizable) surfactants. Polymerizable surfactants (surfmers) can covalently bind to the dispersed phase and as such have a distinct advantage over conventional surfactants that are only physically adsorbed and that can be displaced from the interface by shear forces (e.g., during the polymerization process itself or during transport through pipes) or physical state change (e.g., freeze-thaw) and result in latex destabilization. Furthermore, if the substrate is coalesced to produce decorative or protective films, conventional surfactants tend to concentrate in the water phase and migrate to the surface of the film, resulting in reduced adhesion, increased water sensitivity and modification of the hardness, barrier, and optical properties of the film. There are also potential economic and environmental advantages for the use of surfmers. The binding to the dispersed phase makes these surfactants an

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integral part of polymer and enhances the yield in active matter. It furthermore prevents the release of surfactants in the water effluents on production and application and, as such, reduces the environmental impact during the production of polymers and use of the commercial formulations.

In 1958, Freedman et al.¹ reported the first synthesis of vinyl monomers, which also functioned as emulsifying agents. Since this time, especially over the last 15 years or so, surfmers have received much attention. A wide variety of surfmers have been synthesized and studied by different groups worldwide.^{2–7} A vast amount of literature exists in this field and there are a number of excellent reviews.^{8–12} Sherrington and Hamid¹³ have published a number of articles describing the synthesis and characterization of a wide scope of mono-and divalent quaternary ammonium cationic surfmers^{13–19} and a series of alkyl pyridinium bromide maleate diester surfmers.²⁰

In previous publication Shaffei and Hamed²¹ used the same surfmer functionality but with different backbone structure poly(ethylene glycol) 2,4,6-tris (1phenylethyl) phenyl ether methacrylate.

 $H_2C = C (CH_3) CO_2 (CH_2CH_2O)_n C_6 H_2 [CH (CH_3) C_6 H_5)]_3$

(Mol wt average $M_n \sim 1600$) with four bulky benzene rings in the backbone and found obviously greater stability of the produced poly butyl acrylate (BuA) emulsion lattices.

In this article, a new study on the effect of backbone structure of a surfmer on the stability, morphology and the course of emulsion polymerization of methyl methacrylate (MMA) and BuA using different surfmer concentrations.

EXPERIMENTAL

MMA monomer (stabilized with 14 ppm hydroquinone) provided by BDH. BuA monomer (stabilized with 14 ppm hydroquinone) was provided by Merck-Schuchardt, Germany, both MMA and BuA were redistilled before use and stored at -20° C, potassium persulfate (KPS) was supplied by Merck-Schuchardt, Germany, and recrystallized from water by methanol, and the final crystals were vacuum-dried. Sodium bisulphate, potassium hydroxide, acetone, methanol, and hydroquinone (Quinol) were products of El-Nasr Pharmaceutical Chemical Company (Adwic), Egypt. Poly(ethylene glycol) behenyl ether methacrylate (PEGBEMA)



was provided by sigma-Aldrich, Germany. All water used was purified by distillation, acetone sodium bisulfite adduct was prepared by the addition reaction of sodium bisulfite on the carbonyl group of acetone.

The critical micelle concentration (CMC) for surfmers were determined by conductivity measurements²² using conductivity meter (JENWAY 4510).

The polymerization technique and the number of polymer particles per unit volume of water were carried out as mentioned previously,^{23,24} The polydispersity of polymer particles were calculated by a computerized image analyzer equipment (BILDA-NALYZE IBAS 1 and 2) to find the maximum diameter (D_{max}), circular diameter (D_{circle}), the deviation from spherical morphology (D_{circle}/D_{max}), and the number of polymer particles per unit volume of water (N_t).

The stability studies concern with the determination of surface charge density (SCD) of the emulsion latex particles using conductometric titration that give information about the storage life of emulsion was carried out using (JENWAY 4510) conductivity meter and (JANWAY 1000) hotplate and stirrer.

RESULTS AND DISCUSSION

Determination of CMC of PEGBEMA surfmer

The CMC of poly(ethylene glycol) behenyl ether methacrylate (PEGBEMA) was taken from Figure 1 and found to be 0.0058 mol/L from the relationship between the concentration of the surfmer (mol/L) versus the conductivity in (μ S) of surfmer solution at different temperatures 23 and 70°C. This value is close to the CMC of poly(ethylene glycol) 2,4, 6-tris (1-phenylethyl) phenyl ether methacrylate (PEGTPMA) which is 0.0048 mol/L.

Kinetic study of the emulsion polymerization of BuA and MMA in the presence of (PEGBEMA) surfmer in comparison with that in presence of (PEGTPMA) surfmer

Understanding of emulsion required considering mechanism involving free radical formation, latex



Figure 1 Determination of the critical micelle concentration (CMC) of (PEGBEMA) surfmer at 23°C. Using conductivity measurements in micro siemens.



Figure 2 The conversion-time curves of butyl acrylate monomer using PEGBEMA surfmer.

particle formation, propagation modes, and aqueous phase events which become more important if a partially water soluble monomer is used. The first reasonably accurate qualitative model of an emulsion polymerization system was given by Harkins²⁵ which was shortly thereafter quantified by Smith and Ewart²⁶ (micellar nucleation), Roe²⁷ (homogeneous nucleation), and HUFT²⁸ (Hansen, Uglestad, Fitch and Tsai) theories gives a general description of particle nucleation with HUFT theory recognizing three different loci for particle nucleation, i.e., (micellar, homogeneous, and droplet nucleation).

Figures 2 and 3 show that maximum rate of polymerization, Rp_{max} for BuA and MMA with PEG-BEMA as surfmer at 30–60% conversion and the polymerization reaction reaches maximum for 15–50 min for the polymerization process of MMA with PEGBEMA while it reaches 60–100 min for the polymerization process of BuA with PEGBEMA as surfmer.

Figures 2 and 3 indicates that the rate of polymerization abruptly increases initially and 60% conversion occurs during 6 min (in case of MMA polymerization using 0.5% PEGBEMA) and during 57 min (in case of BuA polymerization using 0.5% PEGBEMA) however, after this the polymerization rate is slow and final conversion is achieved in many hours.

In principle, this could be attributed to several possible factors since the rate of polymerization is given by

$$R_p = K_p[\mathbf{M}]_p \ n \ N/N_A$$

where K_p is the propagation rate constant, $[M]_p$ is monomer concentration in particle, *n* is the average



Figure 3 The conversion-time curves of methyl with acrylate monomer using PEGBEMA surfmer.



Figure 4 Determination of double logarithmic plot of R_p and [Surfmer] mol/L of PBuA using PEGBEMA surfmer.

number of free radicals per reaction locus, N is the number of polymerization locii, N_A is Avogadro's number.

Initially, the number of particles increases due to the formation of new particles via homogeneous nucleation, resulting in more polymerization locii. This could be one reason for the abrupt increase in the initial R_p . The monomer concentration in the polymer particles increases initially due to the diffusion of monomer from the large initiated monomer droplets leading to the increase in the rate of polymerization, however, after 60% the large monomer droplets disappear and monomer concentration in the particles starts decreasing as a result the polymerization rate falls.

Furthermore, from the conversion-time curves of emulsion polymerization of MMA and BuA in PEG-BEMA and PEGTPMA surfmers it can be seen that all the reactions tend to rapidly overcome the starved conditions. The use of the surfmer did not retard the polymerization which have been the result if extensive chain transfer to surfmer occurred because of the formation of quite stable radicals.²⁹

Figures 2 and 3 show the conversion-time curves of BuA monomer and MMA in the presence of (PEGBEMA) surfmer at different concentrations 3.33, 6.66, and 10×10^{-3} mol/L using of redox initiator KPS/ASBS [6.25 × 10^{-3}]/[12.5 × 10^{-3}], respectively, at 70°C.

Figures 4–6 show the double logarithmic plot of R_p and surfmer concentration mol/L for PBuA it



Figure 5 Determination of double logarithmic plot of R_p and [surfmer] mol/L of PBuA using PEGTPMA surfmer.

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Figure 6 Determination of double logarithmic plot of R_p and [surfmer] mol/L of PMMA using PEGBEMA surfmer.

was found that the power with respect to (PEG-BEMA) surfmer was 0.8 and for (PEGTPMA) surfmer was 2.6.

This means greater kinetic tendency for BuA monomer to (PEGTPMA) surfmer than that to (PEG-BEMA) surfmer. Also it is clear that the power of polymerization reaction with respect to (PEGBEMA) surfmer was found to be 0.32 for PMMA and 0.8 for PBuA.

It has been reported that for anionic surfmers,³⁰ the higher the concentration of the surfmer the lower its conversion, it can be seen that the use of large



Figure 7 Effect of different surfmer (PEGBEMA) concentrations on the size and morphological characteristics of the emulsion latex particles of PMMA and PBuA lattices prepared at 70°C in the presence of redox initiator KPS/ASBS [6.25 $\times 10^{-3}$]/[12.5 $\times 10^{-3}$], respectively. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]



Figure 8 Effect of two different surfmers (PEGBEMA) and (PEGTPMA) concentrations on the size and morphological characteristics of the emulsion latex particles of PBuA lattices Prepared at 70°C in the presence of redox initiator KPS/ASBS $[6.25 \times 10^{-3}]/[12.5 \times 10^{-3}]$, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

amounts of PEGTPMA and PEGBEMA resulted in a lower polymerization rate at the beginning of the reaction, on the other hand, the decrease in the polymerization rate can be related to the low reactivity of the surfmer. On the other hand, this decrease could be due to mass transfer limitations for radical entry created by the dense hairy layer formed by the nonionic surfactant.^{31–33}

TABLE IEffect of Different Surfmers (PEGBEMA) and (PEGTPMA) Concentrations on the D_v^- , D_w^-/D_n^- and N_t of the Emulsion Latex Particles of PBuA Lattices Prepared at 70°C in the Presence of Redox InitiatorKPS/ASBS [6.25 × 10⁻³]/[12.5 × 10⁻³], Respectively

Monomer	[Surfmer] $\times 10^{-3}$ mol/L	D_v^- (nm)	D_n^- (nm)	D_w^- (nm)	D_w^-/D_n^-	$N_t \ (\times 10^{15})$
BuA (1.11 mol/L) using surfmer (PEGBEMA)	3.33	186.3	185.1	189.8	1.025	2.23
	6.66	162.8	160.4	169.4	1.056	3.35
	10	153.2	150.8	159.8	1.060	4.02
BuA (1.21 mol/L) using surfmer (PEGTPMA)	3.125	964.7	961.5	974.1	1.013	0.02
	6.25	892.8	884.8	917.5	1.037	0.02
	9.375	560.9	552.5	583.9	1.057	0.08

TABLE II
Effect of Different Surfmers (PEGBEMA) and
(PEGTPMA) Concentrations on the D_{max} , D_{circle} and
$D_{\text{circle}}/D_{\text{max}}$ (the Deviation from the Spherical
Dimensions) of the Emulsion Latex Particles of PBuA
Lattices Prepared at 70°C in the Presence of Redox
Initiator KPS/ASBS $[6.25 \times 10^{-3}]$
$[12.5 \times 10^{-3}]$, Respectively

	3)	1	5	
Monomer	[Surfmer] $\times 10^{-3}$ mol/L	D _{max} (nm)	D _{circle} (nm)	D _{circle} / D _{max} (%)
BuA (1.11 mol/L) using surfmer (PEGBEMA)	3.33 6.66 10	2.5 2.1 1.9	2.3 1.9 1.7	92.93 89.63 86.76
BuA (1.21 mol/L) using surfmer (PEGTPMA)	3.125 6.25	11.7 11.0	10.8 9.9	92.01 90.15

Morphological characteristics of PBuA and PMMA latex particles in presence of (PEGBEMA) and (PEGTPMA) surfmers

Figure 7 shows the photos of polymer particles of PMMA and PBuA using (PEGBEMA) surfmer and Figure 8 shows PBuA using (PEGBEMA) surfmer and PBuA using (PEGTPMA) surfmer.

Tables I and II show the morphological parameters, D_v volume average diameter, $D_{\text{circle}}/D_{\text{max}}$ spherical morphology, D_w/D_n poly dispersity and N_t the number of polymer particles per unite volume of water for polymer particles of PBuA using the (PEG-BEMA) and (PEGTPMA) surfmers.

It is clear that the D_v of PBuA decreases dramatically when using PEGBEMA instead of PEGTPMA, also the poly dispersity index D_w/D_n of PBuA particles (and hence broad distribution of particle size) increases when using PEGBEMA instead of PEGTPMA surfmer.

The N_t values of PBuA particles increases when using PEGBEMA surfmer instead of PEGTPMA.

The greater particle size produced when using PEGTPMA surfmer could be rationalized to the greater micelle size produced by this surfmer because of the steric hindrances caused by the four bulky benzene rings in the backbone structure of the surfmer, this also means that PEGTPMA surfmer produces more defined particles of PBuA rather than PEGBEMA, this also could be rationalized to the presence of four bulky benzene rings found in PEGTPMA surfmer which tend to form more regular particles than straight chain surfmer PEGBEMA.



Tables III and IV show D_v , $D_{\text{circle}}/D_{\text{max}}$, D_w/D_n and N_t for polymer particles of PBuA and PMMA using PEGBEMA surfmer, from these data it can be concluded that the D_v of PMMA particles is greater than D_v of PBuA particles. Also the N_t of polymer particles for PBuA is greater than that for PMMA.

Gan et al.³⁴ found an unusual behavior while polymerizing MMA in emulsion and microemulsion media and found that with increase of SDS (sodium dodecyl sulfonate) concentration decreased percentage conversion, rate of polymerization, final number of latex particles, and increase in particle size was observed.

Stability of emulsion lattices for PBuA in presence of PEGBEMA and PEGTPMA surfmers

Principles of stabilization of colloidal particles

Table V summarizes the key features of the principle kinds (I–III) of latex particle stabilization. Each kind of stabilization has at least one special advantage that makes this particular kind of stabilization useful, but for technical polymer dispersion application of a well-balanced mix of all stabilization possibilities is necessary. This is especially so if during storage and application of water-based dispersions both the ionic strength and the temperature change con-

TABLE IIIEffect of Different Surfmer (PEGBEMA) Concentrations on the D_v^- , D_w^-/D_n^- and N_t of the Emulsion Latex
Particles of PMMA and PBuA Lattices Prepared at 70°C in the Presence of Redox Initiator KPS/ASBS
[6.25×10^{-3}]/[12.5×10^{-3}], Respectively

Monomer	[Surfmer] $\times 10^{-3}$ mol/L	D_v^- (nm)	D_n^- (nm)	D_w^- (nm)	D_w^-/D_n^-	$N_t \; (imes 10^{15})$
MMA (1.41 mol/L)	3.33	347.7	345.4	355.0	1.028	0.34
	6.66	210.9	208.5	219.0	1.051	1.54
	10	136.8	134.4	142.5	1.061	5.65
BuA (1.11 mol/L)	3.33	186.3	185.1	189.8	1.025	2.23
	6.66	162.8	160.4	169.4	1.056	3.35
	10	153.2	150.8	159.8	1.059	4.02

TABLE IV
Effect of Different Surfmer (PEGBEMA) Concentrations
on the D_{max} D_{circle} and $D_{\text{circle}}/D_{\text{max}}$ (the Deviation from
the Spherical Dimensions) of the Emulsion Latex
Particles of PMMA and PBuA Lattices Prepared at 70°C
in the Presence of Redox Initiator KPS/ASBS [6.25
$\times 10^{-3}$]/[12.5 $\times 10^{-3}$]. Respectively

		-	•	
Monomer	$\begin{array}{c} [\text{Surfmer}] \times \\ 10^{-3} \text{ mol/L} \end{array}$	D _{max} (nm)	D _{circle} (nm)	D _{circle} / D _{max} (%)
MMA (1.41 mol/L)	3.33	4.5	4.2	93.68 89.61
	10	1.7	1.5	87.65
BuA (1.11mol/L)	3.33 6.66	2.5 2.1	2.3 1.9	92.93 89.63
	10	1.9	1.7	86.76

siderably the most effective way to realize electronic stabilization is via the application of low-molecularweight ionic surfactants such as alkyl sulfate (prominent example: sodium dodecylsulfate), or alkyl sulfonates, or alkyl ammonium compound (prominent example: cetyltrimethylammonium bromide). Depending on the charge sign of the stabilizer either anionic (most prominent peroxodisulfate) or cationic initiator (such as 2, 2'-azobis (2-amidinopropane) dihydrochloride) are used. But it has been shown that nonionic, water-soluble initiators such as symmetrical poly(ethylene glycol)-azo compound might also be advantageous.³⁵ Moreover, the same investigations showed that much smaller particles were obtained with polymerization recipes containing ionic species than in completely nonionic polymerization. These results clearly indicate that for effective stabilization some ions arising from the initiator, or ionic surfactants, or ionic comonomers are needed at the particle surface. Furthermore, ionic emulsifiers are obviously more effective in stabilizing polymer particles than nonionic stabilizers. The drawback of purely electrostatic stabilization is the proneness to decrease with addition of electrolyte as the repulsive potential decreases exponentially with increasing ionic strength (see Table V). In contrast, the use of nonionic stabilizers has a dramatic effect on the electrolyte stability of latex particle. For instance, the additional stabilization of negatively charged polystyrene particles with dodecyl hexaoxy ethylene glycol monoether causes an increase in the critical coagulation concentration (determined with lanthanum nitrate) by an order of magnitude.³⁶ Besides, increased stability against electrolyte another advantage of steric stabilization is the frequently observed

TABLE V Principles of Stabilization of Colloidal Particles

Electrostatic(I) Electrostatic repulsion of equally charged particles; repulsive potential (V_R) around charged particles at distance (d) decays as: $V_R \propto f(\psi) \exp\left(\frac{-d}{\lambda_D}\right)$ Charge density at the interface, surface potential (ψ) , ionic strength (I_s) ; Debye screnning length (λ_D) $\lambda_D = \left(\frac{\varepsilon \cdot \varepsilon_0 \cdot k_B \cdot T}{\sum_l (z_l \cdot e)^2 \cdot C_{salt}}\right)^{0.5}$ Steric(II) Osmotic and entropic forces between overlapping stabilizer layers of approaching particles $V_R \propto \frac{C_{s,L}^2}{v_{c,P} \cdot \rho_{s,L}^2} (\psi_1 - \chi_{s,cp})$ $\left[[\Delta R - d/2]^2 [3D/2 + 2\Delta R + d/2]\right]$ Electrosteric(III) Competition between the osmotic pressure induce by counterion condensation inside the polyelectrolyte corona, which stretches the polyelectrolyte chain into the aqueous phase, and entropic polymer elasticity, which pulls the chains back to the surface $\Delta R \propto I_s^a; a = -1/5$	Stabilization	Action forces	Important parameters
$V_R \propto f(\psi) \exp\left(\frac{-d}{\lambda_D}\right) \qquad \qquad \lambda_D = \left(\frac{\varepsilon \cdot \varepsilon_0 \cdot k_B \cdot T}{\sum_i (z_i \cdot e)^2 \cdot C_{salt}}\right)^{0.5}$ Steric(II) Osmotic and entropic forces between overlapping stabilizer layers of approaching particles $V_R \propto \frac{C_{s,L}^2}{v_{c,P} \cdot \rho_{s,L}^2} (\psi_1 - \chi_{s,cp}) \\ \left[[\Delta R - d/2]^2 [3D/2 + 2\Delta R + d/2]\right]$ Electrosteric(III) Competition between the osmotic pressure induce by counterion condensation inside the polyelectrolyte chain into the aqueous phase, and entropic polymer elasticity, which pulls the chains back to the surface $\Delta R \propto I_s^a; a = -1/5$	Electrostatic(I)	Electrostatic repulsion of equally charged particles; repulsive potential (V_R) around charged particles at distance (d) decays as:	Charge density at the interface, surface potential (ψ) , ionic strength (I_s) ; Debye screnning length (λ_D)
Steric(II)Osmotic and entropic forces between overlapping stabilizer layers of approaching particlesSolution state of stabilizing polymer molecules (interaction parameter between stabilizing polymer and continuous phase); temperature ionic strength as far as both influence the solution state of the lyophilic polymer $V_R \propto \frac{C_{s,L}^2}{v_{c,P} \cdot \rho_{s,L}^2} (\psi_1 - \chi_{s,cp})$ $\left[[\Delta R - d/2]^2 [3D/2 + 2\Delta R + d/2] \right]$ Ionic strength as far as both influence the solution state of the lyophilic polymerElectrosteric(III)Competition between the osmotic pressure induce by counterion condensation inside the polyelectrolyte corona, which stretches the polyelectrolyte chain into the aqueous phase, and entropic polymer elasticity, which pulls the chains back to the surface $\Delta R \propto I_s^a; a = -1/5$ Ionic strength solution state of the polyelectrolyte chain, ration corona (D); corona shrinks upon increasing ionic strength		$V_R \propto f(\Psi) \; \exp\left(rac{-d}{\lambda_D} ight)$	$\lambda_D = \left(\frac{\varepsilon \cdot \varepsilon_o \cdot k_B \cdot T}{\sum\limits_i (z_i \cdot e)^2 \cdot C_{\text{salt}}}\right)^{0.5}$
Electrosteric(III) Competition between the osmotic pressure induce by counterion condensation inside the polyelectrolyte corona, which stretches the polyelectrolyte chain into the aqueous phase, and entropic polymer elasticity, which pulls the chains back to the surface $\Delta R \propto I_s^a; a = -1/5$ Ionic strength, conformation and charge density of the polyelectrolyte chain, ration corona (D); corona shrinks upon increasing ionic strength	Steric(II)	Osmotic and entropic forces between overlapping stabilizer layers of approaching particles $V_R \propto \frac{C_{s,L}^2}{v_{c,P} \cdot \rho_{s,L}^2} (\psi_1 - \chi_{s,cp}) \\ \left[[\Delta R - d/2]^2 [3D/2 + 2\Delta R + d/2] \right]$	Solution state of stabilizing polymer molecules (interaction parameter between stabilizing polymer and continuous phase); temperature. ionic strength as far as both influence the solution state of the lyophilic polymer
$\Delta R \propto ~I_s^a; a=-1/5$	Electrosteric(III)	Competition between the osmotic pressure induce by counterion condensation inside the polyelectrolyte corona, which stretches the polyelectrolyte chain into the aqueous phase, and entropic polymer elasticity, which pulls the chains back to the surface	Ionic strength, conformation and charge density of the polyelectrolyte chain, ration corona (D); corona shrinks upon increasing ionic strength
		$\Delta R \propto ~ I_s^a; a = -1/5$	

(Pincus brush behavior)

 C_{salt} is the molar bulk concentration of the ions, $k_B T$ is the thermal energy, ε and ε_0 are the permittivity in the continuous phase and in vacuum, z is the stoichiometric valency of the electrolyte, and e is the elementary charge; $C_{s,L}$ is the concentration of lyophilic polymer per unit volume inside the corona; $v_{c,p}$ is the molar volume of the continuous phase $\rho_{s,L}$ is the density of the lyophilic polymer, ψ_1 is an entropy parameter for mixing of the overlap region, and $\chi_{s,cp}$ is the interaction parameter between the lyophilic polymer and the dispersion medium.

	TA	BLE VI				
Relationship	Between	Surfmer	Type	and	Surfac	e
-	Charg	e Densit	v			

Monomer	[Surfmer] $\times 10^{-3}$ mol/L	Surface charge density (SCD) µC
BuA (1.11 mol/L) using	3.33	39.44
(PEGBEMA) surfmer	6.66	34.46
	10	32.44
BuA (1.21 mol/L) using	3.125	204.22
(PEGTPMA) surfmer	6.25	189.01
	9.375	131.93

reversibility of the flocculation process, which occurs if the conditions that have caused the flocculation are removed again. This reversibility requires that the stabilizers are strongly adsorbed or covalently bound to the particles. Also, an increase in the molecular weight of the steric stabilizer can kinetically retard the displacement of otherwise only weakly anchored stabilizers. Finally, as the name already indicates, electrosteric stabilization should combine features of the two other principles.

Table VI shows SCD versus surfmer concentrations for PBuA emulsion lattices prepared in the presence of PEGBEMA and PEGTPMA surfmers.

From these data it is clear that there is a greater decrease in the SCD (from 204 to 39 μ C at 0.5% surfmer) and hence decrease in the stability of the emulsion particles prepared using PEGBEMA instead of PEGTPMA, this could be rationalized to the greater stabilization of the PEGTPMA surfmer resulting from steric hindrance caused by the presence of four adjacent bulky phenyl groups.

From the structure of PEGTPMA and PEGBEMA surfmers it is clear that both surfmers are of nonionic character and their stabilization are of steric types II (Table V), furthermore, the steric stabilization of PEGTPMA is of great amount due to the presence of four adjacent phenyl groups instead of straight chain of PEGBEMA and this is in agreement with the higher SCD (204.2 μ C) Table VI for the emulsions prepared in the presence of PEGTPMA compared with lower charge density 39.4 μ C for the emulsions prepared in the presence of PEGBEMA surfmer.

Stability of emulsion lattices for PMMA and PBuA in presence of PEGBEMA surfmers

Table VII show the effect of different surfmer (PEG-BEMA) concentrations on the stability and SCD in micro coulomb (μ C) of emulsion latex particles of PMMA and PBuA lattices prepared at 70°C in the presence of redox initiator KPS/ASBS [6.25 × 10⁻³]/ [12.5 × 10⁻³], respectively

From Tables VI and VII it is clear that increasing surfmer concentration decreases SCD and hence decreases the stability of the emulsion lattices and it is also clear that the PMMA emulsion lattices show greater stability than PBuA lattices when using PEG-BEMA as surfmer.

Initiation system

Tsaur and Fitch³⁷ and Schoonbrood and Asua³⁸ reported that the surface yield (the surfmer adsorbed or reacted that contributes to colloidal stability) of the surfmer depend on the initiator system for this purpose PPS/ASBS was used because this system PPS/ASBS yields hydrophobic organic radicals where as KPS/SBS yields hydrophilic inorganic radicals.

Mechanism

$$(CH_3)_2 - C(OH) - SO_3^- + S_2O_8^{-2}$$
$$\longrightarrow SO_4^{-2} + SO_4^{--} + (CH_3)_2 - C(OH) - SO_3^{\bullet}$$

Initiation

$$(CH_3)_2 - C(OH) - SO_3^{\bullet} + M + X$$
$$\longrightarrow (CH_3)_2 - C(OH) - SO_3 - X - M^{\bullet}$$

Propagation

$$(CH_3)_2 - C(OH) - SO_3 - X - M^{\bullet} + M$$
$$\longrightarrow (CH_3)_2 - C(OH) - SO_3 - X - M - M^{\bullet}$$

$$\begin{array}{c} (CH_3)_2 - C(OH) - SO_3 - X - M^{\bullet}_{(x-1)} + M \\ & \longrightarrow (CH_3)_2 - C(OH) - SO_3 - X - M^{\bullet}_x \end{array}$$

Termination

$$\begin{array}{l} (CH_3)_2 - C(OH) - SO_3 - X - M_x^{\bullet} \\ + (CH_3)_2 - C(OH) - SO_3 - X - M_y^{\bullet} \\ - \longrightarrow (CH_3)_2 - C(OH) - SO_3 - X - M_{(x+y)} \\ - X - SO_3 - C(OH)(CH_3)_2 \end{array}$$

TABLE VII
Stability of Emulsion Lattices of PMMA and PBuA
Using Different Surfmer Concentration

Monomer	[Surfmer] $\times 10^{-3} \text{ mol/L}$	Surface charge density (SCD) μC
MMA (1.41 mol/L)	3.33	73.60
	6.66	49.61
	10	34.75
BuA (1.11 mol/L)	3.33	39.44
	6.66	34.46
	10	32.44

Poly(ethylene glycol) behenyl ether methacrylate (PEGBEMA) or poly(ethylene glycol) 2,4,6-tris (1-phenylethyl) phenyl ether methacrylate (PEGTPMA) = X.

CONCLUSIONS

In this manuscript, a new study of the effect of surfmer backbone structure on the stability and the course of the emulsion polymerization of MMA and BuA was carried out. Poly(ethylene glycol) behenyl ether methacrylate (PEGBEMA) was used as surfmer and compared with poly(ethylene glycol) 2,4,6-(1-phenylethyl) phenyl ether methacrylate tris (PEGTPMA), the bulky surfmer PEGTPMA produces much greater stability than the straight chain PEG-BEMA surfmer, also the bulky surfmer PEGTPMA produced particles of BuA much greater than those produced by PEGBEMA, also the particles of poly (butylacrylate) prepared in the presence of PEGTPMA are of less poly dispersity when prepared using the bulky PEGTPMA surfmer than those when prepared using the chain PEGBEMA surfmer. Finally, BuA shows greater kinetic tendency to PEGTPMA than that to PEGBEMA.

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