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ORIGINAL CONTRIBUTION

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Emulsion copolymerization of styrene and methacrylic acid in the presence of a polyethylene oxide based-polymerizable stabilizer with a shorter chain length

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Abstract The emulsion copolymerization of styrene and methacrylic acid (MAA) was performed in the presence of a relatively new macromonomer, poly(ethylene glycol) ethyl ether methacrylate (PEG-EEM) as a stabilizer. In contrast to similar studies, a macromonomer having relatively shorter polyethylene oxide chain length (i.e., M_n:246, $n \approx 3.0$) was selected for this study. Highly uniform and carboxyl functionalized latex particles in the size range of 0.16–0.50 μm were obtained by changing MAA, PEG-EEM, total monomer, and initiator concentrations. The use of PEG-EEM as a stabilizer resulted in larger monodisperse particles relative to those obtained by the emulsifier-free emulsion copolymerization of styrene and MAA. The particle size decreased and the polymerization rate increased with the increasing MAA feed concentration. The application of power law model indicated that MAA concentration was more effective in the presence of PEG-EEM for control of particle size relative to similar systems. The latex particles with higher numbers of surface-carboxyl groups were obtained with the higher MAA feed concentrations. Although the particle size decreased and the polymerization rate increased with the increasing PEG-EEM concentration in the emulsion polymerization of styrene, both of them remained roughly constant with the increasing PEG-EEM concentration in the presence of MAA.

Key words Styrene · Methacrylic acid · Polyethylene glycolmethacrylate · Polyethylene glycol ethylether methacrylate · Emulsion polymerization · Uniform latex particles

Introduction

Polystyrene latex particles with polar functional groups are widely utilized in biomedical applications, especially in protein adsorption and cell adhesion studies. Suzawa et al. developed an emulsifier-free emulsion copolymerization method to produce polystyrene latex particles with different functionalities [1–4]. By their method, styrene-acrylamide-acrylic acid and styrene-hydroxyethylmethacrylate-acrylic acid copolymer latexes were prepared without emulsifier [1]. The same group also prepared styrene-acrylic acid and styrene-methacrylic acid copolymer latexes by seeded emulsion polymerization [4]. The emulsion polymerization of styrene performed in the presence of carboxylic monomers were extensively investigated by Ceska [5, 6], Sakota and Okaya [7–9], and Vijayendran [10]. Shoaf and Poehlein studied the distribution of acrylic and methacrylic acid between the aqueous and organic phases in the emulsion polymerization of styrene [11]. The kinetics of emulsion polymerization in the presence of functional monomers (including carboxylic monomers) were extensively studied by different researchers [12–17]. A kinetic model was proposed for describing the reaction behavior of emulsion polymerization systems including carboxylic monomers, where significant polymerization occurred in both the particle and the aqueous phases [12]. The effect of neutralization degree of the carboxylic monomers on the kinetics of emulsion polymerization system was investigated by Shoaf and Poehlein [13]. The effect of pH of the polymerization medium on the distribution of carboxylic monomers in the emulsion copolymerization of styrene with different hydrophilic monomers was also investigated [18–22]. The effect of carboxylic monomers on the morphology of latex particles was examined by Okubo et al. [23, 24]. In our previous studies, a series of polystyrene latex particles carrying carboxyl groups on their surfaces were also produced [25–27]. These studies were mainly focused on the determination of size and surface chemistry of latex particles and polymerization rate [26].

An increased stability of latex particles, termed "Enhanced Steric Stabilization" can be obtained by the irreversible chemical bonding of polymeric stabilizer onto the particle surface [28]. The macromonomers containing ethylene oxide (EO) units modified with terminally attached polymerizable groups have attracted significant attention in emulsion polymerization as steric stabilizers. Ottewill and Satgurunathan proposed poly(ethyleneglycol) methylether methacrylate with 40 ethylene oxide units (PEG-MEM) as a polymerizable stabilizer in the emulsion polymerization of styrene [29, 30]. Polystyrene latex particles produced in the presence of PEG-MEM were shown to be very stable to electrolyte concentration [31]. Flocculation behavior of polystyrene latex carrying polyethylene oxide chains was also investigated with regard to the existence of polyethylene oxide as the free polymer [32]. Different types of polyethylene oxide based macromonomers with a terminally attached polymerizable groups were tried as steric stabilizers in the emulsion polymerization of styrene [33]. Poly(ethylene glycol) methylether macromonomers with terminal *p*-styrylalkyl group were also used in the preparation of uniform latex particles by emulsion or dispersion copolymerization [34, 35]. Recently, Ottewill reviewed the colloidal behavior of latex particles produced in the presence of polymerizable polyethylene oxide based stabilizers [36]. EO-based polymerizable stabilizers were also used in the presence of oil soluble initiators to produce latex particles carrying EO chains by dispersion polymerization [37–40].

In our previous study, a relatively new macromonomer with a shorter chain-length, poly(ethyleneglycol) ethyl ether methacrylate (PEG-EEM), was proposed as an efficient polymerizable stabilizer to control the average size in a relatively wider range, in the emulsion polymerization of styrene [41]. Here the emulsion copolymerization of styrene and methacrylic acid was performed by using PEG-EEM as a polymerizable stabilizer. The effects of MAA and PEG-EEM feed concentrations on the polymerization rate, the size, the number density, and the carboxyl content of final latex particles were investigated.

Experimental

Materials

Styrene (St, Yarpet AS, Turkey) was distilled under vacuum. Methacrylic acid (MAA, Merck, A.G., Darmstad, Germany) and poly(ethylene glycol) ethyl ether methacrylate (PEG-EEM, average M_n ca. 246, $n \approx 3$, Aldrich Chem. Co., Milwaukee, WI) were used without further purification. Potassium persulfate (KPS, Analar grade, BDH Chemicals Ltd., Poole, England) was selected as the initiator. Distilled-deionized (DDI) water was used in all experiments.

Emulsion polymerization

The emulsion polymerizations were performed in a magnetic driven, sealed cylindrical reactor (volume: 250 ml) equipped with a temperature control system. A typical procedure applied for the emulsion terpolymerization of styrene, methacrylic acid, and PEG-EEM is given below. The monomer phase was comprised of 15 ml styrene, 1.2 ml MAA, and 2.4 ml PEG-EEM was added into the 180 ml of aqueous KPS solution (0.50 mg/ml) placed in a polymerization reactor at room temperature. The reactor content was stirred at 250 rpm during the monomer addition completed within about 3 min. Then it was purged with bubbling nitrogen for 5 min and the heating was started. The zero-reaction time was defined when the reactor temperature was raised to 68 °C. The emulsion terpolymerizations were conducted for 24 h at 250 rpm stirring rate and a temperature of 68 ± 0.4 °C. In some experiments, the progress of the polymerization was followed by the gravimetric analysis of the samples withdrawn from the sample valve placed at the bottom of the reactor [25]. Overall conversion of monomers to the polymer form was determined by measuring the total solid content of the sample. Unless stated otherwise, these common conditions were used for the emulsion terpolymerizations.

Characterization of latex particles

The average size and the size distribution of latex particles were determined by Scanning Electron Microscopy as described elsewhere [25]. The number (D_n) average diameter of the latex particles was calculated according to Eq. (1) where N_i is the number of particles in diameter D_i (μm). The polydispersity index (U) was calculated by Eq. (2). Here, D_w is the weight average diameter of the latex particles:

$$D_n = \Sigma N_i D_i / \Sigma N_i \tag{1}$$

$$U = D_w / D_n \tag{2}$$

The final latex yield was determined by a using a conventional gravimetric procedure. After polymerization, the produced latex suspension was passed through a coarse filter (44 μm in size) to remove any coagulum, then 10 ml of sample was centrifuged at 20,000 rpm for 20 min and the supernatant was discarded after the centrifugation. The latex particles were redispersed in 10 ml of distilled water by ultrasonication and the resulting dispersion was again centrifuged. This operation was performed three times. The final dispersion was dried in vacuum at 60 °C for 24 h. The latex yield (C_T%, the weight ratio of produced latex particles to the total monomer mass charged into the reactor) was calculated by using the weight of dried particles.

For the determination of mass and surface charge densities, 50 ml of latex dispersion diluted with 50 ml of DDI water was treated with a mixed bed of ion exchange resins containing equal amounts of Dowex 50WX2–100 (H Type) and Dowex 550 A (OH type, both from Aldrich Chem. Co., each 6 g in the mixed bed).

This operation was performed by circulating the latex dispersion in a column-reservoir system. Then aqueous NaCl solution was added to the cleaned latex suspension to obtain a NaCl concentration of 0.003 N in the final dispersion. The conductometric titration of the resulting suspension was performed with 0.01 N NaOH solution in a Jenway 4020 conductometer. By using the inflection points observed in the titrations, the mass charge density (Q, meq/g) and the surface charge density (Q_s, $\mu C/cm^2$) of the produced latexes were determined for strong and weak acidic groups.

Results and discussion

In our previous study, we investigated the effects of initiator, polymerizable stabilizer, and monomer concentrations on the properties of the styrene/PEG-EEM copolymer latexes [41]. Then we compared the behavior of St-PEG-EEM system with the previously studied emulsion polymerizations of styrene performed with the poly(ethylene oxide) carrying polymerizable stabilizers with higher molecular weights [29–31, 33]. In the presented study, PEG-EEM was used as a polymerizable stabilizer in the emulsion copolymerization of St with a highly water soluble functional monomer, methacrylic acid (MAA). First, we examined the effects of two conventional parameters (i.e., initiator concentration and monomer/water volume ratio) on the latex yield, average size, size distribution, and surface properties of the final latexes. Then, we tried to identify the effects of short chain polymerizable stabilizer and functional comonomer concentrations on the same properties. St-PEG-EEM-MAA emulsion terpolymerization system provided latex particles in the size range of 0.16–0.50 μm. Some of these latexes are exemplified in Fig. 1. As seen here, the latex particles were obtained in the highly monodisperse form. The highly ordered view of particles was obtained with most of the tried conditions. Owing to the calculated polydispersity index (PDI) values of these latexes being around 1.001, the PDI value was not separately given for the monodisperse latexes. In the following section, this value was only included for the latexes showing appreciable polydispersity. The effects of process variables are presented below.

KPS concentration

In this set, KPS concentration was changed between 1.23–5.56 mmol/l by fixing St, MAA, and PEG-EEM concentrations at 75.25 g/l, 6.77 g/l, and 14.7 g/l, respectively (i.e., the volumes of St, MAA and PEG-EEM in 180 ml of aqueous phase were 15 ml, 1.2 ml, and 2.4 ml, respectively). The emulsion polymerizations were performed for 24 h at 68 °C at 250 rpm stirring rate. The properties of latex particles produced in this set are given in Table 1. As seen here, no significant effect of initiator concentration was observed on the latex yield. The latex yield was satisfactorily high for all initiator concentrations. The average particle size slightly increased with the increasing KPS concentration. The variation of particle size and the particle number density with the KPS concentration is shown in logarithmic coordinates in Fig. 2. By selecting the KPS concentration as the independent variable, the application of power law model gave the exponent values

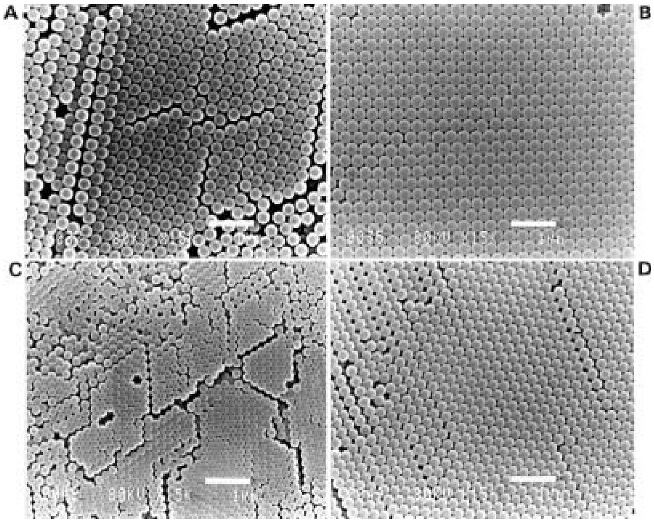

Fig. 1A–D The sample electron micrographs of St-MAA-PEG-EEM terpolymer latex particles produced with different combinations of experimental variables. Magnification:15.000X, Experiment no: **A** SM1; **B** SM2; **C** SM12; **D** SM17

Table 1 The properties of carboxyl functionalized PS latexes produced with different KPS feed concentrations

C_{KPS} (mmol/l)	C_T (wt%)	D_n (μm)	Strong acid		Weak acid		P (A^2/COOH)
			Q (meq/g) × 10^3	Q_s ($\mu C/cm^2$)	Q (meq/g) × 10^3	Q_s ($\mu C/cm^2$)	
(SM1)[a] 1.23	84.8	0.28	4.0	1.9	197.6	93.4	17.2
(SM2) 1.85	85.4	0.31	5.7	3.0	170.5	89.2	18.0
(SM3) 3.70	85.6	0.32	17.5	9.5	193.0	104.2	15.4
(SM4) 5.56	86.9	0.36	27.7	16.8	166.7	101.3	15.8

C_{KPS}: KPS feed concentration, C_T: Latex yield, D_n: Number average size, Q: Mass charge density, Q_s: Surface charge density, P: Actual parking area

[a] Code of the polymerization is given within the parentheses in the first column

of 0.14553 ± 0.03276 and –0.42269 ± 0.09457 in the curve fittings where the average particle size and particle number density were selected as the dependent variable, respectively. In our previous study on the emulsion copolymerization of St and PEG-EEM, the corresponding exponent values were determined as 0.13901 ± 0.04568 and –0.396 ± 0.1186 [41]. As seen here, the exponent values determined for the effect of initiator concentration on the average particle size were reasonably close for St-PEG-EEM and St-PEG-EEM-MAA systems. The same situation was also valid for the exponent values found for particle number densities of the two separate systems. The results of power law fitting indicated that the effects of initiator concentration on the particle size and particle number density did not change by the introduction of MAA into the St-PEG-EEM emulsion system. For conventional emulsion polymerization, the increase in the final size is usually explained by the formation of fewer nuclei with the increasing initiator concentration in the earlier stage of polymerization. By looking at the particle number densities (or determined exponent values for the particle number density), it may be concluded that this explanation is probably valid both for St-PEG-EEM and St-PEG-EEM-MAA systems.

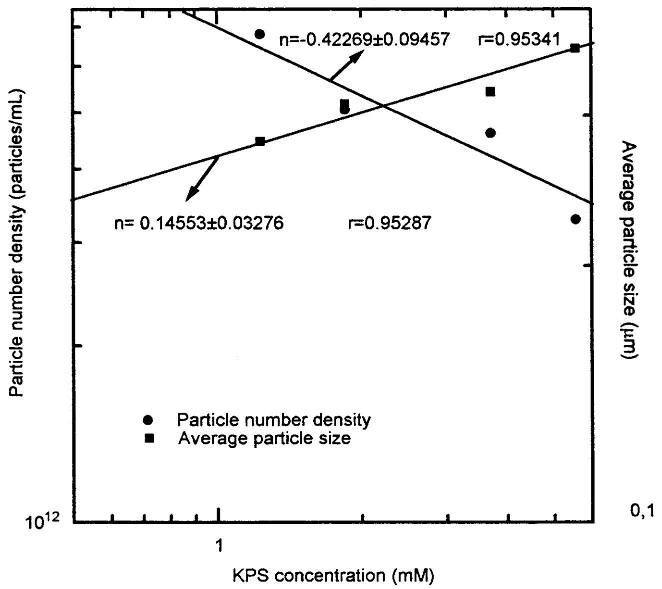

Fig. 2 The variation of particle size and particle number density with the KPS concentration in logarithmic coordinates

The mass and surface charge densities of the latex particles produced by different KPS concentrations are given in Table 1. As seen here, either the mass or the surface charge density originated from the strong acid groups increased with the increasing KPS concentration. This increase is expected since these groups comes from the initiator. In the studied range, no significant effect of KPS concentration was observed both on the mass and surface charge density of carboxyl groups. However, the charge densities of weak acid groups obtained by the use of PEG-EEM in the emulsion copolymerization of St and MAA were higher relative to the particles produced by conventional emulsion copolymerization of styrene and carboxylic monomers [8–10, 20, 42]. In this table, the actual parking area values were also calculated to evaluate the magnitude of the carboxyl content of the particle surface. As seen here, the parking area values ranging between 15.4 and 18.0 A^2/COOH were obtained for the carboxyl carrying-latex particles produced with different initiator concentrations. The close-packed parking area occupied by one carboxyl group is approximately 20 A^2 [42]. Therefore high surface charge densities corresponding to the parking area values lower than 20 A^2 should not be evaluated as a conventional surface charge and probably indicate the presence of poly(methacrylic acid) or copolymer chains grafted onto the particle surface because these values are determined after the cleaning of latex particles by ion-exchange.

Total monomer/water volume ratio

Total monomer/water volume ratio (M/W) was varied between 0.052–0.13 by fixing MAA/St and PEG-EEM/St volume ratios to 0.08 and 0.16. In these experiments, KPS concentration in the aqueous phase were 1.85 mmol/l. The polymerizations were performed for 24 h at 68 °C at 250 rpm stirring rate. The properties of latex particles are presented in Table 2. As seen here, no significant change was observed both in the latex yield and average size with the increasing total monomer

Table 2 The properties of carboxyl functionalized PS latexes produced with different monomer/water ratios

M/W (ml/ml)	C_T (wt%)	D_n (μm)	Strong acid		Weak acid	
			Q (meq/g) × 10^3	Q_s (μC/cm^2)	Q (meq/g) × 10^3	Q_s (μC/cm^2)
(SM5)^{a}9.30/180.0	78.3	0.32	21.2	11.5	175.0	94.6
(SM6) 14.1/180.0	81.6	0.32	11.8	6.4	189.6	102.4
(SM2) 18.6/180.0	85.4	0.31	5.7	3.0	170.5	89.2
(SM7) 23.4/180.0	84.8	0.32	5.6	3.1	166.7	90.1

M/W: Monomer/water ratio, C_T: Latex yield, D_n: Number average size, Q: Mass charge density, Q_s: Surface charge density

[a] Code of the polymerization is given within the parentheses in the first column

concentration in the studied range. It should be noted that either the latex yield or the average size markedly increased with the increasing total monomer concentration in the emulsion polymerization of styrene by using PEG-EEM as the stabilizer [41]. The presence of MAA in the same polymerization system prevented the effect of monomer volume on these parameters. The linear relation between the particle size and monomer volume in logarithmic coordinates, proposed by Smigol et al. for the emulsifier free emulsion polymerization of styrene, was not valid for St-PEG-EEM-MAA system [43]. However, the validity of the same relation was shown elsewhere for the emulsion copolymerization of styrene and PEG-EEM [41].

Based on the strong acid groups, higher total monomer concentrations provided latex particles with relatively lower mass and surface charge densities (Table 2). This behavior may be explained as follows. In these experiments, KPS feed concentration in the aqueous phase was kept constant at 1.85 mmol/l. Then the amount of initiator used per mass of total monomer decreased with the increasing monomer volume which in turn resulted in a decrease in the charge density originated from the strong acid groups. Either the mass or the surface charge densities for -COOH groups did not change significantly with the increasing total monomer concentration. This behavior may originate from the use of constant feed ratio for MAA/St and PEG-EEM/St in all experiments of this set.

Methacrylic acid concentration

In this set, MAA feed concentration was changed between 1.69 g/l and 27.1 g/l by fixing styrene and PEG-EEM concentrations to 75.25 g/l and 14.7 g/l, respectively. The initiator concentration was 1.85 mmol/l. The copolymerizations were performed for 24 h at 68 °C at 250 rpm stirring rate. The properties of produced latexes are presented in Table 3. As seen here, higher MAA concentrations led to higher latex yields. The variation of overall monomer conversion with time is given in Fig. 3 for different MAA feed concentrations. The polymerization rates were calculated based on these curves. The variation of polymerization rate with the MAA feed concentration is given in Fig. 4. As seen here, the polymerization rate increased with increasing MAA feed concentration. Similar tendencies for different emulsion polymerization systems including carboxylic comonomers were reported elsewhere [5, 9, 20, 44]. As also seen in Table 3, the average size markedly decreased with the increasing MAA concentration in the studied system. Some of the previously performed studies on the emulsion copolymerization of styrene with carboxyl carrying comonomers are summarized in Table 4 [5, 9, 20, 43]. In these studies, the data indicating the effect of carboxylic monomer concentration on the polymerization rate and the average particle size were available. By selecting the carboxylic monomer concentration as the independent variable, we also applied the power law model either to the polymerization rate or the average

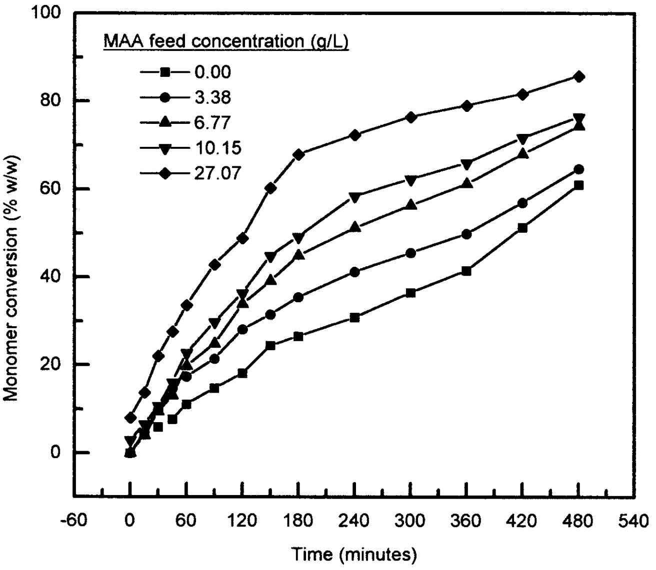

Fig. 3 The variation of overall monomer conversion with the time for different MAA feed concentrations

Table 3 The properties of carboxyl functionalized PS latexes produced with different MAA feed concentrations

C_{MAA} (g/l)	C_T (wt%)	D_n^a (μm)	Strong acid		Weak acid		P (A^2/COOH)
			Q (meq/g) × 10^3	Q_s (μC/cm^2)	Q (meq/g) × 10^3	Q_s (μC/cm^2)	
(S3)[b] 0.00	84.8	0.51	3.2	2.8	–	–	–
(SM8) 1.69	81.5	0.48	1.5	1.2	11.3	9.0	175.0
(SM9) 3.38	80.5	0.36	2.1	1.3	30.3	18.4	87.0
(SM2) 6.77	85.4	0.31	5.7	3.0	170.5	89.2	18.0
(SM10) 10.15	88.7	0.29	8.3	4.1	242.1	118.5	13.5
(SM11) 27.07	88.1	0.27(1.1886)	26.4	14.3	410.2	187.0	8.6

C_{MAA}: MAA feed concentration, C_T: Latex yield, D_n: Number average size, Q: Mass charge density, Q_s: Surface charge density

[a] Except for SM11, all samples were monodisperse, the polydispersity index of SM11 was given in the parentheses

[b] Code of the polymerization is given within the parentheses in the first column

particle size. Then the exponent values (n) of the power law relation were determined. The exponent values are given in Table 4 together with the coefficient of variation (r) values of the curve-fits performed. The determined r values indicated that the power law model was reasonably consistent with the reported data of the selected systems. For our study, higher exponent values relative to similar emulsion polymerization systems were obtained.

Then it may be concluded that the carboxylic monomer (i.e., MAA) concentration is a highly effective variable on both polymerization rate and average particle size in the emulsion copolymerization of St and MAA performed by using a short-chain polymerizable stabilizer (i.e., PEG-EEM). As stated in the literature, the effect of carboxylic acid monomer on the rate of an emulsion polymerization system including styrene was closely related to its hydrophobicity (i.e., distribution properties between the aqueous and styrene phases) [5]. MAA was found to be the most effective carboxylic monomer structure affecting the particle formation process under identical conditions relative to the other carboxylic comonomers (i.e., acrylic acid and itaconic acid) [5]. For this reason, comparison of our exponent values with those of the emulsion systems involving MAA clearly indicated the greater effect of MAA concentration both on the polymerization rate and final particle size when PEG-EEM was used as the stabilizer.

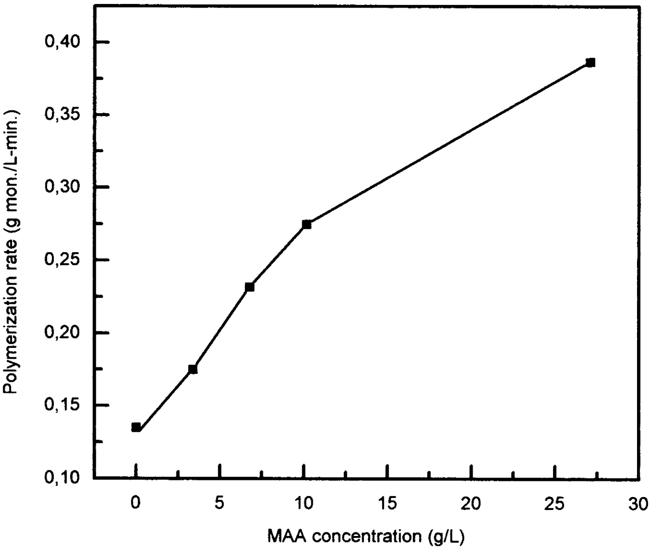

Fig. 4 The variation of polymerization rate with the MAA feed concentration

The variation of particle number density with the MAA feed concentration is sketched in logarithmic coordinates in Fig. 5. Only the polymerizations providing monodisperse particles were included in this plot. The exponent value for the power law dependency of particle number density on the MAA concentration was determined as 0.93334 ± 0.09359. This result indicated that approximately a linear relation between particle number density and methacrylic acid concentration was valid in the St-PEG-EEM-MAA emulsion polymerization system. By changing the MAA concentration in the polymerization medium, the relation obtained between the polymerization rate and the particle number density is as given in Fig. 6. As seen here, the polymerization rate increased linearly with the particle number density as described in the Smith-Ewart relation [45].

The variation of charge density originated from the strong acid groups with the MAA feed concentration is given in Table 3. As seen here, the mass charge density of strong acid groups increased linearly with the increasing MAA concentration. Although the average size decreased (i.e., the specific surface area increased) with the increasing MAA feed concentration, the surface charge density of strong acid groups also increased. In the presence of more MAA in the aqueous phase, the usability of free sulfate radicals by the MAA molecules increases because MAA is more hydrophilic component

Table 4 The determined exponent values (n) based on the power law relation between particle size/polymerization rate and carboxylic monomer concentration in different emulsion polymerization systems

Monomer	Hydrophobic comonomer	Carboxylic comonomer	Stabilizer	Exponent (n)	r	Reference
Dependent variable: Particle size						
Independent variable: Carboxylic comonomer concentration						
St	None	AA	LS	−0.12355 ± 0.01983	0.95847	9
St	Butadiene	ITA	None	−0.28183 ± 0.02093	0.99453	5
St	Butyl acrylate	MAA	None	−0.15980 ± 0.03019	0.96611	20
St	None	MAA	PEG-EEM	−0.27798 ± 0.03982	0.98009	Our work
Dependent variable: Polymerization rate						
Independent variable: Carboxylic comonomer concentration						
St	None	AA	None	0.31506 ± 0.04078	0.99173	44
St	None	AA	None	0.21009 ± 0.02768	0.98773	5
St	None	MAA	None	0.26595 ± 0.06331	0.98721	5
St	None	MAA	PEG-EEM	0.38128 ± 0.01272	0.99889	Our work

AA: Acrylic acid, ITA: Itaconic acid, LS: Lauryl sulfate

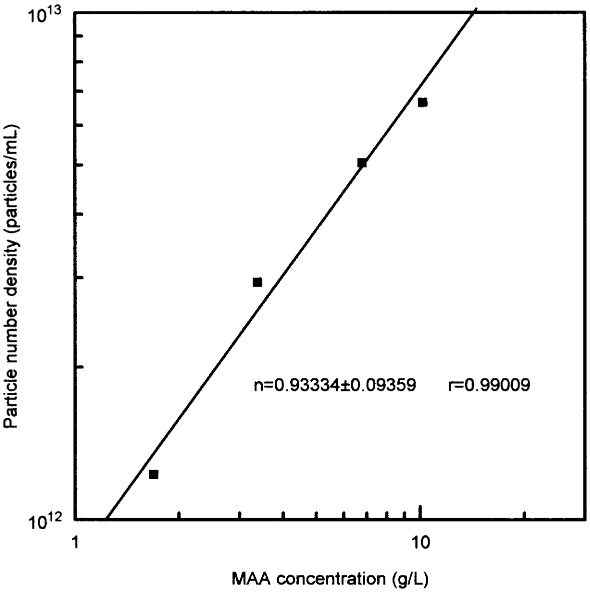

Fig. 5 The variation of particle number density with the MAA feed concentration in logarithmic coordinates

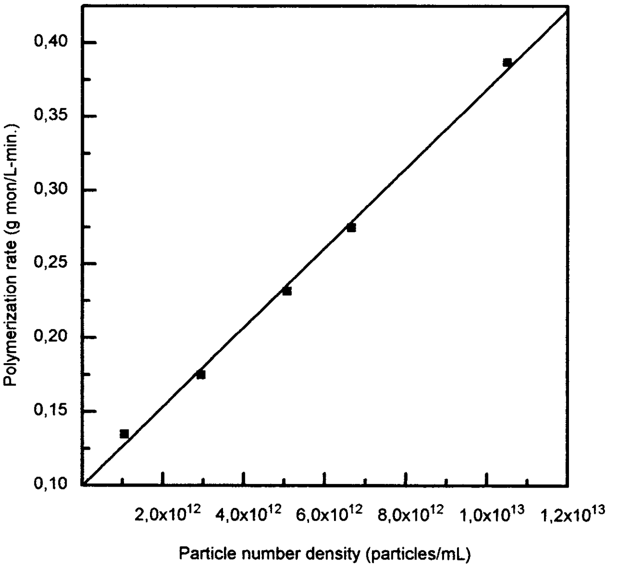

Fig. 6 The variation of polymerization rate with the particle number density in St-PEG-EEM-MAA system. The change in the particle number density was obtained by varying the MAA feed concentration

relative to styrene and PEG-EEM. This is probably the reason for the increase observed in the surface charge density of strong acid groups with the increasing MAA feed concentration.

Both the mass and surface charge densities originated from the weak acid groups (i.e., COOH) increased with the increasing MAA feed concentration. A similar result for the surface charge density of carboxyl groups was reported elsewhere for the emulsion terpolymerization of St, MAA, and butyl acrylate by Guillaume et al. [20]. As also seen in Table 3, the actual parking area of the carboxyl groups significantly decreased with the increasing MAA feed concentration. This probably leads to the better stabilization of final particles. A clear decrease in the actual parking area of carboxyl groups with the increasing concentration of carboxylic monomer was reported elsewhere for the emulsion copolymerization of St and acrylic acid [9].

MAA distribution after completion of the polymerization is shown in Table 5. Percent of MAA located on the particle surface – calculated based on the MAA fed into the reactor – increased with increasing MAA feed concentration. These values were determined by applying two different clean-up procedures (i.e., ion-exchange and successive centrifugation-decantation performed by using DDI water). The MAA percent values determined after applying the centrifugation-decantation method were given within the parentheses in the second column. These values were higher than those determined by ion-exchange cleaning because the centrifugation-decantation procedure likely gave the total MAA (i.e., physically adsorbed and covalently bound) on the particle surface while ion-exchange provided only the covalently bound fraction of MAA on the particle surface. Therefore the difference between these two values should be roughly considered as the fraction of non-grafted MAA on the particle surface.

The percent of MAA values remaining in the aqueous phase after polymerization was expressed in two different bases in the third column of Table 5. The values on the left side of this column were calculated based on the MAA fed into the reactor. These values decreased with increasing MAA feed concentration. On the other hand, the values given in parentheses were calculated by taking the ratio of the amount of MAA remaining in the aqueous phase to the total monomer mass charged into the reactor. Here, the base of total monomer mass was included because the same base was also used to express

Table 5 The effect of initial MAA concentration on the distribution of carboxyl groups after polymerization

C_{MAA} (g/l)	MAA on the particle surface (wt%)	MAA in the aqueous phase (wt%)	Solid content of aqueous phase (wt%)[a]
(SM8) 1.69	4.2 (4.3)[b]	25.4 (0.48)[c]	3.6
(SM9) 3.38	5.7 (9.9)[b]	11.8 (0.43)[c]	4.5
(SM3) 6.77	17.7 (20.8)[b]	5.6 (0.40)[c]	4.6
(SM10) 10.15	18.0 (25.3)[b]	5.7 (0.58)[c]	4.6
(SM11) 27.07	13.3 (19.9)[b]	6.1 (1.43)[c]	8.2

[a] These values were based on the total monomer mass fed into the reactor

[b] Weight percent of MAA on the particle surface determined after cleaning of particles by serum replacement

[c] Weight percent of MAA remained in the aqueous phase based on total monomer fed into the reactor

the solid content of the aqueous phase after polymerization. It should be noted that the rest of the MAA – not shown in Table 5 – were found both within the particles and coagulum obtained at the end of polymerization.

The ratio of solid material in the aqueous phase to the total monomer mass was given in the fourth column. As can be seen here, 3.6–8.2 wt% of total monomer mass were found in the aqueous phase by the conventional gravimetric analysis. Solid content of aqueous phase should be originated from the solution polymerization leading to the soluble polymeric products probably comprised of both homopolymer and copolymers of MAA. Order of magnitude of the solid material ratios calculated for the aqueous phase indicated that the "final soluble polymer yield" was reasonably lower to the latex yield in the studied system. The ratio of solid material in the aqueous phase was approximately constant when the ratio of MAA remaining in the aqueous phase to the total monomer mass did not change significantly (i.e., the values within the parentheses in the third column). Only for the last experiment was an appreciable increase observed in the ratio of solid material, in which the ratio of MAA remaining in the aqueous phase to the total monomer mass was higher. This increase probably originated from the solution polymerization taking place in the aqueous phase in the case of reasonably high MAA feed concentration. As also seen in Table 3, the final yield of latex particles was 80–90% in most of the experiments. The data collected in the preliminary experiments showed that approximately 5–10% of total monomer mass were found in the coagulum. By considering these data, it could be concluded that approximately 10–15 wt% of initial monomer mass were converted into the undesired polymeric products (i.e., coagulum and soluble polymer) in the emulsion copolymerization of styrene and MAA conducted in PEG-EEM. The mass balance obtained by considering the latex yield, the solid content of aqueous phase (i.e., soluble polymer), and the amount of coagulum indicated nearly quantitative conversions of monomer to polymer in most of the randomly selected experiments.

The effect of MAA feed concentration on the final latex properties were investigated without neutralizing the acidic comonomer (i.e., MAA) at the beginning of the polymerization Then, all polymerizations were initiated at the pH value originated from the amount of MAA fed into the polymerization medium. The initial pH value was very close to 2.0 in these polymerizations. The effects of neutralization degree of the acidic comonomer (i.e., MAA) on the average particle size and final latex yield were investigated in a separate set of experiments. To change the degree of neutralization of MAA, precalculated volumes of aqueous NaOH solution (5 wt%) were added to the initial polymerization medium. In this set, the other conditions were identical to those used in the polymerization encoded as SM2. Monodisperse particles were obtained with all neutralization degrees (i.e., CV < 1.001). The variation of average particle size and particle number density with the degree of neutralization of MAA is given in Fig. 7. Here, the final latex yields were also given. As can be seen here, complete neutralization of MAA provided a reasonably lower latex yield. Particle size increased and

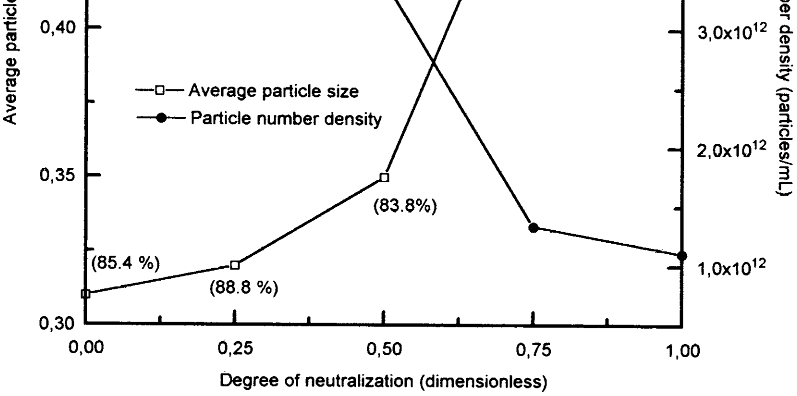

Fig. 7 The effects of degree of neutralization of MAA on the size and particle number density of final latexes. The final latex yields (wt%) were given within the parentheses on the points indicating average size

particle number density decreased as the degree of neutralization of MAA increased. These results may be attributed to a decrease in the polymerization rate with the increasing degree of neutralization. It should be noted that similar tendencies were also reported and explained for the conventional emulsion copolymerization systems including St and MAA or AA [8, 9, 13, 22].

PEG-EEM feed concentration

To investigate the effect of PEG-EEM feed concentration on the size and surface properties of latex particles, two separate sets of experiments were designed. In each set, PEG-EEM feed concentration was varied within the range 0.0–22.1 g/l. MAA feed concentration was fixed at 6.77 g/l and 10.15 g/l, in the first and second set of polymerizations, respectively. In both of these sets, KPS and St concentrations were fixed at 1.85 mmol/l, 75.25 g/l, respectively. The polymerizations were performed for 24 h at 68 °C at 250 rpm stirring rate. The properties of produced latexes are given in Table 6. By changing the PEG-EEM feed concentration in the above range, and by using identical polymerization conditions, a separate set of polymerization were also performed in the absence of MAA. The properties of St-PEG-EEM copolymer latexes produced by this set are given in Table 7. In the presence of MAA, no significant change was observed in the final monomer conversion with the increasing PEG-EEM concentration (Table 6). This behavior was observed for both of the studied MAA feed concentrations. However, an appreciable effect of PEG-EEM feed concentration on the final monomer conversion was detected for the emulsion copolymerizations performed in the absence of MAA. To investigate the kinetic behavior, the variation of overall monomer conversion with the polymerization time was determined both in the absence and existence of MAA with different PEG-EEM feed concentrations. The monomer conversion-time curves obtained in the absence and presence of MAA are given in Fig. 8.

Polymerization rates calculated based on the data given in Fig. 8 are sketched against PEG-EEM feed concentration in Fig. 9. The variation of particle number density with the PEG-EEM feed concentration was also compared for both cases in Fig. 10. As expected, either the polymerization rate or the particle number density increased with the increasing polymerizable stabilizer (i.e., PEG-EEM) concentration in the absence of MAA (Figs. 9 and 10). Similar tendencies were also reported elsewhere for the emulsion polymerization systems containing a hydrophobic monomer (i.e., mostly styrene) and a polyethylene oxide-based polymerizable stabilizer (i.e., polyethylene glycol methacrylate, polyethylene glycol methylether methacrylate, etc.) [33]. To quantify the behavior of selected polymerizable stabilizer (i.e., PEG-EEM) in the polymerizations performed in the absence of MAA, the power law model was applied. The results are given in Table 8. As seen here, the exponent value (*n*) for the dependency of polymerization rate to the PEG-EEM feed concentration was found to be 0.30993 ± 0.07248. A positive exponent value is usually an expected result for the power law relation between the polymerization rate and stabilizer concentration. In the study performed by Brown et al., the emulsion polymerization of styrene in

Table 7 The properties of PS latexes produced with different PEG-EEM feed concentrations

$C_{PEG\text{-}EEM}$ (g/l)	C_T (wt%)	D_n (μm)	Strong acid ($-OSO_3^-$)	
			Q(meq/g) × 10^3	Q_s(μC/cm^2)
(S1)[a] 0.00	80.5	0.69(1.040)	8.5	9.9
(S2) 7.37	85.3	0.58	5.1	5.0
(S3) 14.73	84.8	0.51	3.2	2.8
(S4) 22.10	94.9	0.46	1.4	1.1

$C_{PEG\text{-}EEM}$: PEG-EEM feed concentration, C_T: Latex yield, D_n: Number average size, Q: Mass charge density, Q_s: Surface charge density. The polydispersity index value of S1 was included within the parentheses in the third column

[a] Code of the polymerization is given within the parenthesis in the first column.

Table 6 The properties of carboxyl functionalized PS latexes produced with different PEG-EEM feed concentrations

$C_{PEG\text{-}EEM}$ (g/l)	C_T (wt%)	D_n (μm)	Strong Acid		Weak Acid	
			Q(meq/g) × 10^3	Q_s(μC/cm^2)	Q(meq/g) × 10^3	Q_s(μC/cm^2)
(SM12)[a] 0.00	86.1	0.16	25.5	6.9	112.2	30.3
(SM13) 7.37	85.0	0.32	9.1	4.9	159.1	86.0
(SM2) 14.73	85.4	0.31	5.7	3.0	170.5	89.3
(SM14) 22.10	87.4	0.34	4.4	2.6	131.6	75.6
(SM15) 0.00	87.5	0.16	33.7	9.1	238.7	64.5
(SM16) 7.37	86.5	0.18	21.6	6.6	280.1	85.1
(SM17) 14.73	88.1	0.24	9.2	3.7	262.4	106.3
(SM18) 22.10	88.4	0.28	5.6	2.7	253.5	119.8

$C_{PEG\text{-}EEM}$: PEG-EEM feed concentration, C_T: Latex yield, D_n: Number average size, Q: Mass charge density, Q_s: Surface charge density

[a] Code of the polymerization is given within the parentheses in the first column

the presence of EO containing macromonomers having different chemical structures was investigated [33]. Among them, the exponent value of 0.47 ± 0.02 was obtained with the most similar structure to the polymerizable stabilizer used in our study, polyethylene glycol methyl ether methacrylate [33]. As also seen in Table 8, the particle size decreased with increasing PEG-EEM feed concentration and this tendency gave the exponent value of –0.20836 ± 0.01804 for the power law relation between the average particle size and PEG-EEM feed concentration.

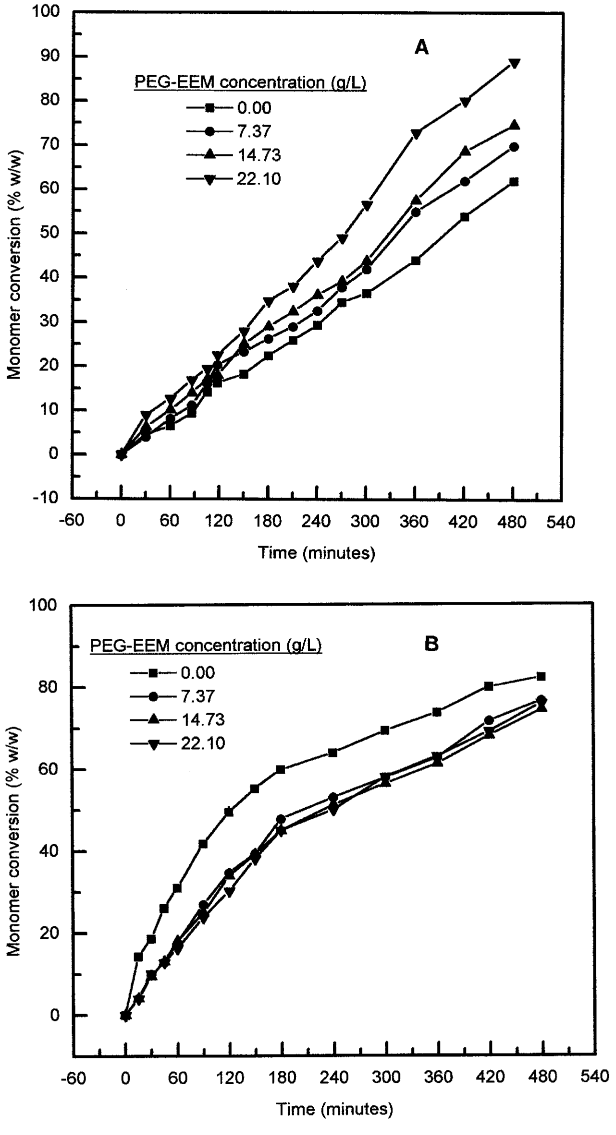

Fig. 8A, B The variation of monomer conversion with the time for different PEG-EEM feed concentrations: **A** in the absence of MAA; **B** MAA feed concentration 6.77 g/l

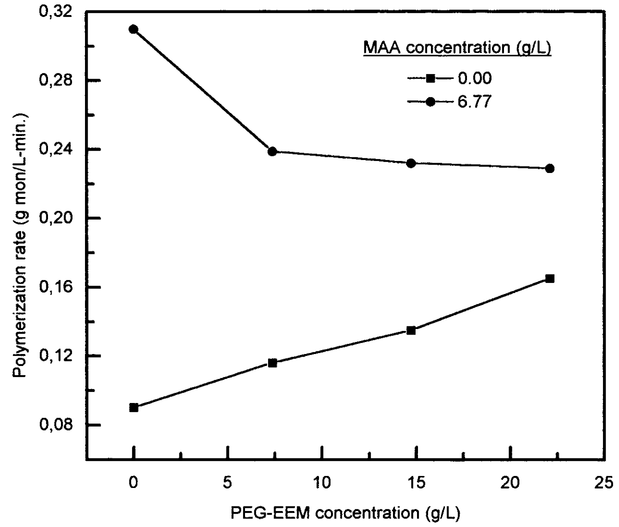

Fig. 9 The variation of polymerization rate with the PEG-EEM feed concentration in the absence and presence of MAA

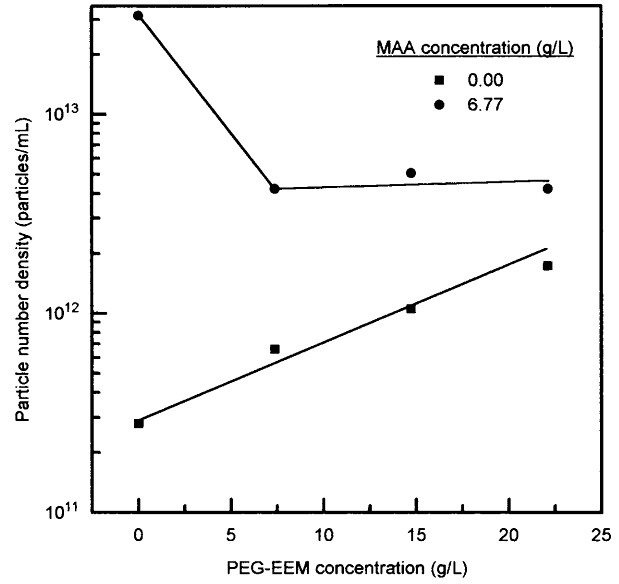

Fig. 10 The variation of particle number density with the PEG-EEM feed concentration in the absence and presence of MAA

Table 8 The exponent values determined by the application of power law model on the data collected from the emulsion copolymerization of St and PEG-EEM

Independent variable	Dependent variable	Exponent (*n*)	Coefficient of variation (r)
PEG-EEM concentration	Polymerization rate	0.30993 ± 0.07248	0.97373
PEG-EEM concentration	Particle number density	0.85528 ± 0.14737	0.98548
PEG-EEM concentration	Average particle size	–0.20836 ± 0.01804	0.99627

However, the behavior of PEG-EEM in the presence of MAA was reasonably interesting. In this case, lower polymerization rates were obtained with the PEG-EEM containing formulations relative to that observed with St-MAA system (Fig. 9). In other words, the introduction of PEG-EEM into the emulsion polymerization system including St and MAA resulted in an increase in the average particle size (Table 6) and a decrease in the particle number density (Fig. 10). It should be noted that all these tendencies were contrary to the behavior observed with the St-PEG-EEM system. In the presence of MAA, both the polymerization rate and the particle number density (also the particle size) seemed independent of PEG-EEM feed concentration (Figs. 9 and 10). Then it is not meaningful to apply the power law model for the variations of polymerization rate, particle number density, and average size with the PEG-EEM feed concentration. The variation of polymerization rate with the particle number density is given in Fig. 11 both for St-PEG-EEM and St-PEG-EEM-MAA systems. As seen here, lower particle number densities and polymerization rates were obtained with the St-PEG-EEM system in which the polymerization rate linearly increased with the increasing particle number density (i.e., the increasing PEG-EEM concentration). This behavior was also consistent with the Smith-Ewart relation [45]. However, the points obtained with different PEG-EEM concentrations in St-PEG-EEM-MAA system were accumulated in a certain region of this graph (i.e., three points located at the high left corner). The point belonging to the St-MAA system located at the right corner (i.e., PEG-EEM free emulsion copolymerization of St and MAA) was reasonably far from these points. Then, a linear relation between the polymerization rate and particle number density could not be observed by changing the PEG-EEM feed concentration in St-PEG-EEM-MAA system.

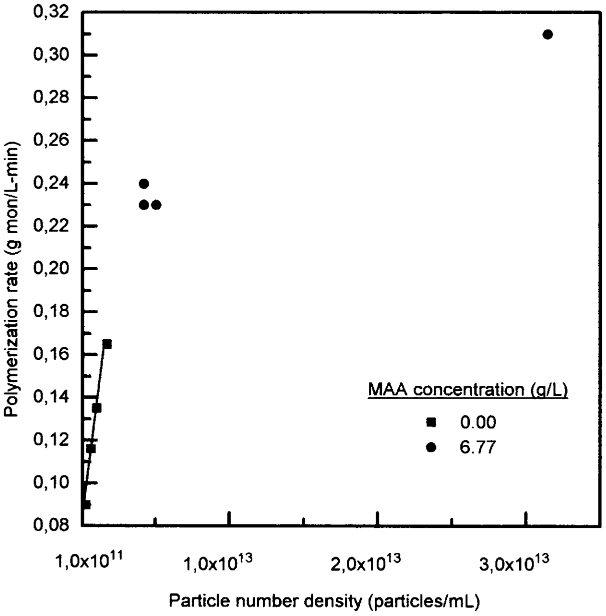

Fig. 11 The variation of polymerization rate with the particle number density in St-PEG-EEM and St-PEG-EEM-MAA systems. The change in particle number density was obtained by varying the PEG-EEM feed concentration in both system

As seen in Table 6, the introduction of PEG-EEM into the emulsion copolymerization of St and MAA resulted in a significant decrease both in the mass and surface charge densities of strong acid groups. It should be noted that a similar tendency was also obtained in the emulsion copolymerization system including only St and PEG-EEM (Table 7). For the emulsion polymerization system including only St and PEG-EEM, this behavior was explained by the nucleation of fewer number of oligomer chains having longer chain length with the increasing PEG-EEM feed concentration [41]. For the weak acid groups, the lowest mass and surface charge densities were obtained by the St-MAA system in the absence of PEG-EEM (Table 6).

In both sets, the mass and especially surface charges of the particles produced by using PEG-EEM were higher relative to those obtained without using PEG-EEM. These results indicated that the use of PEG-EEM in the emulsion copolymerization led to the preparation of uniform latex particles with higher MAA contents relative to those obtained by the conventional emulsion copolymerization of St and MAA (i.e., polymerizations encoded as SM12 and SM15). Although MAA is infinitely soluble within water, the solubility of PEG-EEM is around 4 wt% [41]. Then PEG-EEM is more hydrophilic than styrene, but more hydrophobic than MAA. Owing to the solubility properties of the monomeric components, the interaction possibility of MAA rich-radicals formed in the aqueous phase with the PEG-EEM molecules is probably higher relative to the other hydrophobic monomer (i.e., styrene). To establish this conclusion, the carboxyl content of aqueous medium was determined after completion of the polymerization and is given in Table 9. Here, all values were expressed based on the amount of MAA fed into the reactor. For the fraction

Table 9 The effect of PEG-EEM feed concentration on the distribution of carboxyl groups

$C_{PEG\text{-}EEM}$ (g/l)	MAA in the aqueous phase wt%	MAA on the particle surface wt%
(SM12) 0.0	12.7	10.1
(SM13) 7.37	5.8	15.3
(SM2) 14.73	5.6	17.7
(SM14) 22.10	6.4	15.0
(SM15) 0.0	17.6	15.1
(SM16) 7.37	9.4	18.9
(SM17) 14.73	5.8	19.4
(SM18) 22.10	6.5	20.1

of MAA remaining in the aqueous medium, reasonably lower values were obtained in both sets with the polymerizations performed in the existence of PEG-EEM. The use of PEG-EEM also provided an increase in the carboxyl groups covalently bound onto the surface. Note that the MAA percent on the particle surface was determined after cleaning of latex particles by ion-exchange. Hence, these values probably indicated the covalently bound fraction of MAA. These results showed that the transport of MAA rich-radicals from the aqueous phase to the forming particles became easier when PEG-EEM was included in the copolymerization recipe.

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