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Emulsion copolymerization of styrene and poly(ethylene glycol) ethyl ether methacrylate

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Abstract

In this study, a relatively novel macromonomer having a relatively shorter chain length, poly(ethylene glycol) ethyl ether methacrylate (PEG-EEM) was used to increase the stability of styrene–water emulsion. The uniform latex particles in the range of 0.4–1.2 μm were prepared by the emulsion copolymerization of styrene (S) and PEG-EEM. The copolymerizations were achieved by using potassium persulphate (KPS) as the initiator in an aqueous emulsion medium including NaCl. To achieve uniform copolymer particles with different size and surface properties, PEG-EEM/S volume ratio, KPS concentration, monomer/water ratio and NaCl concentration were changed. The results indicated that the average particle size decreased with the increasing PEG-EEM/S ratio. Higher PEG-EEM/S ratios provided copolymer latex particles with higher yield and higher monodispersity. The copolymer latex particles with lower mass and surface charge densities were obtained with the higher PEG-EEM/S ratios. The power law dependency of particle number density on the PEG-EEM concentration was also determined. The average particle size increased with the increasing KPS and NaCl concentrations. Excess KPS or NaCl concentrations led to copolymer latex particles with a bimodal size distribution. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Styrene; Polyethylene glycol; Polyethylene glycol methacrylate

1. Introduction

Various emulsion and dispersion copolymerization procedures were proposed for the production of polystyrene latex particles carrying polar functional groups on their surfaces. In these methods, styrene was copolymerized with the highly water soluble, acrylate based monomers by applying single or multi-step polymerization procedures providing latex particles usually comprised of a hydrophobic core and a hydrophilic surface layer [1–5].

The steric stabilizers called as "protective colloids" (i.e. poly(vinyl alcohol), poly(ethylene oxide) (PEO), poly(vinylpyrrolidone), cellulose and starch derivatives) also stabilize the polymer dispersions in aqueous phase by forming a dense protective layer on the latex particles [6]. The surface layer can be formed by the physical adsorption of the steric stabilizer onto the forming latex particles [7]. The chemical bonding of the steric stabilizer onto the colloidal surface by a grafting reaction is another mechanism for the formation of protective surface layer [8]. The irreversible chemical bonding of the polymeric stabilizer onto the latex particles provides an increased stability termed as "Enchanced Steric Stabilization" [9]. An important group of steric stabilizers utilized in emulsion polymerization are the macromonomers with PEO chains modified with terminally attached polymerizable groups. Poly(ethyleneglycol) methylether methacrylate (PEG-MEM) with 40 ethylene oxide units was tried as a polymerizable stabilizer in an emulsion polymerization of styrene [10,11]. The polystyrene latexes stabilized by PEG-MEM were found to be very stable to the addition of electrolyte [12]. The flocculation behaviour of polystyrene latex anchored with PEO chains was also investigated in the existence of PEO as a free polymer [13]. The micelle formation properties of a PEO based macromonomer including eight ethylene oxide (EO) units with ω-methacrylate end group and its polymers were determined [14,15]. In the another study performed by Brown et al., different types of non-ionic water-soluble polymers and macromonomers with PEO chains modified with terminally attached polymerizable groups were investigated as steric stabilizers in the batch emulsion polymerization of styrene [6]. Poly(ethylene glycol) methylether macromonomers carrying terminal *p*-styrylalkyl groups were also utilized in the preparation of uniform latex particles by emulsion or dispersion copolymerization with a large excess of styrene or butyl methacrylate [16,17]. Recently, Ottewill reviewed the colloidal behaviour of the

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latex particles stabilized by the polymerizable surfactants carrying EO units [18]. Various direct dispersion polymerization procedures using an oil soluble initiator for the synthesis of PEO carrying latex particles were also proposed [19–21]. Recently, a direct dispersion copolymerization procedure was obtained for producing latex particles made of styrene and PEO macromonomers carrying methoxy group on one (α-) end methacryloyloxyhexyl or methacryloyloxydecyl group on the other (ω-) end [22].

In this study, a reasonably novel macromonomer having a relatively shorter chain-length, poly(ethyleneglycol) ethyl ether methacrylate (PEG-EEM) was used for the synthesis of uniform polystyrene particles carrying polyethylene glycol residues. A single step method (i.e. emulsion copolymerization) was proposed for the production of uniform styrene–PEG-EEM particles. The effect of polymerization conditions on the monomer conversion, the average size, the size distribution and the charge density of the copolymer particles were investigated.

2. Experimental

2.1. Materials

Styrene (Yarpet AS, Turkey) was distilled under vacuum before use. PEG-EEM (Average M_n for the whole molecule: ca. 246, number of ethylene oxide units: ~3, Aldrich Chem. Co., Milwaukee, WI) was used without further purification. Potassium persulphate (KPS, Analar grade, BDH Chemicals Ltd., Poole, UK) was selected as the initiator. The ionic strength of aqueous polymerization medium was adjusted by sodium chloride (Merck AG, Darmstad, Germany).

2.2. Emulsion copolymerization

The emulsion copolymerizations were performed in the sealed cylindrical reactors (volume: 150 ml) placed in a shaking water bath equipped with a temperature control system. A typical procedure for the emulsion copolymerization of styrene and PEG-EEM is presented below: 5 ml styrene and 1 ml PEG-EEM were added into 45 ml of aqueous KPS solution (0.44 mg/ml) in a polymerization reactor. The reactor was purged with bubbling nitrogen for 5 min. The sealed reactor was placed into a shaking water bath at room temperature. The emulsion copolymerization was conducted for 24 h with 200 cpm shaking rate at a temperature of 68 ± 0.2°C.

2.3. Characterization of latex particles

The average size and the size distribution latex particles were evaluated by scanning electron microscopy as described elsewhere [4]. The number of average diameter (D_n) of the latex particles was calculated according to Eq. (1); where, N_i is the number of particles in diameter D_i (nm). The polydispersity index (U) was calculated by Eq. (2).

$$D_n = \sum N_i D_i / \sum N_i, \tag{1}$$

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

In Eq. (2), D_w is the weight average diameter of latex particles calculated by Eq. (3).

$$D_w = \left\{ \sum N_i D_i^6 / \sum N_i D_i^3 \right\}^{1/3}. \tag{3}$$

The particle number density (N_p, in particles per ml of water) was calculated according to Eq. (4) [6]; where, D_n is the number-average particle diameter, X_m is the fractional conversion of total monomer (i.e. styrene and PEG-EEM), M_0 is the total amount of both monomers initially charged per ml of water, and ρ_p is the density of copolymer particles. The density was determined for several latex samples by a picnometric method and 1.05 g/ml was used as an average value for the calculation of N_p in all samples.

$$N_p = 6 M_o X_m / (\pi D_n^3 \rho_p). \tag{4}$$

The latex yield was determined by using a gravimetric procedure. After polymerization, the 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 centrifuge. 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.

The charge density of the copolymer latex particles were determined by a potentiometric titration method [23]. The latex suspension (30 ml) was treated with 6 g of ion exchange resin mixture consisting of equal mass of Dowex, G55-OH anion exchange resin (OH type) and Dowex, 50WX2-200 cation exchange resin (H type), (Aldrich Chem. Co.) in a magnetic stirrer. After the ion exchange, pH of latex suspension was brought to 3.0 by adding 0.01 N HCl solution. The resulting suspension was titrated with 0.005 N NaOH solution, potentiometrically. A titration was also performed with an equal volume of blank solution having the same pH (i.e. 3.0). 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 latex particles were calculated.

3. Results and discussion

The macromonomers with relatively longer PEO chains have been tried as the polymerizable stabilizers in the emulsion or dispersion copolymerization systems [6,10–12,

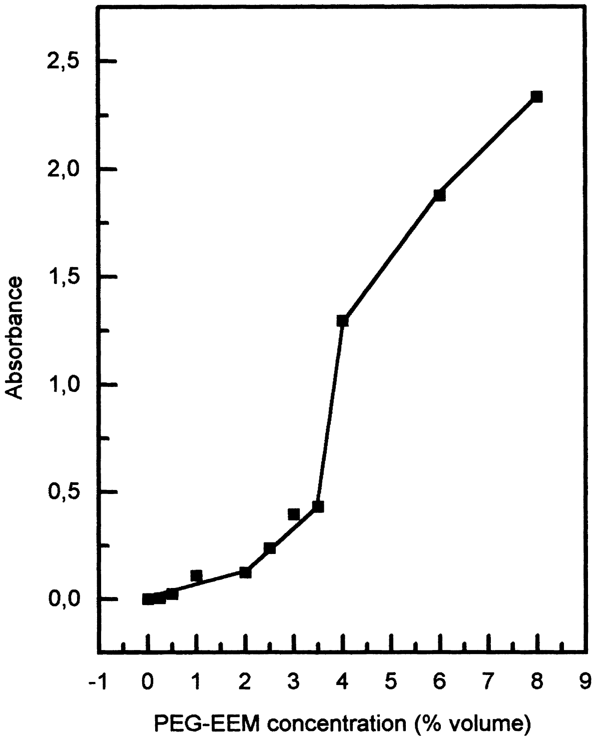

Fig. 1. The variation of absorbance of PEG-EEM–water mixtures with the PEG-EEM concentration ($\lambda = 500$ nm).

16–22]. The number of EO units in the macromonomers utilized in the emulsion polymerization of styrene were approximately 40–45 [6,10–12]. In our study, the macromonomer selected as the polymerizable stabilizer (PEG-EEM) includes only three EO units. Therefore, the length of the PEO chain in the macromonomer is reasonably shorter relative to previously examined structures. In other words, the weight ratio of the polymerizable hydrophobic group (i.e. methacrylate) to the more hydrophilic chain (i.e. PEO) is higher in the selected macromolecule, which affects either the solubility or the copolymerization characteristics. To have an idea about the behaviour of a polymerizable stabilizer having relatively shorter PEO chain length, PEG-EEM was tried in the emulsion polymerization of styrene. Then, this study allowed the comparison of examined behaviour with previously tried macromonomers with longer PEO chains [18].

In our study, the solubility characteristics of PEG-EEM and the stability of styrene–water emulsions in the existence of PEG-EEM were investigated. To have an idea about the solubility of PEG-EEM in distilled water, the absorbances of PEG-EEM–water mixtures prepared with different PEG-EEM concentrations were measured in a UV–Vis spectrophotometer at a wavelength of 500 nm. To achieve the solubilization/emulsification of PEG-EEM in water, the prepared mixtures were sonicated at 200 W for 5 min before recording the absorbance value. The variation of absorbance of PEG-EEM–water mixtures with the PEG-EEM concentration is given in Fig. 1. The aqueous PEG-EEM mixtures containing PEG-EEM up to 3.5% (v/v) were mainly transparent. It could be stated that the maximum solubility of PEG-EEM in water was around 3.5% (v/v). However, a sudden increase in the absorbance (also indicating a sudden increase in the turbidity of aqueous mixture) was detected at 4.0% (v/v) PEG-EEM concentration. The aqueous PEG-EEM mixtures prepared with the PEG-EEM concentrations higher than 4.0% (v/v) were in the form of a typical emulsion.

The effect of PEG-EEM concentration on the stability of styrene–water emulsion was also examined. In these group of experiments 5 ml of styrene was emulsified with distilled water (45 ml) by including PEG-EEM at different concentrations ranging from 0 to 4.4% by volume. The emulsions were prepared within the cylindrical glass tubes by ultrasonication of the styrene–water mixtures at 200 W for 3 min. By the breaking of the emulsion, the height of the light phase increased. Then, the breaking of emulsion could be expressed by the determination of the appeared fraction of the light phase (including styrene and PEG-EEM) on the photographs taken at different time values. This parameter was calculated by taking the ratio of the height of the light phase at any time to the height of the light phase after complete separation of two phases (i.e. at infinite time). The behaviour of emulsions are quantified in Fig. 2(A). Here, the variation of the appeared fraction of the light phase was plotted against the time for the each emulsion. The water–styrene emulsion was rapidly broken within about 5 min in the absence of PEG-EEM. However, the formation rate of the light phase decreased with the increasing PEG-EEM concentration. In other words, the breaking rates of emulsions prepared with different PEG-EEM concentrations were reasonably slower relative to the emulsion including no PEG-EEM. Note that, the breaking rate of water–styrene emulsion prepared with 4.4% (v/v) of PEG-EEM concentration was slower relative to the others. This concentration was slightly higher than that in which a sudden increase in the turbidity of the water–PEG-EEM mixture was observed. These results indicated the stability of water–styrene emulsion increased with the increasing PEG-EEM concentration.

The effect of PEG-EEM on the stability of styrene–water emulsion was also studied with an emulsion medium including NaCl at a concentration of 15.2 mM. The same method with the previous one was used and the PEG-EEM concentration in the emulsion medium was changed between 0.0 and 4.4% (by volume). The variation of the appeared fraction of the light phase with the time for the styrene–water emulsions prepared by including NaCl and with different PEG-EEM concentrations are given in Fig. 2(B). As seen here, the formation rate of the light phase for the emulsions prepared with 1.1 and 2.2% of PEG-EEM (i.e. the breaking rate of emulsion) was close to that observed with the emulsion including no PEG-EEM. This behaviour possibly originated from the strong salt-out effect of NaCl present in the emulsion medium. However, the styrene–water emulsion

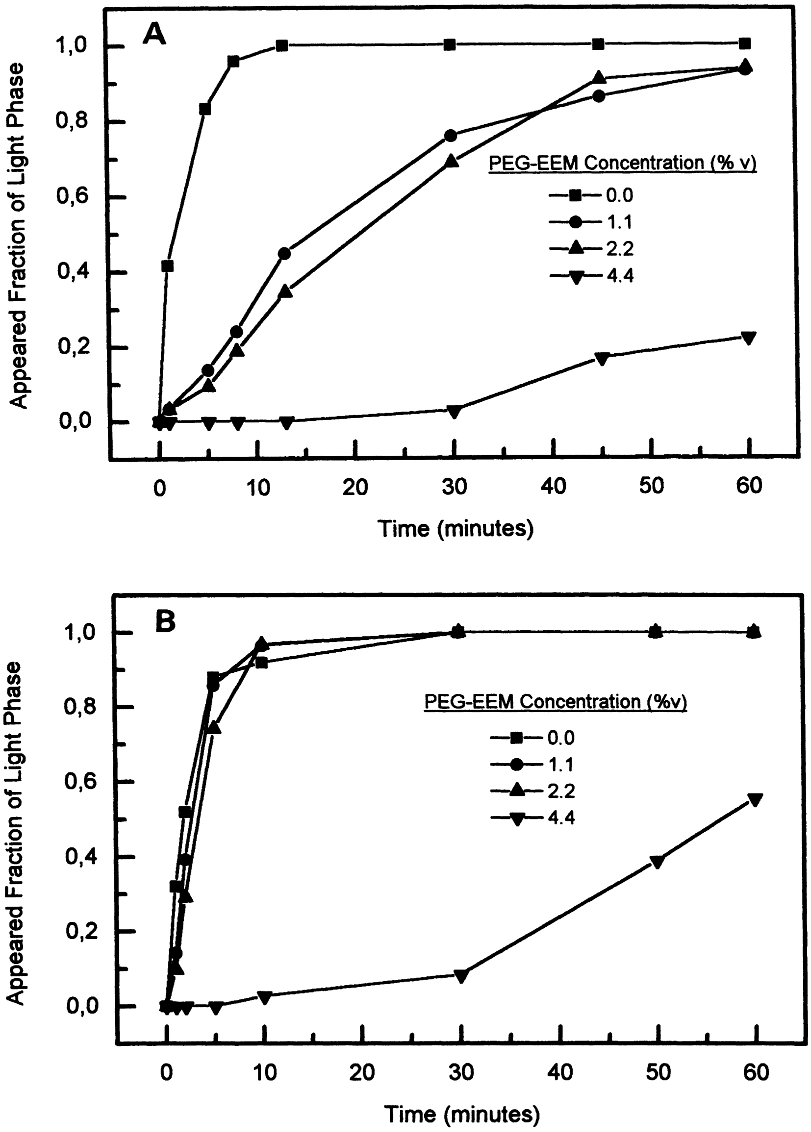

Fig. 2. The variation of appeared fraction of the light phase with the time during the breaking of styrene–water emulsions prepared with different PEG-EEM concentrations. Medium Type (A) No salt, (B) 15.2 mM NaCl.

prepared with 4.4% PEG-EEM was reasonably stable in this case. These results again indicated that the stability of styrene–water emulsion increased by the introduction of PEG-EEM into the emulsion medium including NaCl. To use this property of PEG-EEM in the emulsion polymerization of styrene, several sets of experiments were designed. In the emulsion copolymerization experiments, the concentrations of initiator, styrene and PEG-EEM were changed to prepare the latex particles with different size and surface properties. The effects of copolymerization conditions on the properties of latex particles are presented below.

3.1. Macromonomer/styrene (PEG-EEM/S) volume ratio

The effects of PEG-EEM/S volume ratio on the size and surface properties of the copolymer latex particles were investigated both in the absence and existence of electrolyte (i.e. NaCl). For this purpose, four sets of experiments were designed with different combinations of experimental variables. In the first set, KPS concentration was fixed to a low value (i.e. 1.64 mM) in the aqueous emulsion medium including no salt. Here, PEG-EEM/S volume ratio was changed between 0.05 and 0.30 ml/ml by fixing the styrene concentration to 11.1% (by volume). The properties of the produced latexes are presented in Table 1. Note that, PEG-EEM concentration in the aqueous medium was also given within the parentheses in the first column of Table 1. In the second set, PEG-EEM/S volume ratio was changed in the above range in the presence of a higher initiator concentration (3.28 mM) in an emulsion medium also including no salt. Here, a poly(styrene) latex was also synthesized in the absence of PEG-EEM as a reference material for the evaluation of copolymer latexes produced in this set. The properties of latex particles are also presented in Table 1. In the

Table 1
The properties of latex particles produced by different PEG-EEM/S ratios (the concentration of PEG-EEM in the emulsion medium (% (v/v)) was given in the parentheses)

PEG-EEM/S (ml/ml)	C_T (%)	D_n (nm)	U (D_w/D_n)	Q (meq/g) × 10^3	Q_s (μC/cm^2)
First set conditions: No salt, KPS: 1.64 mM, S: 11.1% (v/v)					
0.05 (0.56)	72.8	1209	1.031	10.9	22.1
0.20 (2.22)	94.0	824	1.001	7.16	9.92
0.30 (3.33)	86.2	580	1.003	8.26	8.05
Second set conditions: No salt, KPS: 3.28 mM, S: 11.1% (v/v)					
0.00 (0.00)	60.2	1192	1.009	25.9	51.8
0.05 (0.56)	74.9	1349	1.016	17.6	39.9
0.10 (1.11)	81.6	777	1.014	7.71	10.1
0.20 (2.22)	77.7	583	1.005	6.25	6.11
0.30 (3.33)	71.1	541	1.002	6.78	6.16
Third set conditions: NaCl: 15.2 mM, KPS: 3.28 mM, S: 11.1% (v/v)					
0.00 (0.00)	86.4	936	1.041	5.61	8.82
0.10 (1.11)	88.4	1125	1.025	3.68	6.95
0.20 (2.22)	84.7	1248	1.002	3.57	7.49
0.30 (3.33)	78.8	854	1.021	2.72	3.90
0.40 (4.44)	61.0	825	1.009	3.43	4.76
Fourth set conditions: NaCl: 15.2 mM, KPS: 3.28 mM, S: 2.22% (v/v)					
0.00 (0.00)	56.0	684	1.003	75.1	86.3
0.05 (0.11)	87.0	580	1.007	31.2	30.5
0.10 (0.22)	91.9	579	1.005	31.3	30.4
0.20 (0.44)	80.2	456	1.004	29.2	22.4
0.40 (0.88)	74.8	459	1.002	44.6	34.4

first set, the latex yield was lower with the lowest PEG-EEM/S ratio (i.e. 0.05 ml/ml) relative to the other runs. Higher latex yields were obtained when PEG-EEM was included in the emulsion copolymerization recipe. In the second set, the behaviour for the latex yield was also similar to that of the first one. The lowest latex yield was obtained with the latex produced in the absence of PEG-EEM. The latex yields achieved with different PEG-EEM/S ratios were reasonably higher relative to the yield obtained in the absence of PEG-EEM. However, the formation of significant amount of coagulum (21% of the total monomer mass) in the last run of the second set performed with the PEG-EEM/S ratio of 0.30 ml/ml caused a decrease in the latex yield.

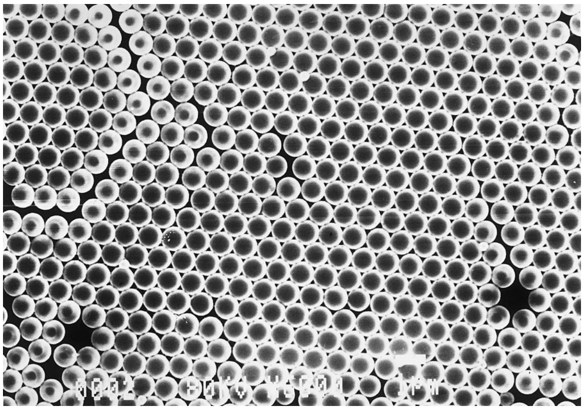

Fig. 3. SEM photograph of the monodisperse styrene–PEG-EEM copolymer latex particles, Magnification: 6000 ×, Polymerization conditions; KPS:1.64 mM, No NaCl, S: 11.1% (v/v), PEG-EEM/S:0.20 ml/ml.

These findings indicated that the introduction of PEG-EEM into the emulsion polymerization of styrene resulted in an increase in the overall monomer conversion when PEG-EEM/S ratio was kept at a suitable level. This increase may be explained by considering two factors: the first one is possibly related to the solubility of monomers. The solubility of PEG-EEM in the aqueous medium is reasonably higher relative to styrene. This factor makes the initiation of the copolymerization in the aqueous medium in the presence of a water-soluble initiator (KPS) easier; the second factor causing an increase in the monomer conversion is possibly related to the emulsification function of PEG-EEM. As emphasized previously, the stability of styrene–water emulsion increased with the increasing PEG-EEM concentration. In other words, the introduction of PEG-EEM into the styrene–water mixture resulted in a significant reduction in the size of organic phase droplets within the aqueous phase. Either the number or the total surface area of the monomer stock droplets increases with the decreasing droplet size. Both of them make easier the monomer diffusion from the stock droplets to the forming latex particles at the late stages of the emulsion copolymerization process. As a result of these two reasons, the monomer conversion was possibly higher in the existence of PEG-EEM. As seen in Table 1, PEG-EEM also affected the monodispersity of latex particles. Higher polydispersity index values indicating wider size distributions were calculated for the latex particles produced without using PEG-EEM or with the lower PEG-EEM/S ratio (i.e. 0.05 ml/ml) both in the first and second sets of runs (Table 1). Highly monodisperse copolymer particles were obtained with the

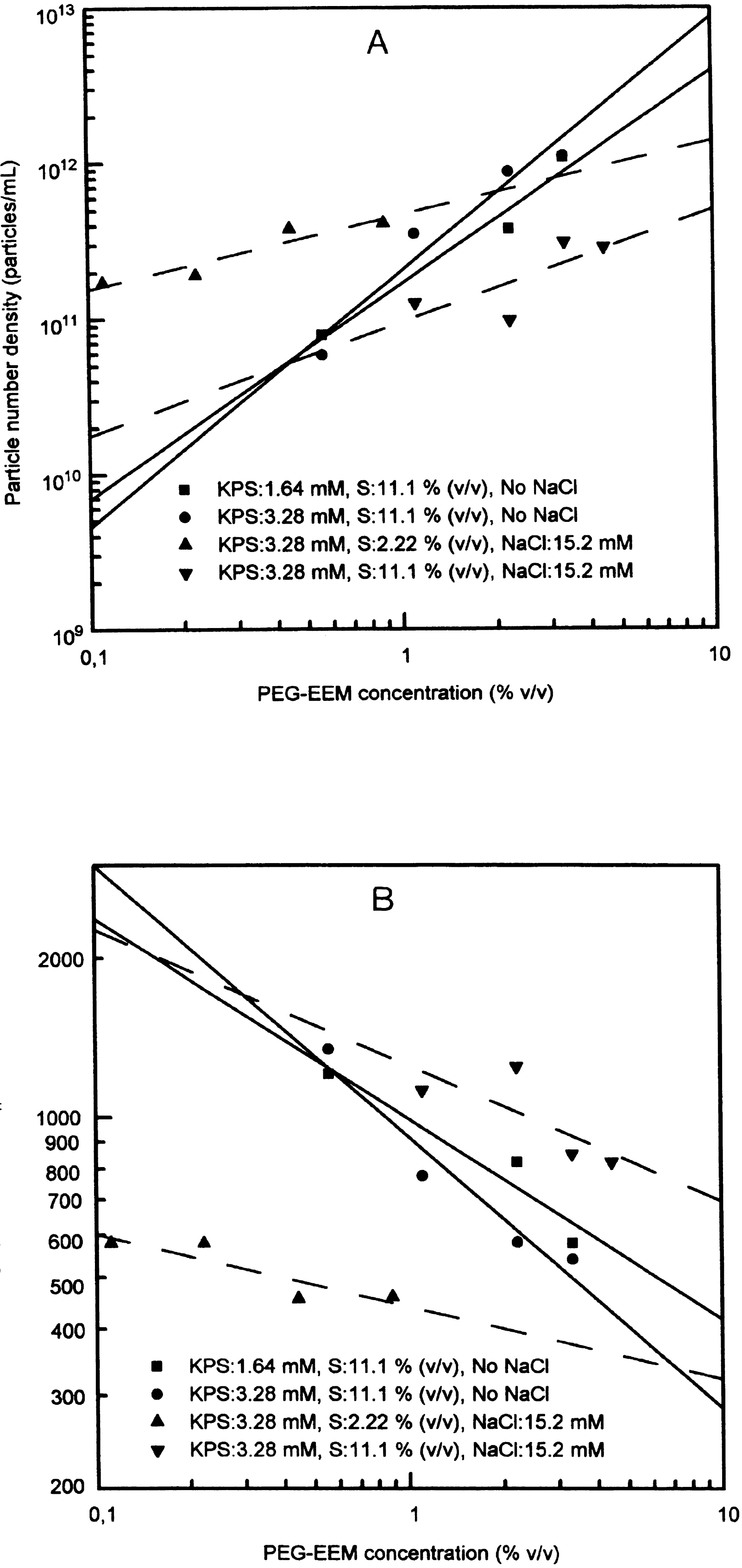

Fig. 4. The variation of particle number density and average particle size with the PEG-EEM concentration for different combinations of experimental variables: (A) particle number density; (B) average particle size.

Table 2
The exponent (n) values for the power law dependencies of particle number density (N_p) and average particle size (D_n) on the PEG-EEM concentration

KPS (mM)	Styrene (%v/v)	NaCl (mM)	n for N_p	n for D_p
1.64	11.1	0.0	1.38 ± 0.27	− 0.38 ± 0.11
3.28	11.1	0.0	1.64 ± 0.30	− 0.51 ± 0.09
3.28	2.22	15.2	0.48 ± 0.12	− 0.16 ± 0.05
3.28	11.1	15.2	0.73 ± 0.45	− 0.26 ± 0.16

higher PEG-EEM/S ratios. A representative SEM photograph of the monodisperse copolymer latex particles produced in the existence of PEG-EEM is given in Fig. 3. The average particle size decreased with the increasing PEG-EEM/S ratio for both the initiator concentrations. This result indicated that PEG-EEM was effective on the formation of primary particles (i.e. particle number density).

In the third group of runs, a new emulsion medium was prepared by adding NaCl at a concentration of 15.2 mM, into the emulsion medium used in the second set. The properties of latex particles are presented in Table 1. The lowest latex yield with the highest PEG-EEM/S ratio (i.e. 0.40 ml/ml) originated from the formation of coagulum (26.0% of the total monomer mass). Although the latex yield was satisfactorily high for the polystyrene latex produced in the absence of PEG-EEM, the size distribution of this sample was wider ($U = 1.041$) relative to the other copolymer latexes produced in this set. The use of PEG-EEM as a comonomer again resulted in an improvement in the particle size distribution in the presence of salt.

In the fourth group of runs, PEG-EEM/S ratio was changed between 0.05 and 0.40 ml/ml while the total monomer/water ratio was reduced for producing smaller particles relative to the other sets. Here, the styrene concentration in the aqueous medium was set to a lower value (i.e. 2.22% v/v). The aqueous medium prepared in the third set was also used in the fourth one. The properties of copolymer latexes are also presented in Table 1. A decrease in the average particle size with the increasing PEG-EEM/S ratio was also detected in the emulsion media including NaCl (i.e. third and fourth sets). The results again indicated that the number of polymerization loci (i.e. the number of formed nuclei) increased with the increasing PEG-EEM/S ratio (i.e. the increasing PEG-EEM concentration within the aqueous medium).

In all sets, PEG-EEM/S ratio was changed by increasing the amount of PEG-EEM while the amount of styrene was kept constant. This case involves the distribution of same amount of styrene into the more forming particles with the increasing PEG-EEM concentration in the aqueous phase. Therefore, the size of final particles decreased with the increasing PEG-EEM/S ratio.

The results in Table 1 indicated that either the mass charge density or the surface charge density were lower when the emulsion polymerization was performed with a higher PEG-EEM/S ratio. In the existence of PEG-EEM, the number of primary particles is higher relative to the conventional emulsifier-free emulsion process. However, each primary particle is possibly formed by the flocculation of less number of oligomer chains with longer chain length. In the earlier step of the emulsion copolymerization, a competition occurs between the solubilized PEG-EEM and styrene molecules for binding onto the SO_4 carrying monomer radicals. The binding of PEG-EEM molecules onto the growing chains is easier due to their more polar character (i.e. higher water solubility). The longer chain length before the nucleation is only possible when the growing chains include dominant PEG-EEM units. The more polar character of these chains allows them to remain in the solubilized form until reaching a higher molecular weight. Therefore, the nucleation in an emulsion medium prepared with a higher PEG-EEM/S ratio results in smaller particles with the lower mass charge densities. The increase in the specific surface area of the particles due to their lower size also reduces the surface charge density.

The variation of particle number density (N_p) with the PEG-EEM concentration is given in Fig. 4(A). For different combinations of experimental conditions, an approximate a linear relation was obtained between particle number density and PEG-EEM concentration in the logarithmic coordinates. The exponent (n) value in the power law was determined by using a conventional least-squares algorithm. In Fig. 4(A), to show the predicted particle number density values according to power law, the solid and the segmented lines were used for the emulsion copolymerizations performed in the absence and existence of NaCl, respectively. The exponent values determined for different combinations of experimental conditions are given in Table 2. For the emulsion copolymerizations performed in the absence of NaCl, the exponent values of 1.38 and 1.64 were obtained with the KPS concentrations of 1.64 and 3.28 mM, respectively. A similar analysis was made by Brown et al. for the emulsion copolymerization of styrene with different poly(ethylene glycol) carrying macromonomers [6]. They also used an aqueous emulsion medium containing no electrolyte. In their study, the exponent values of approximately 1.0 were obtained for five different macromonomers synthesized on the basis of the monomethyl ether of PEO having M_n of 2000 g/mol [6]. In our study, higher exponent values obtained under similar conditions showed the stronger effect of PEG-EEM concentration on the particle number density. Here, it should be noted that Smith–Ewart Theory predicts the exponent of stabilizer as 0.6 for the emulsion polymerization of water-insoluble monomers [24]. The reported experimental values of this exponent were in the range of 0.47–0.7 [25]. In the case of PEG-EEM, the exponent values are almost twice the maximum value determined for the emulsion polymerization of styrene. As seen in Fig. 4(A), the slopes of the segmented lines were reasonably lower relative to those of the solid lines. Then, lower exponent values (i.e. 0.48 and 0.73) were obtained for the emulsion copolymerizations performed within the aqueous

Table 3
The properties of latex particles produced by different KPS concentrations

C_{KPS} (mM)	C_T (%)	D_n (nm)	U (D_w/D_n)	Q (meq/g) $\times 10^3$	Q_s (μC/cm^2)
First set conditions: No salt, S: 11.1% (v/v), PEG-EEM: 1.11% (v/v)					
0.82	83.6	728	1.001	3.01	3.68
3.28	81.6	777	1.009	7.71	10.1
4.92	84.6	930	1.007	10.4	16.3
8.22	89.6	1007	1.015	9.83	16.7
Second set conditions: NaCl: 15.2 mM, S: 11.1% (v/v), PEG-EEM: 2.22% (v/v)					
0.82	74.9	795	1.052	6.17	8.25
1.64	86.9	1040	1.001	2.66	4.65
3.28	84.7	1248	1.002	3.57	7.49
6.56	84.6	420–1200	Bimodal	4.17	–
13.12	80.9	300–900	Bimodal	3.72	–

media including 15.2 mM NaCl (Table 2). It could be concluded that the concentration of PEG-EEM was less effective on the particle number density in the existence of electrolyte (i.e. NaCl). Here, it should be also noted that the higher exponent value was obtained with the higher styrene concentration.

In Fig. 4(B), the variation of average particle size with the PEG-EEM concentration is given in the logarithmic coordinates. The power law dependency of average particle size on the PEG-EEM concentration was also determined. The exponent values estimated for different combinations of experimental conditions are given in Table 2. For the copolymerizations performed in the absence of NaCl, the exponent values of −0.38 and −0.51 were obtained with the constant initiator concentrations of 1.64 and 3.28 mM, respectively. To compare our results with the literature, we applied the power law model on the data collected by Brown et al. and obtained exponent values between −0.32 and −0.53 for four PEO carrying macromonomers which were the most effective ones on the average size among the tried structures [6]. The magnitude of the exponent values obtained in our study showed that the polymerizable stabilizer (PEG-EEM) was covalently incorporated onto the latex particles [6,26]. The exponent values of −0.16 and −0.26 may be attributed to the weaker dependency of average particle size on the PEG-EEM concentration in the existence of NaCl.

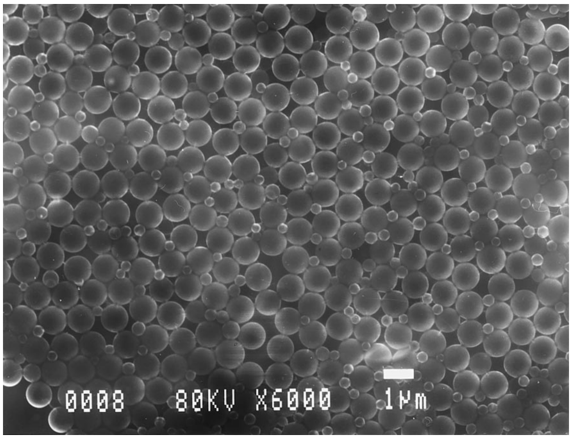

Fig. 5. SEM photograph of the bimodal styrene–PEG-EEM copolymer latex particles, Magnification: 6000×, Polymerization conditions; KPS:13.12 mM, NaCl:15.2 mM, S:1.11% (v/v), PEG-EEM/S:0.20 ml/ml.

3.2. KPS concentration

In the first set of these experiments, the effect of initiator concentration on the particle size and size distribution was investigated in an emulsion medium containing no electrolyte. Here, KPS concentration was changed between 0.82–8.22 mM. The polymerization conditions and the properties of latex particles are given in Table 3. As seen in the first part of Table 3, the latex particles were obtained with the satisfactory latex yields. The average particle size increased with increasing KPS concentration. The best monodispersity was obtained with the lowest KPS concentration (i.e. 0.82 mM). The highest KPS concentration provided a broader size distribution ($U = 1.015$) relative to others. In the second set of experiments, the effect of initiator concentration was investigated in the existence of an electrolyte. Here, KPS concentration was changed between 0.82 and 13.12 mM in an aqueous emulsion medium including 15.2 mM NaCl. The properties of latex particles produced in this set are given in Table 3. As seen here, the average particle size also increased with increasing KPS concentration in the range of 0.82–3.28 mM. The lower initiator concentrations usually provided the latex particles with reasonably narrow size distribution. The best monodispersity in this set was obtained with the KPS concentration of 1.64 mM. A bimodal size distribution was observed with higher KPS concentrations (i.e. 6.56 and 13.12 mM). A representative SEM photograph of the copolymer particles with bimodal size distribution is given in Fig. 5. Some amount of coagulum causing a decrease in the latex yield was also observed with the KPS concentrations of 6.56 and 13.12 mM. For monomodal size distribution, an approximate linear increase was observed in the average particle size with increasing KPS concentration in both sets of experiments. This increase may be explained as follows: the increase in the initiator concentration causes an increase

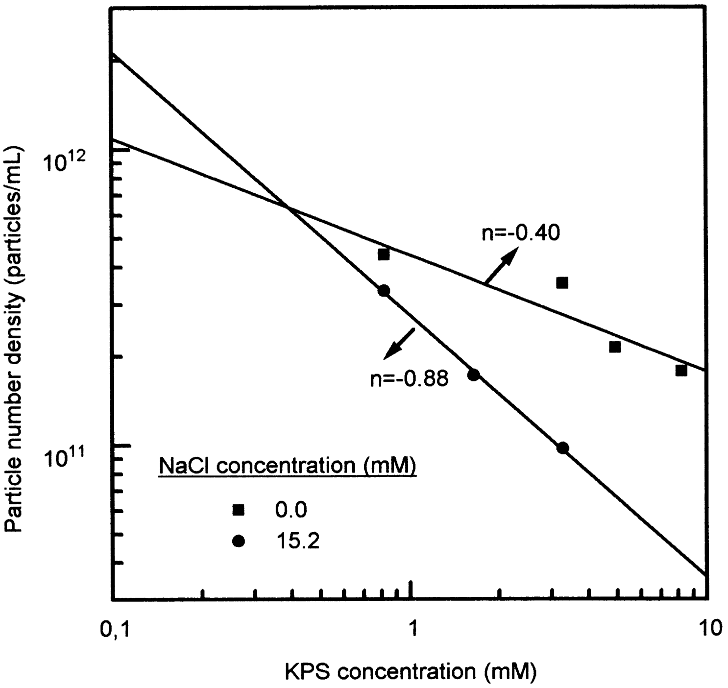

Fig. 6. The variation of particle number density with the initiator concentration in the absence and existence of NaCl (*n*:slope).

in the number of free sulphate radicals produced in the earlier stage of copolymerization. The presence of PEG-EEM in the aqueous emulsion medium is also a factor causing an increase in the solubility of oligomer chains. So, higher initiator concentration leads to lower molecular weight oligomer chains, which are more soluble in the aqueous medium. At the higher initiator concentrations, due to the low concentration of high molecular weight chains, fewer polymerization nuclei are produced by the nucleation, which possibly leads to a lower number of particles but with larger size. The variation of particle number density with the KPS concentration is given in Fig. 6. The particle number density decreased by increasing the KPS concentration. Based on the linear relation observed in the logarithmic coordinates, the exponent values for the power law dependency of particle number density on KPS concentration were determined as -0.40 and -0.88 for the emulsion copolymerizations performed in the absence and existence of NaCl, respectively. The comparison of the initiator exponents indicated that KPS concentration was more effective on the particle number density in the presence of an electrolyte (i.e. NaCl). The mass and surface charge densities of the latex particles produced by different KPS concentrations are also presented in Table 3. As seen here, either the mass or the surface charge density increased with the increasing KPS concentration for the latex particles produced in the emulsion medium including no salt. This increase is an expected case since the surface charge of the latex particles arises from the strong acidic groups coming from the initiator. However, the increase in the mass charge density with the increasing KPS concentration was not so clear for the emulsion medium including 15.2 mM NaCl.

3.3. NaCl concentration

In these group of experiments, NaCl concentration was changed between 0 and 38.0 mM. The polymerization conditions and the properties of latex particles are presented in Table 4. High latex yields were obtained up to the NaCl concentration of 15.2 mM. The formation of significant

Table 4
The properties of latex particles produced by different NaCl concentrations (KPS: 3.28 mM, S:11.1% (v/v), PEG-EEM: 2.22% (v/v))

C_{NaCl} (mM)	C_T (%)	D_n (nm)	U (D_w/D_n)	Q (meq/g) × 10^3	Q_s (μC/cm^2)
0.00	77.7	583	1.005	6.25	6.11
3.80	89.7	681	1.009	5.16	5.90
7.60	88.8	893	1.002	3.61	5.41
15.2	84.7	1248	1.002	3.57	7.49
22.8	80.3	1232	1.013	3.29	6.81
38.0	67.3	200–1200	Bimodal	6.05	–

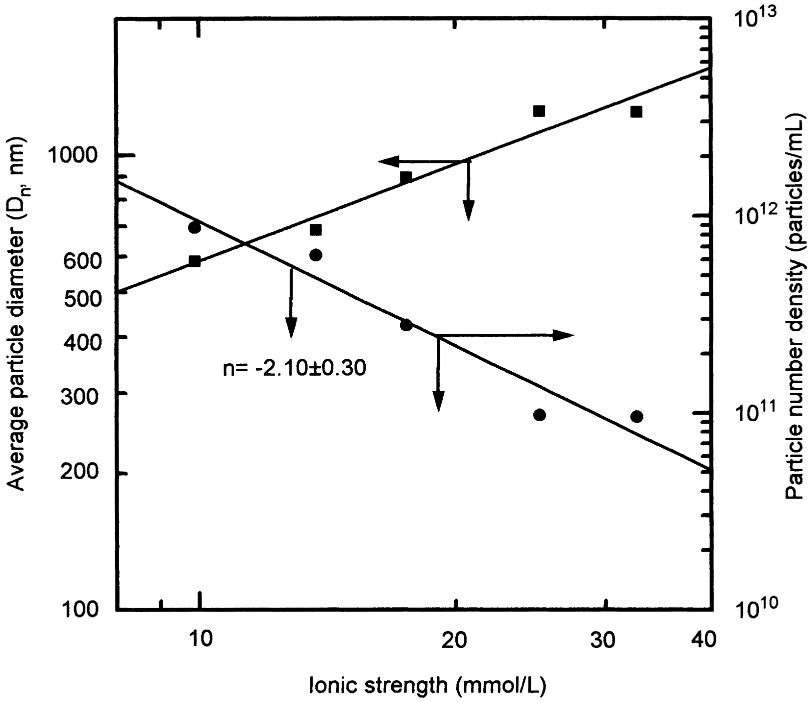

Fig. 7. The variation of average particle size and the particle number density with the ionic strength of the aqueous emulsion medium (*n*:slope).

amount of coagulum with the NaCl concentrations of 22.8 and 38.0 mM resulted in a decrease in the latex yield. As seen in Table 4, the latex particles with reasonably narrow size distribution could be obtained with the NaCl concentrations up to 15.2 mM. An appreciable size distribution was first observed with the NaCl concentration of 22.8 mM. The highest NaCl concentration (38.0 mM) provided a bimodal size distribution including significant amount of small particles. The results indicated that the average particle size increased with increasing NaCl concentration (i.e. increasing ionic strength of the aqueous medium). A linear dependence between the particle diameter and ionic strength of the aqueous phase in logarithmic coordinates was observed by Smigol et al. in the emulsifier free-emulsion polymerization of styrene [27]. Goodwin et al. also reported a similar tendency for the preparation of smaller particles starting from styrene [28]. For our copolymerization system, the variation of particle diameter with the ionic strength of the aqueous medium is shown in Fig. 7. As seen here, a linear relation between the particle diameter and the ionic strength of the aqueous medium in logarithmic coordinates was also valid for the emulsion copolymerization of styrene with PEG-EEM. The variation of particle number density with the ionic strength is also shown in Fig. 7. The exponent of -2.10 was obtained for the power law dependency of particle number density on the ionic strength. An exponent value of -0.9 was predicted by the “Coagulative Nucleation Theory” proposed by Feeney et al. for the conventional emulsion polymerization of styrene [29]. The experimental data of Goodwin et al. provided the exponent value of -0.7 for the same system [28,30]. Our result indicated that the ionic strength was a more effective parameter on the particle number density in the existence of a polymerizable stabilizer (PEG-EEM). As seen in Table 4, either the mass charge density or the surface charge density did not change significantly with the NaCl concentration in the aqueous emulsion medium. The surface charge density was not calculated for the latex particles obtained with the highest NaCl concentration (38.0 mM) since the determination of specific surface area was difficult in the presence of bimodal size distribution.

3.4. Monomer/water volume ratio

Total monomer/water volume ratio (M/W) was changed between 0.027 and 0.133 ml/ml by fixing PEG-EEM/S

Table 5
The properties of latex particles produced by different monomer/water volume ratios (KPS: 3.28 mM, NaCl: 15.2 mM, PEG-EEM/S: 0.2 ml/ml)

M/W (ml/ml)	C_T (%)	D_n (nm)	U (D_w/D_n)	Q (meq/g) × 10^3	Q_s (μC/cm^2)
0.027	60.2	456	1.004	29.2	22.4
0.067	80.1	723	1.008	5.43	6.60
0.133	84.7	1248	1.002	3.57	7.49

volume ratio to 0.2 ml/ml. The copolymerization conditions and the properties of latex particles are presented in Table 5. As seen here, the latex yield was relatively lower with the lowest monomer/water ratio (i.e. 0.027 ml/ml). As seen in Table 5, all tried monomer/water ratios provided latex particles with reasonably narrow size distribution. The results also indicated that the particle diameter significantly increased with the increasing monomer/water ratio. The amount of monomer present in the aqueous medium is especially effective at the extended polymerization times [27]. After completion of the nucleation period, the number of primary latex particles is constant and these particles grow by the diffusion of monomer through the aqueous phase [27]. The monomer diffusion continues up to the disappearance of the stock droplets. Therefore the particle diameter increases with the increasing amount of monomer available (i.e. in the form of stock droplets) within the polymerization medium [27,28]. A linear relation between the particle size and monomer concentration was observed in logarithmic coordinates by Smigol et al. for the emulsifier free emulsion polymerization of styrene [27]. For the emulsion copolymerization of styrene and PEG-EEM, the particle size increased linearly with the increasing monomer concentration in the studied range. As seen in Table 5, either the mass or the surface charge densities were reasonably higher for the latex particles produced with the lowest monomer concentration (i.e. 0.027 ml/ml). The higher monomer concentrations provided latex particles with relatively lower charge densities. During the experiments, the concentration of KPS in the aqueous phase was kept constant. For this reason, the amount of initiator used per mass of the monomer decreased with the increasing amount of monomer. Therefore, the charge density originated from the strong acidic group content of the latex particles decreased.

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