A New Investigation with the Salting-Out Effect on Emulsifier-Free Emulsion Polymerization of Methyl Methacrylate

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ABSTRACT: The effects of the various salts onto the emulsifier-free emulsion polymerization of methyl methacrylate (MMA) were investigated. It was found that the kind and amount of the salts were very effective on the polymerization even onto the polymeric products. It is known that the ionic strength of the electrolyte is effective for the polymerization. However, our investigation with the same ionic strength of different electrolyte produced the different effect on the polymerization. It was found that the Stokes radiuses of ions are very important for the reaction kinetics and type of the product. At the same electrolyte concentration, as increased Stokes radii of cation of salts that not react (the fragments of initiator, ions, etc.) in polymerization, polymerization rate and average molecular weight of polymer decreased, polymer particle diameter increased. In the case of Br$^-$ and SO$_4^=$ the anions of the salt are also demonstrated some unexpected reactions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2494–2500, 2007

Key words: colloids; emulsifier-free emulsion polymerization; methyl methacrylate; ionic strength; salting-out effect

INTRODUCTION

The emulsifier-free emulsion polymerization has received much attention as a method for producing ''clean'' lattices.[1–5] This method have advantages of having no added emulsifier for applications in adhesive, coating, calibration standards, and supports for biomolecules. This technique also allows preparing highly monodisperse polymer particles with well-defined surface properties, which are often used as model system to study rheology of colloids.[6] Knowledge of disperse medium effects on the polymerization kinetics is important to understand events that occur in emulsifier-free emulsion polymerization. Several mechanisms for the emulsifier-free emulsion polymerization have been proposed.[7–9] The mechanism are dependent on the solubility of the monomers in the water. The polarity of the monomers[4,10] and the effect of the solvents[11–14] in the aqueous medium have been studied and well documented. Also, the effects of electrolyte that changes the features of polymerization medium is available in literature,[15–17] although the effects of ionic strength were ignored in the basic theories of emulsion by Smith and Ewart.[18] But, the researchers have not considered the importance of electrolyte type in all their studies.

The salting-out efficiency of an electrolyte depends on the tendencies of its ions to be hydrated. Thus, cations and anions can be arranged in the following lyotropic series of approximately decreasing salting-out power: Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}.[19] The salting-out power reflects the size of the ions and their polarizabilities. In fact, this tendency increases with the increasing the effective nuclear charge of ion (Z^*). While the hydration numbers are related to the Stokes radius, it is possible to use Stokes radius instead of hydration numbers. With increasing Stokes radius of ions, the number of water molecules in the vicinity of the ion increases, this cause to the decrease of the mobility.[20] It is, therefore, hardly surprising that they should have a determining effect on various aspect of both kinetic and equilibrium behavior of colloidal systems in emulsion-free emulsion polymerization.

In the present work, further investigations of electrolyte effects on persulphate-initiated emulsifier-free emulsion polymerization of methyl methacrylate was investigated with various salts, such as NaCl, LiCl, NaBr, NaI, Na$_2$SO$_4$, MgCl$_2$, CaCl$_2$, and BaCl$_2$.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was freed from phenolic inhibitors by shaking with 5% aqueous NaOH, washing with water, and drying over Na$_2$SO$_4$ and then distilled under reduced pressure. The initiator, potassium

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TABLE I
Recipe of Emulsifier-Free Emulsion Polymerization of Methyl Methacrylate at 75°C and an Agitation Rate of 240 rpm

Contents	Type	Amount (g)	Concentration (mol L^{-1})
Water	Double distilled	952.5	–
Initiator	$K_2S_2O_8$	0.1288	4.00×10^{-1}
Monomer	MMA	38.7	5.00×10^{-4}
Salt	NaCl, NaBr, NaI, LiCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, Na_2SO_4	Variable	Variable

persulphate (KPS), was a product of Fluka, Germany. Double distilled water was used in all the stages of the workup. The conductivity of water was measured about 1.0–1.5 μs cm^{-1} at 25°C. The salts, NaCl, NaBr, NaI, LiCl, $MgCl_2$, $BaCl_2$, $CaCl_2$ (purchased from Aldrich), were used without further purification. The chloroform was purified stirring with 98% H_2SO_4 at least for 1 day, and shaking with aqueous NaOH and drying over Na_2CO_3.[21]

Polymerization procedure

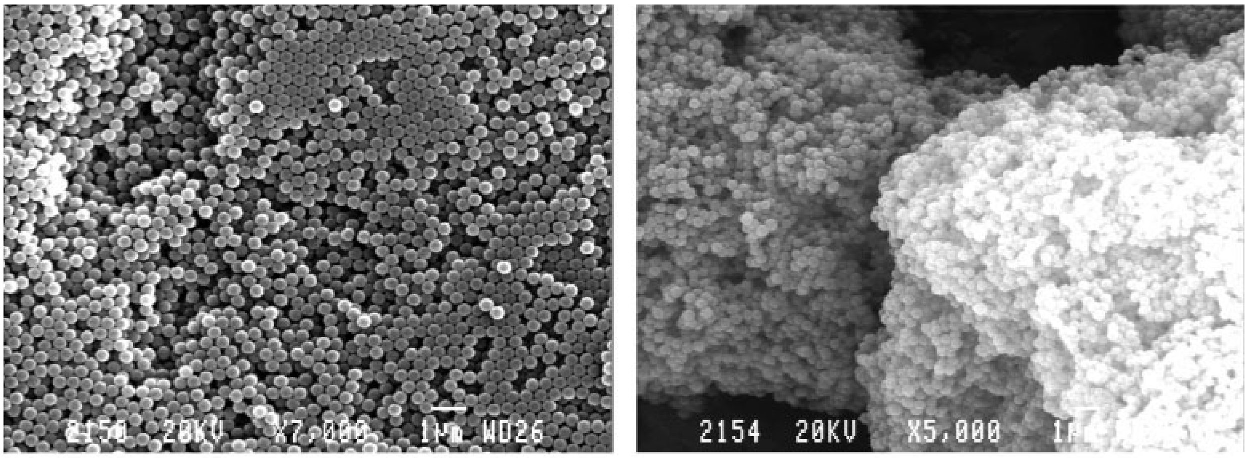
Polymerization was carried out at 75°C in a 1-L round-bottomed, four-necked glass flask equipped with a mechanical stirrer, nitrogen inlet, thermometer (±0.1°C), and condenser fitted with pipette outlet. The reactor was immersed in a thermostated water bath to maintain constant temperature. The stirring speed was adjusted to 240 rpm with a digital controller. First, the appropriate amounts of water (800–900 mL), salt solution (a desired amount of the salt dissolved in 30 mL water), and MMA were charged into the reactor and stirred under nitrogen atmosphere for at least 20 min to remove oxygen from the reaction system. Temperature equilibrium was attained and the aqueous phase was saturated with monomer. 0.1288 g initiator, potassium persulphate dissolved in 40 mL water, was added into the reactor and the reaction was allowed to proceed at 75°C for about 3 h. The synthesis conditions of lattices are shown in Table I.

After the start of the polymerization, 1–2 mL of the reaction mixture was sampled at a definite time interval for conversion measurement. The sample was placed in a tared weighed dish along with hydroquinone to stop the reaction and dried. The conversions were determined gravimetrically from dried sample weights based on the total amount of the monomer used.

Characterization

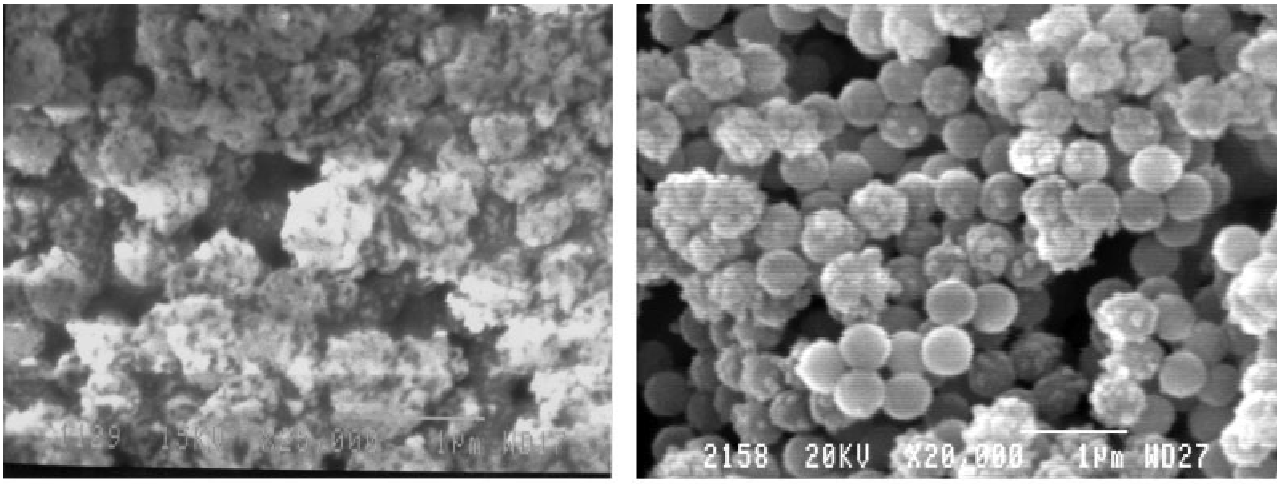
Bead size and distribution are examined in a scanning electron microscope (SEM), JSM 840 CX.[13] The weight–average molecular weight and molecular weight distribution of polymers were determined by gel-permeation chromatography (Agilent 1100) equipped with refractive index detector, at a flow rate of 0.3 mL/min in THF at 30°C using poly(methyl methacrylate) standards. The viscosity–average molecular weights were obtained from viscosity measurements in chloroform at 20°C with an Ubbelohde viscosimeter using the Mark-Houwink constants $K = 0.0055$ mL/g and $a = 0.79$. Before the viscosity measurements, the solid beads are separated from latex by freezing[3] and washed with deionized water for five times to remove the salt.

The surface charge of beads calculated on the basis of the number–average molecular weights and the average particle diameter.[22] In the calculations, it was assumed that all initiator radicals involve the reaction and all poly(methyl methacrylate) (PMMA)



(a) (b)

Figure 1 The agglomeration of beads in lattice as related to the medium properties. (a) 0.1×10^{-2} mol Na_2SO_4/L water and (b) 0.5×10^{-2} mol Na_2SO_4/L water. See Table I for details.



(a) (b)

Figure 2 The appearing beads at SEM photographs, after beads that covered with LiCl (2×10^{-2} mol L^{-1}) were washed, where (a) is for unwashed sample, (b) is for washed sample.

chain radicals' undergone termination by disproportionation. This approach has been accepted. All of the experiments were performed at the same standard condition except salts concentration. This can only bring a systematical fault.

RESULTS AND DISCUSSION

Monodisperse PMMA lattices were obtained by adding various salts have different concentrations at 75°C. A reaction without any salt was also carried out for comparison. Polymerization recipe is shown in Table I. As it can be clearly seen from the Figure 1(b), the agglomerization was observed at high salt concentrations. Interestingly, at the higher salt concentrations, the salt crystals were observed on the beads of lattices, which are shown in the SEM photomicrographs at Figure 2(a). The lattices were washed with double distilled water for five times, when the SEM photomicrographs of beads were taken to again demonstrate that these are salt crystals. It was seen that most of these salts crystals on the beads were removed [Fig. 2(b)]. When NaI used as a salt in the polymerization system, the polymer could not obtained, only the red solution was obtained due to reaction as shown eq. (1).[23]

$$S_2O_8^{2-} + 3I^- \rightarrow 2SO_4^{2-} + I_3^- \tag{1}$$

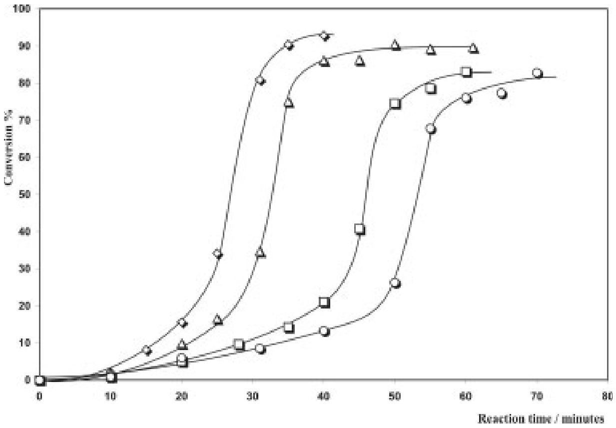


Figure 3 Reaction kinetics for different NaCl concentrations; (◇) without the salt, (Δ) 0.5×10^{-2} mol NaCl/L water, (□) 1×10^{-2} mol NaCl/L water, (○) 2×10^{-2} mol NaCl/L water.

Kinetics

The addition of the salt to the reaction media were caused to increase in the duration of the first interval of the reaction due to decreasing the solubility of monomer in the aqueous phase.[13,24] Thus, there has been an extension at the reaction period. As seen in Figures 3–5, the finishing times of interval I extended from 20 to 60 min with the increasing salt concentrations, except Na_2SO_4.

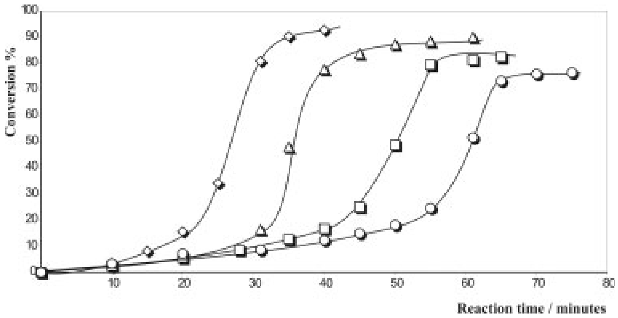


Figure 4 Reaction kinetics for different NaBr concentrations; (◇) without the salt, (Δ) 0.5×10^{-2} mol NaBr/L water, (□) 1×10^{-2} mol NaBr/L water, (○) 2×10^{-2} mol NaBr/L water.

Na_2SO_4 showed very interesting behavior. At lower salt concentration, the reaction rate was slower and an increase in the reaction rate was observed by the addition of the salt to an optimum. On the higher concentration of the Na_2SO_4, the decrease in the reaction rate was observed again. This feature can easily be seen in Figures 6 and 7. It was assumed that the interaction between $S_2O_8^{2-}$ and SO_4^{2-} ions effect the reaction rate due to the possible reaction between $S_2O_8^{2-}$ and SO_4^{2-} as shown in eq. (2);[25]

$$S_2O_8^{2-} + 2e^- \rightleftarrows 2SO_4^{2-} \qquad (2)$$

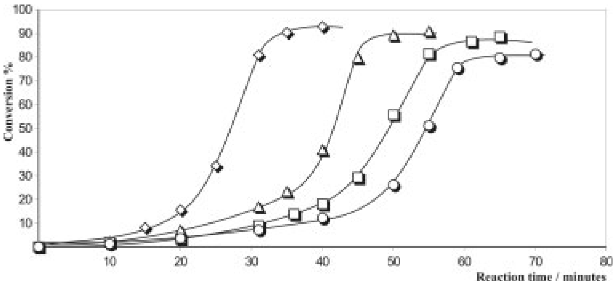


Figure 5 Reaction kinetics for different LiCl concentrations; (◇) without the salt, (Δ) 0.5×10^{-2} mol LiCl/L water, (□) 1×10^{-2} mol LiCl/L water, (○) 2×10^{-2} mol LiCl/L water.

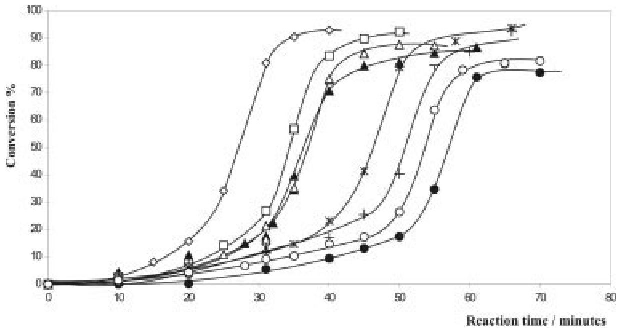


Figure 6 Reaction kinetics for different Na_2SO_4 concentrations; (◇) without the salt, (□) 0.1×10^{-2} mol Na_2SO_4/L water, (Δ) 0.25×10^{-2} mol Na_2SO_4/L water, (∗) 0.3×10^{-2} mol Na_2SO_4/L water, (▲) 0.5×10^{-2} mol Na_2SO_4/L water, (+) 0.6×10^{-2} mol Na_2SO_4/L water, (●) 0.75×10^{-2} mol Na_2SO_4/L water, (○)1×10^{-2} mol Na_2SO_4/L water.

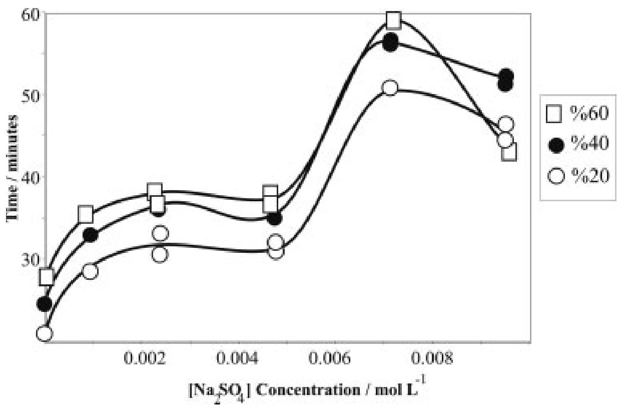


Figure 7 Plots of reaction time versus Na_2SO_4 concentration at conversion 20, 40, 60%.

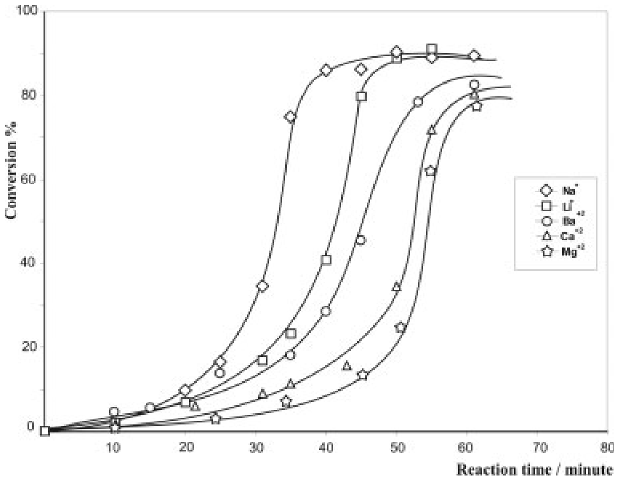


Figure 8 Effect of cation type on the polymerization kinetic, with a constant ionic strength of 5.0×10^{-3} and common Cl^-.

When the NaBr has been used as a salt, the reaction rate is slower than used NaCl (Figs. 3 and 4). This can be attributed to the to the reaction of Br^- with the initiator $S_2O_8^{2-}$ as follows[26];

$$2Br^- + S_2O_8^{2-} \rightarrow Br_2 + 2SO_4^{2-} \qquad (3)$$

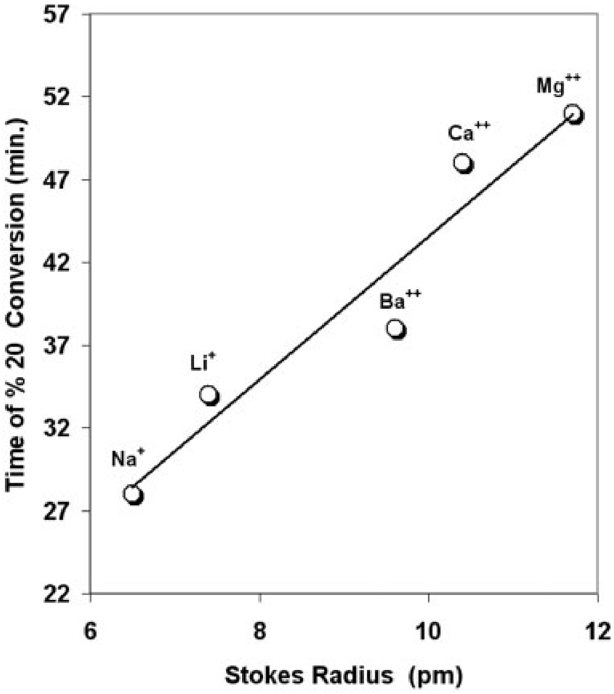


Figure 9 Dependence of Stokes radius of ion on time of 20% conversion at ionic strength of 5.0×10^{-3} and with presence common Cl^-.

The color changes to the light yellow may support the suggestion.

LiCl, NaCl, $CaCl_2$, $MgCl_2$, and $BaCl_2$ have not participated in the any chemical interaction in polymerization medium. So, we can easily observe the salting-out efficiency of salts on the kinetic of the polymerization using with these salts. Although salts have generated the same ionic strength, they have showed the different effects on the reaction rates as seen in Figure 8. This is due to the different the salting-out power or Stokes radius of ions.[20] Thus, it was found that there is a linear relation between the Stokes radius[20] of cations and time of 20% conversion. It was clearly demonstrated in Figure 9.

Latex characterization

It was observed that the beads have been undergone more agglomeration as increased the amounts of the salt as shown in the SEM photomicrographs at Figure 10.

Table II summarizes the average molecular weights ($\overline{M}_{\bar{n}}$, $\overline{M}_{\bar{w}}$, and $\overline{M}_{\bar{v}}$) of polymers formed at different ionic strengths. The average molecular weights of polymers have decreased generally increasing the ionic strength of the aqueous phase[17] as seen in Table II. This inverse relation between the molecular weight of polymer and the ionic strength is due to the decreasing monomer solubility in the aqueous on raising ionic strength, which decrease the number of primary particles that occur in the first period of the polymerization.[3,4] Thus, the radical concentration per the particle increases, the termination reactions accelerate inside the particle, and the average molecular weight decreases.

When it was used the same concentrations of inert salts, which have valency of +1 or +2, the average molecular weights of polymer have decreased with increasing Stokes radius of ions.[20] For example, it was found that the average molecular weight of polymer that have been obtain at medium with $MgCl_2$ was smaller than with NaCl one at the same ionic

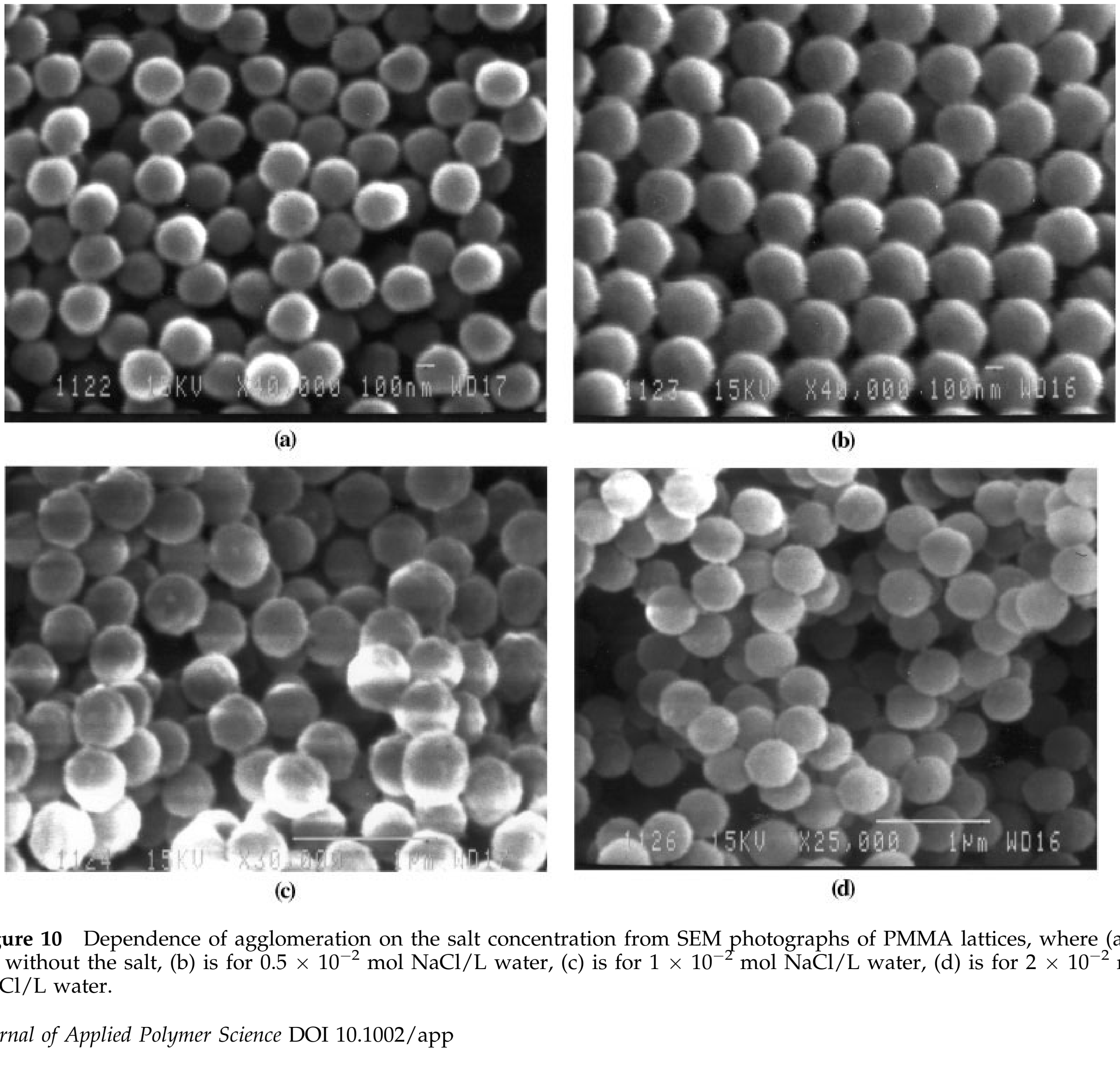


Figure 10 Dependence of agglomeration on the salt concentration from SEM photographs of PMMA lattices, where (a) is for without the salt, (b) is for 0.5×10^{-2} mol NaCl/L water, (c) is for 1×10^{-2} mol NaCl/L water, (d) is for 2×10^{-2} mol NaCl/L water.

TABLE II
The Effects of Ionic Strength and Salt Type on the Average Molecular Weights

Ionic Strength	Salt	M_v (kg mol^{-1})	M_w (kg mol^{-1})	M_n (kg mol^{-1})
0.005	NaCl	550	798	401
	LiCl	480	786	398
	$BaCl_2$	371	716	295
	$CaCl_2$	458	643	275
	$MgCl_2$	416	675	326
0.005	NaCl	550	798	401
	NaBr	374	707	332
0.01	NaCl	526	753	382
	NaBr	353	689	385
	Na_2SO_4	463	788	357
0.02	NaCl	495	683	264
	LiCl	328	605	229

strength ($I = 0.05$), as seen in Table II, because Mg^{2+} ion has the bigger Stokes radius.

The motion of ions have the big Stokes radius at around surface of bead are slower. In this case, the diffusion of monomer gets difficult and the probability of radical entry into growing particles increases and so leads to shorter kinetic chains. Thus, reduced the average molecular weight of polymer with increasing Stokes radius is due to reduce ratio of R_p/R_t in the bead.

Br_2 becomes from the reaction that is shown equation (2) and it gives radicals easy.[26] Apolar Br_2 prefers to enter apolar phase, the monomer-swollen particles. It causes increasing the termination reactions as the result of more producing radical. The results of experiments have supported this statement. Table II shows that the average molecular weight of polymer has more decreased with increasing the concentration of Br^-.

At medium with Na_2SO_4, the average molecular weights of polymers have decreased increasing the ionic strength of the aqueous phase. However, it was observed unsystematic behaviors at ionic strengths between 0.07 and 0.015 as seen in Figure 12.

TABLE III
The Effect of Salt Type on Bead Size and the Surface Charge of Bead, with Constant Ionic Strength

Ionic Strength	Salt	Stokes radius of cation (pm)	Bead size (nm)	Surface charge (μC/cm^2)
0.005	NaCl	6.5	278 ± 5	0.89 ± 0.05
	LiCl	7.4	386 ± 6	3.59 ± 0.17
	$BaCl_2$	9.6	538 ± 21	6.43 ± 0.75
	$CaCl_2$	10.4	524 ± 19	5.68 ± 0.62
	$MgCl_2$	11.7	584 ± 14	6.33 ± 0.46
0.005	NaCl	6.5	278 ± 05	0.89 ± 0.05
	NaBr	6.5	277 ± 06	1.31 ± 0.08
0.01	NaCl	6.5	423 ± 14	1.42 ± 0.14
	NaBr	6.5	418 ± 16	2.00 ± 0.23
	Na_2SO_4	6.5	432 ± 09	3.30 ± 0.23
0.02	NaCl	6.5	465 ± 16	1.66 ± 0.17
	LiCl	7.4	495 ± 10	5.34 ± 0.32

The salt reduces the water solubility of monomer.[17] Zou and colleagues reported that the final bead size increases with decreasing solubility of the monomer in water.[24] The obtaining results confirm this expectation and the bead size has increased as seen Table III. In this view, the aqueous reaction of initiator fragments and monomer molecules rapid, so that the number of oligomeric radicals produced increases with the instantaneous concentration monomer in water even tough the diffusion of monomer, from monomer droplets in to the aqueous phase, maintains a constant monomer concentration in water. Alternatively, it is possible that particle size is primarily determined by the stability of oligomeric chain radicals. Then, oligomeric chains resulting from more water-soluble monomer may grow larger before they nucleate into particles. In any case, it must be pointed out that primary particles probably undergo limited coagulation to form the final particles. Therefore, both rates nucleation and coagulation are involved in establishing the final particle numbers.

For the inert salts, it was found that there is a linear relation between the bead size and Stokes radius of cation as seen Figure 11. To explain the experimental findings, it should be borne in mind both rates nucleation and coagulation. As increases Stokes radius of ions, both of them also increase. The particles undergo coagulation to maintain the stability of them in disperse medium. So the surface charges of them also increase as shown Table III. However, at presence $BaCl_2$, the bigger particles have become unexpectedly, because Ba^{2+} ions interact strongly with sulfate ions involved in stabilization of particles leading to bigger particles.

Equation (3), which indicates the reaction of Br^-, has effected on the reaction kinetics and the average

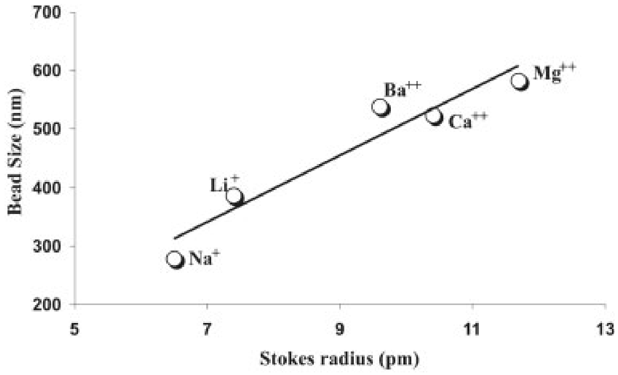


Figure 11 The relation between Stokes radius of cation (Na^+, Li^+, Ba^{2+}, Ca^{2+}, Mg^{2+}) and bead size, with a constant ionic strength of 5.0×10^{-3} and common Cl^-.

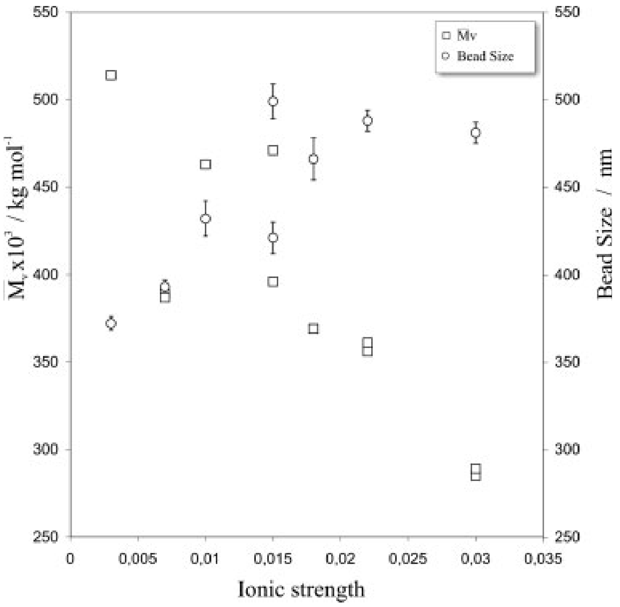


Figure 12 At medium with Na_2SO_4, the effects of ionic strength on the average molecular weight and bead size.

molecular weight distribution. But, this effect was not observed on the bead size.

At medium with Na_2SO_4, it was also obtained the linear relation between the bead size and the ionic strength of the aqueous phase. However, like the molecular weights of polymers, it was observed unsystematic behaviors at ionic strengths between 0.07 and 0.015 as seen in Figure 12.

CONCLUSIONS

The emulsifier-free emulsion polymerization of MMA was carried out with $K_2S_2O_8$ as initiator in the presence of aqueous phase that has various ionic strengths at 75°C. Monodisperse PMMA lattices with particle diameters varying between 277 and 584 nm and polymer molecular weight of the order 229–798 kg mol^{-1} were prepared. When the different salts at the same ionic strength are used, the polymerization kinetics and the features of final product have changed. In other words, the name of salt is very important for the polymerization process and product such as ionic strength. With increasing Stokes radius[20] of cation, the polymerization rate linearly decreased (Fig. 8) and increased the bead size (Table III). In addition it was observed that the amount of SO_4^{2-} ion in aqueous phase influences activity of $K_2S_2O_8$. The SO_4^{2-} ion on the surface of the bead interacts with Ba^{2+} ion strongly. As a result of this behavior, the surface charge has decreased and the bead size has increased. These findings will get new approaches related to the effects of the salt type on to emulsifier-free emulsion polymerization systems.

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