Pickering emulsion polymerization of styrene using Ludox HS-30 as solid particles stabilizer: The dependence on the pH

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ABSTRACT

Solid nanoparticles can be used as stabilizers for oil/water emulsions instead of the conventional surfactants. Silica nanoparticles can aquire different particle size as a function of pH, which is thought to influence its emulsification potency. Emulsion polymerization of styrene, as an example of polymerizable oil, was started in the current study after ultrasonication of the monomer into the aqueous phase, with the aid of silica nanoparticles as sole stabilizer for the process, as a function of pH, either before or after the ultrasonication process, while the concentrations of the monomer, initiator and silica were fixed. The results revealed that when the pH was adjusted before sonication, the emulsification of the styrene proceeded more effective at low pH (2 and 4) while when the pH was adjusted after sonication the affect of the pH on the stability disappeared completely. This was attributed to surface charge density and consequent extent of electrostatic repulsion when the pH was changed before sonication whereas after sonication a compact protective layer of the silica nanoparticles was already surrounding the styrene drops in water and could not be destroyed by changing the pH. Accordingly, the emulsion polymerization was conducted with the pH adjusted before sonication and it was found that both the conversion %, as well as the average molecular weight of the resulting emulsion polymer increase, associated by a remarkable decrease in the particle size of the composite latex particles. © 2014 Trade Science Inc. - INDIA

INTRODUCTION

Pickering stabilization of emulsion derived its name from the American scientist Pickering who suggested this principle in 1907[1]. In the subsequent decades, huge number of articles focusing on this topic have been published[2,3]. It was observed by Pickering that solid-stabilized emulsions (Pickering emulsion) could be obtained when fine solid particles were mixed with water and oily solvents, without the need for any true surfactants[1,4]. Numerous types of inorganic nanoparticles were suggested for use in Pickering emulsion polymerization such as magnetite[5], cobalt ferrite[6], cerium dioxide[7], titania[8], and silica[9,10]. Many factors affect the

stability of Pickering emulsions, including particles concentration, wettability, size, interaction between the particles, pH, and electrolyte concentration[11]. Thus, this method is characterized by lower toxicity and cost, green to environment in addition to more control over the particles properties. Furthermore, no by-products are produced from this process. The final product comprises a polymer core with a shell of nanoparticles, accordingly can be used in catalysis, electronics, and many others[12-15]

It was found that increasing or decreasing the pH level changes the amount of ions available in the slurry, which affects the charge in the double layer surrounding the particles, suspended in the fluid and so affects

the zeta potential. Presumably, if the zeta potential is too low, the particles will agglomerate and create large clusters, and the particles will be less stable in the colloids. While at high zeta potential values, the particles are more stable in the colloids. The current work will focus on optimization of these conditions whereas making use of silica nanoparticles as the sole stabilizer for styrene in water emulsions, before and after polymerization.

EXPERIMENTAL

Materials

Ludox HS-30 and Styrene were obtained from Aldrich Chemical Company. Potassium persulfate (PPS), sodium hydroxide and hydrochloric acid were obtained from S.d. fine–chem. Ltd

Preparation of pickering emulsion

Distilled water as dispersion medium and Ludox HS-30 were stirred for two min. under magnetic stirring. The required amount of monomer was sonicated in the dispersion medium for three min. at 50% power using CPX 750, Cole-Parmer ultrasonic processor, U.S.A., with power 750 watts and a frequency of 20 kHz. The formed emulsion and the required amount of potassium persulfate, dissolved in least amount of water, were then charged into a 250 ml two-necked flask. The polymerization reactions were run ahead at the temperature of interest (± 1°C) in an automatically controlled water bath under mechanical stirring at 350 rpm. In order to determine the conversion % during the polymerization, it was necessary to withdraw samples at various time intervals from the reaction mixture. The withdrawn samples were extremely small so that the composition in the reaction vessel was not seriously affected. Once a sample was removed and put in a watch glass, the reaction was ceased with 7 ppm of hydroquinone and the contents in the watch glass were evaporated at room temperature then dried in an electric oven until constant weight was reached. Since the composition in the reaction vessel at the sampling time is known, the conversion % can be calculated gravimetrically.

Characterizations

The hydrodynamic particle size and zeta potential were determined by dynamic light scattering using a Zetasizer from Malvern Instruments (model 3000-HS) using a He-Ne laser at a wavelength of 632 nm. The dispersions were diluted with water in a plastic cuvette before the measurements. Particle sizes and zeta potentials are given as the average of three measurements. Transmission Electron Microscope of JEM-1230 model, Japan, was used to measure the average particles size for the different polymer latex particles. It works at 120 kV, with maximum magnification of 600×10^3 and a resolution until 0.2 nm. A drop of an aqueous dispersion of the emulsion was placed on a carbon-coated copper TEM grid (300 mesh size) and allowed to air dry for TEM characterization. The samples were examined additionally with scanning electron microscope Model Quanta 250 FEG (Field Emission Gun) (SEM-FEM) attached with EDX Unit (Energy Dispersive X-ray Analyses) while working at accelerating voltage of 30 kV, for characterization of the morphological features on the surface, after gold sputtering using EMITECH K550X sputter coater, England. Fourier transform infrared spectroscopy investigation was performed using a JASCO FTIR-6100E spectrometer, Japan. The average molecular weights of the latexes were determined by Agilent 1100 Gel permeation chromatography (GPC), Germany, using tetrahydrofuran as solvent at 25 °C and narrowly distributed polystyrene (PS) as the standard, while a refractive index detector was used. A series of columns (100, 10^4, 10^5 A) with dimension of 7.5 x 300 mm were connected in series, to cover molecular weight range 10^3-4×10^6 g/mol. Thermogravimetric characterization (TGA) was carried out with a SDYQ-600 thermal analyzer, U.S.A., on about 20 mg samples by heating from 25°C to 600°C at a rate of 10°C/min. under nitrogen atmosphere.

RESULTS AND DISCUSSION

Particles suspended in a fluid are surrounded by a double layer whose charge density is highly sensitive to the pH, which strongly affects the zeta potential. If the zeta potential is too low, the particles will agglomerate and create large clusters therefore the particles will be less stable in the medium. Kim and co-workers[16] found that the particle size of silica was increasing by decreas-
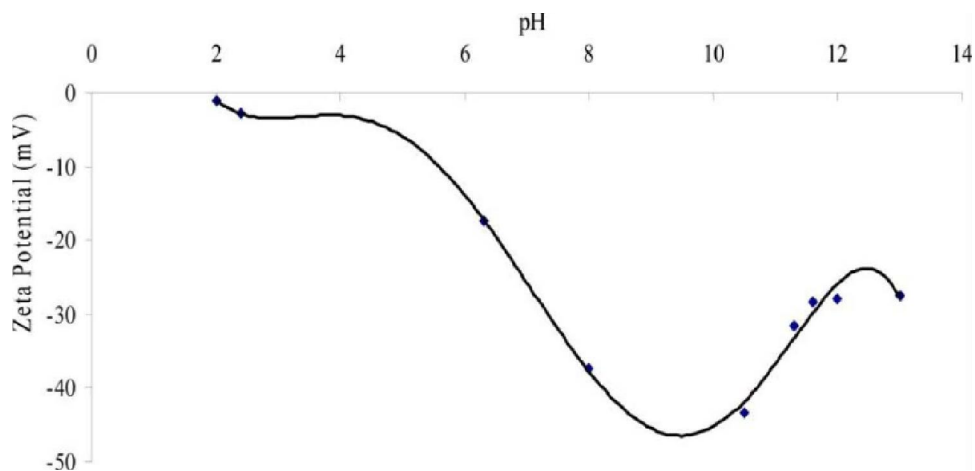
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Figure 1 : Zeta potential as a function of pH for Ludox HS-30

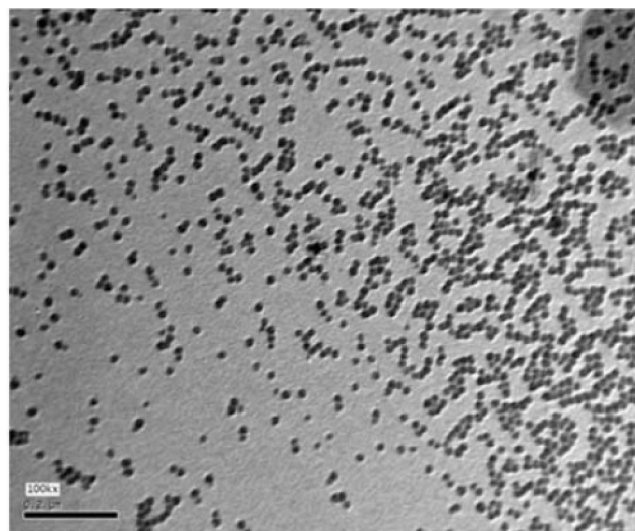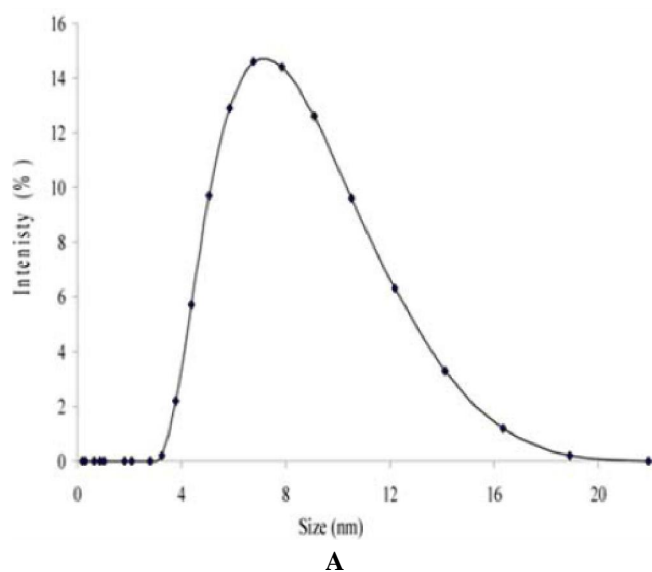A   B

Figure 2 : Dynamic light scattering (A), and TEM (B[x=100.000]) of Ludox Hs-30 (pH = 9.5)

ing the pH. They explained this as some primary particles form few larger flocculated particles whereas the higher the zeta potential values, the more stable the particles in the medium.

The zeta potential of silica nanoparticles in solution (Ludox HS-30) was measured as a function of pH (Figure 1). It is apparent that the zeta potential is increasing in the negative range as the pH increases from 2 and up to 10 then decreases back in the opposite direction up to pH=12 where the maximum acquired zeta potential at this stage was -30 mV. It is implied that the zeta potential of silica increases likely because of the compression of electric double layer when the pH is above 11[17]. In addition, the isoelectric point of the Ludox HS-30 was assigned close to pH 2.

Moreover, the particle size of Ludox Hs-30 was measured at pH 9.5 using dynamic light scattering (DLS) which give rise to size of rage of 3.5 - 17 nm while the average size was 8.8 nm at pH=9.5. On the other hand, it was assigned 14 nm using TEM imaging as shown in Figure 2 which lies in conformity with DLS thus the particles of silica suspension tend to remain as primary particles at pH 9.5.

Styrene, at a concentration of 0.435 mol/L, was sonicated in water using 5 v% of Ludox HS-30 as solid stabilizer at different pH values (2, 4, 8, 10 and 12). The pH was adjusted before and after sonication to supervise the stability of the formed emulsion in each case.

**Effect of pH on the stability of the emulsion before polymerization**
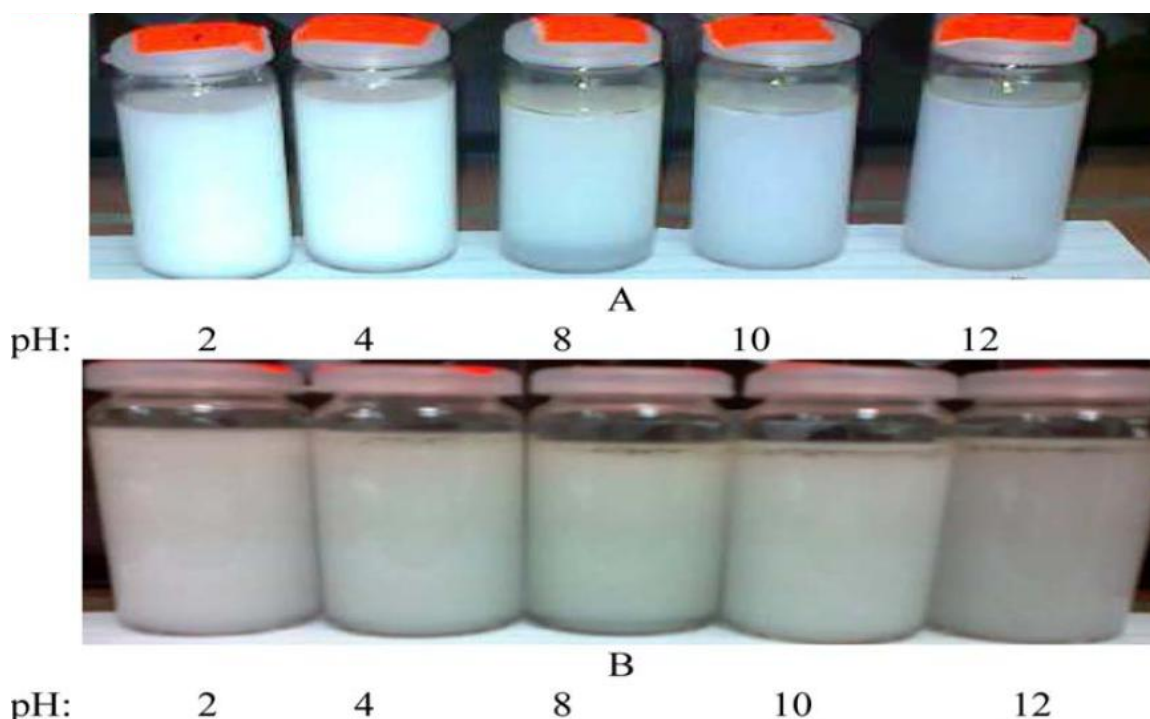
Figure 3 : Digital photographs taken of emulsions after sonication as a function of pH adjusted before the sonication (A) and after the sonication (B) at styrene concentration of 0.435 mol/L: pH=2, 4, 8, 10, 12
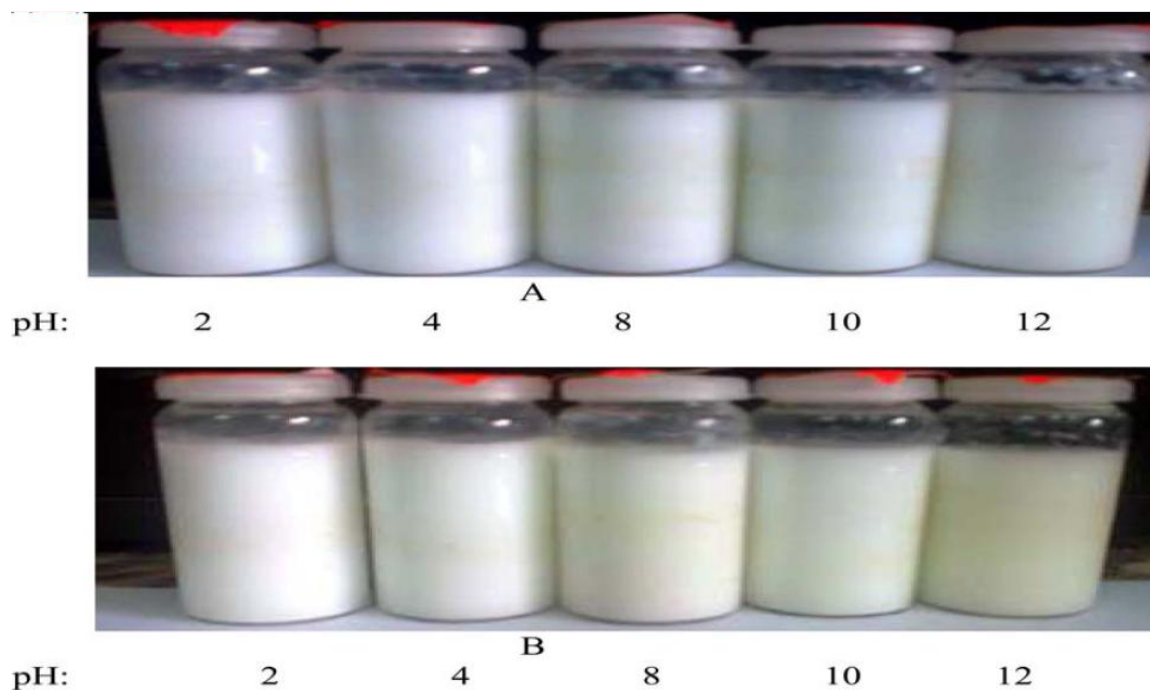
Figure 4 : Digital photographs taken of emulsions after polymerization as a function of pH adjusted before the sonication (A) and after the sonication (B) at styrene concentration of 0.435 mol/L: A; pH=2, B; pH=4, C; pH=8, D; pH=10 and E; pH=12

Figures 3 (A and B) represent the effect of the adjusted pH before and after sonication on the stability of the resulting emulsion at a fixed styrene concentration (0.435 mol/L). It was found that, in case of adjusted pH before sonication, as the pH decreases the emulsion becomes more stable especially at the acidic conditions of pH 2 and 4 (Figure 3A). On the other hand, in case of adjusted pH after sonication, it is obvious that there is absolutely no effect of the pH on the emulsion stability after sonication even at the acidic condi-

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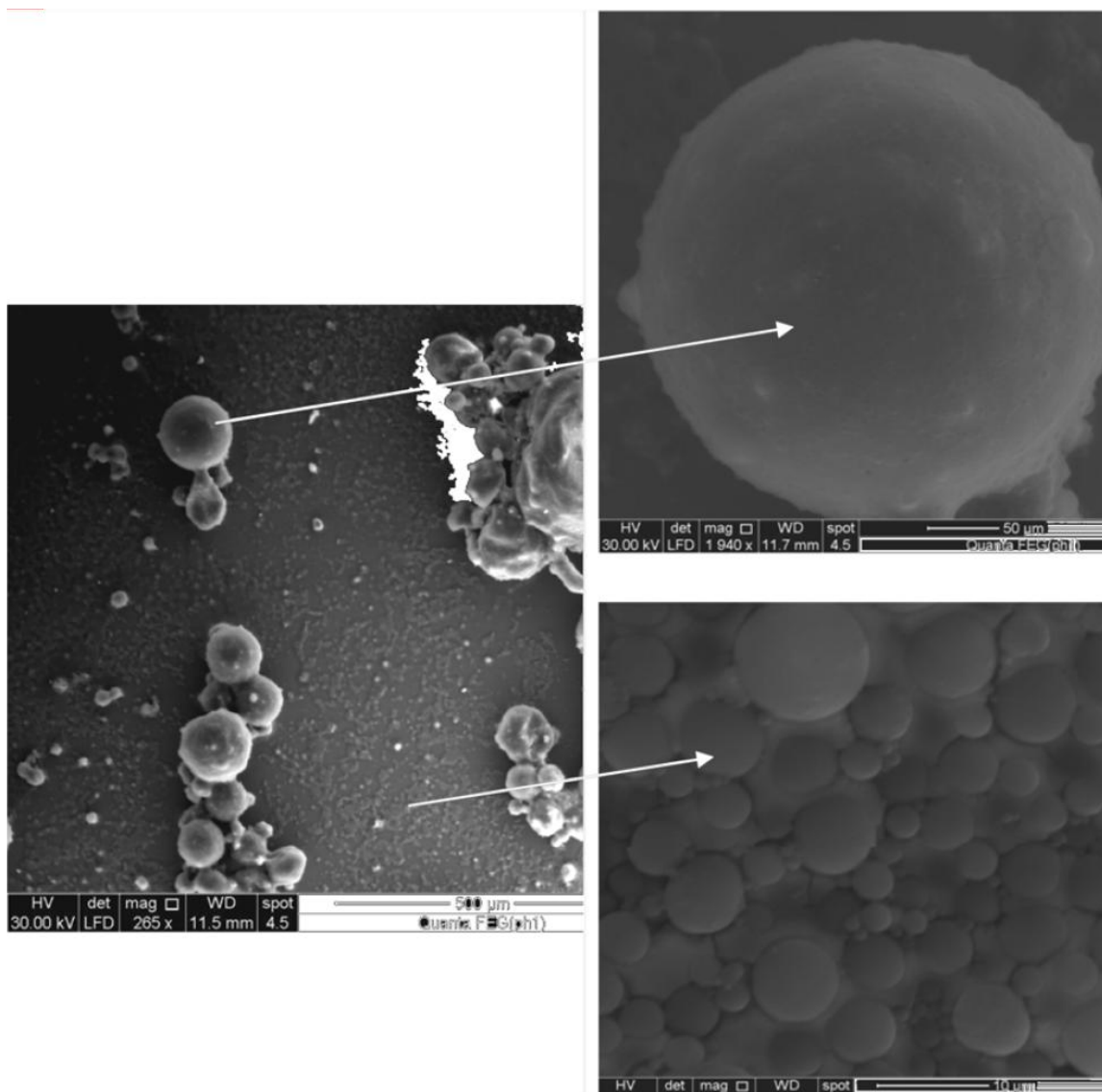
Figure 5 : SEM of polystyrene/Ludox HS-30 composite prepared at pH = 2, using Ludox HS-30 (5 v%) as stabilizer and potassium persulfate as initiator (3.69 mmol/L) at styrene concentration 0.435 mol/L, at different magnifications

tions. However, there was a very small layer of the monomer appearing as top layer, Figure 3 B.

It is known that nano-SiO_2 particles dispersed in aqueous phase can acquire varying surface charge as a function of pH. The surface charge density of nano-SiO_2 particles is determined by the concentration of H^+ and OH^- in the dispersion. According to Yang et al.[18] there should be an energy barrier between the particles dispersed in water and the oil/water interface. Colloidal particles must overcome the energy barrier in order to be adsorbed at the interface. Therefore, the fact that SiO_2 can stabilize Pickering emulsion at acidic conditions (pH=4) rather than at neutral (pH=7) or strong alkaline conditions (pH=13) is ascribed to the dramatic increase of surface charge density leading to increase of energy barrier with the enhancement of electrostatic repulsion between the particles adsorbed at the oil/water interface and the particles in the aqueous phase. A limited adsorption of the particles at the interface results in a loose particle layer on the surface of oil droplets and poor stabilization for the prepared emulsion[19].

In case of pH adjusted after sonication in the presence of the solid particles, there was no effect and this could be ascribed to the fact that SiO_2 nanoparticles were already adsorbed at the oil-water interface in a compact form hence neither H^+ nor OH^- would be able to cause defects in the compact layer with the change of the surface charge density.

TABLE 1 : Effect of pH on the conversion %, weight average molecular weight and average particle size of polystyrene/Ludox HS-30 composite particles prepared using styrene concentration 0.435 mol/L.

Experimental conditions			pH	Conv. %	Mwt X10^{-3} (g/mol)	Particle size (nm)
Water ml	Ludox HS-30 v%	PPS mmol/L				
95	5	3.69	2	78	72.2	1200
95	5	3.69	8	83.8	75.3	328
95	5	3.69	12	89.1	78.5	215
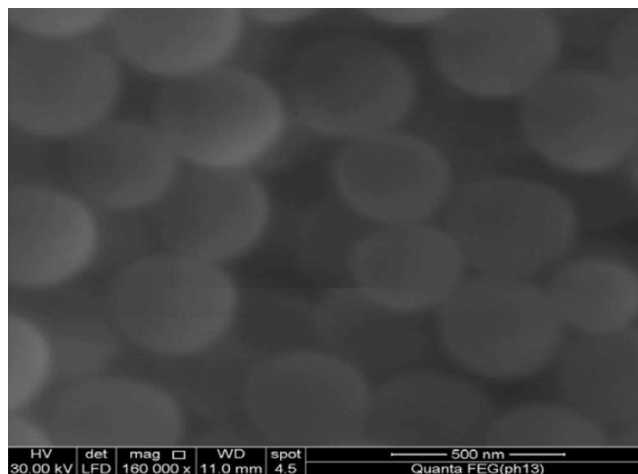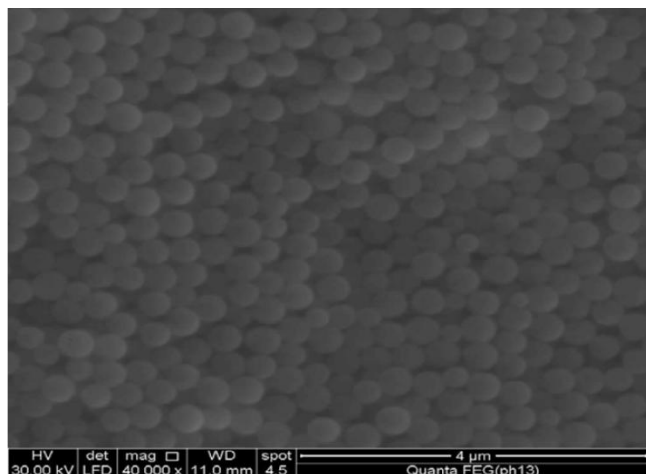
Figure 6 : SEM of polystyrene/Ludox HS-30 composite prepared at pH = 12, using Ludox HS-30 (5 v%) as stabilizer and potassium persulfate as initiator (3.69 mmol/L) at styrene concentration 0.435 mol/L, at different magnifications

Effect of pH on the stability of the emulsion after polymerization

Figures 4 (A and B) reveal the effect of pH adjusted before and after sonication on the stability of the emulsions after polymerization at styrene concentration 0.435 mol/L and potassium persulfate (3.69 mmol/L) as initiator, where the polymerization reactions were conducted at 80°C for 240 min. It could be noticed that the top separated layer of the monomer disappeared completely at the end of polymerization.

TABLE 1 summarizes the effect of the pH on the monomer conversion %, the weight average molecular weight and average particle size of the resulting polymer latexes.

The conversion percent increases with the pH adjusted before sonication and the weight average molecular weight of the composite latex also increases while the average particle size decreases. The emulsion polymerization at pH 2 exhibits the lowest stability where the emulsion was settling and coagulation took place within two weeks which results larger particle size of the emulsion than the usual (Figure 5). This may be correlated with the efficiency of the emulsification pro-

cess of the monomer using the particles under the different employed conditions at the start of the process.

Figures 5,6 show SEM images of polystyrene/ Ludox HS-30 composite latexes, prepared at pH=2 and pH=12, respectively, at different magnifications. At pH 2, a broad particle size distribution in the micrometer range was observed, indicating some coagulation had occurred. This is plausible as electrostatic stabilization through charge repulsion at low pH is poor[20]. At pH 12, the particles appears more uniform in size presumably as a result of more effective electrostatic repulsion.

It was also found that the Ludox HS-30 content has an important impact on the morphology of the products. At low concentration, a core shell microspheres were obtained while at high concentration, hollow microspheres (capsules) were obtained (Figures 5,6). The mechanism of capsule formation was discussed by Essawy and Zhou[21,22]. At high particle content, more ludox HS-30 were available for being adsorbed at the oil-water interface, leading to high coverage at the oil/ water interface and so lead to some inhibition of the formed oligoradicals in the aqueous phase to transfer into the monomer reservoir in the droplets so the poly-
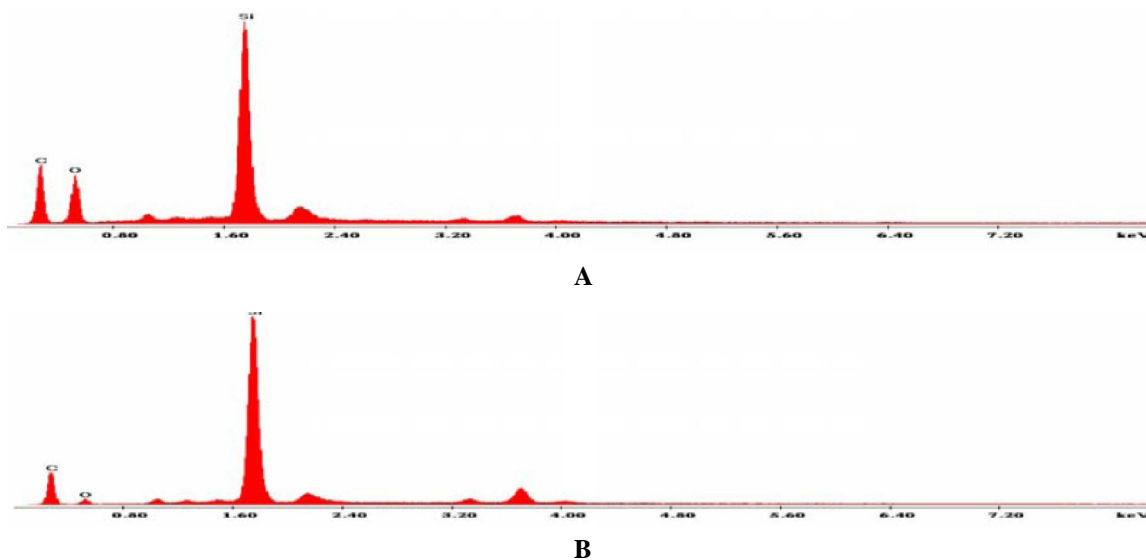
Figure 7 : EDX of polystyrene/Ludox HS-30 composite prepared at pH=2 (A) and pH=12 (B) using Ludox HS-30 (5 v%) as stabilizer and potassium persulfate as initiator (3.69 mmol/L) at styrene concentration 0.435 mol/L, at one spot on the latex particles surface.
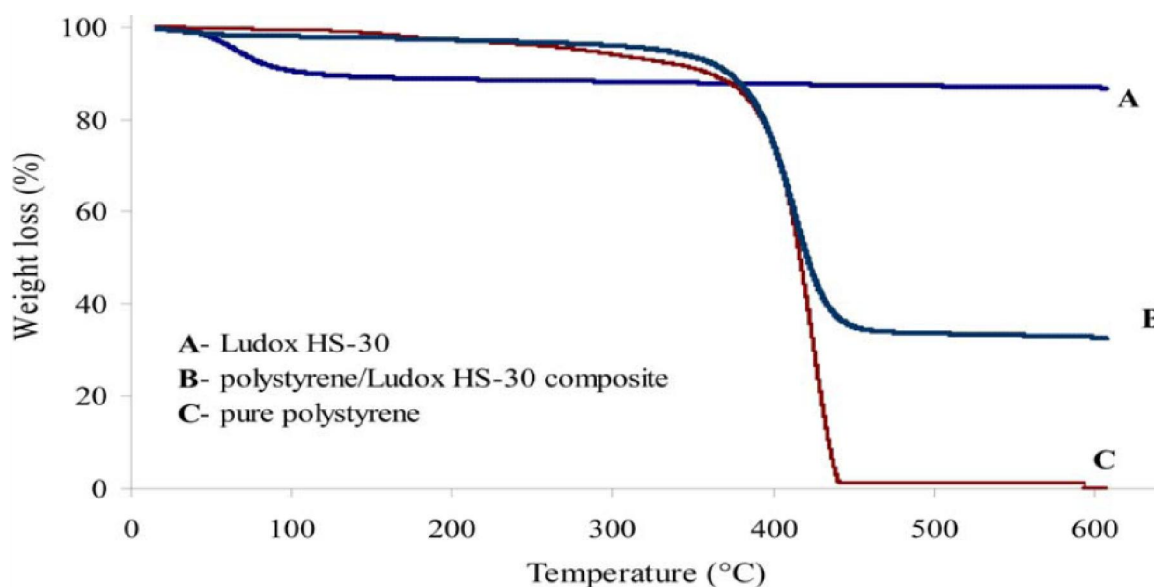

Figure 8 : TG traces of (A) Ludox HS-30, (B) polystyrene/Ludox HS-30 composite and (C) pure polystyrene

merization will take place only at the interface. The conversion of the styrene was rather low for the conditions listed in Figure 6, which is an evidence for retardation of the oligoradicals in the aqueous phase to arrive into the monomer in the core (TABLE 1).

Figures 7 (A and B) show the related EDX for the samples prepared at pH=2 and pH=12, respectively, at single spots on the latex particles. From the EDX spectrum, it can be clearly seen that Si^{4+} and O^{2-} are existing predominately on the composite particle surface which proves that the emulsification process pro-

ceeded via Pickering system.

It is implied that the chemical composition, heating rate, temperature, and inorganic content are the major factors that affect the thermal behavior of materials[23]. Figure 8 displays the gravimetric thermograms of Ludox HS-30, pure polystyrene and polystyrene/Ludox HS-30 composite. It shows that the Ludox HS-30 loses about 11% of its weight in the range 50-150 °C due to removal of physically adsorbed water and then becomes stable. For the pure polystyrene and polystyrene/Ludox HS-30 composite, the weight loss was about 2% at the
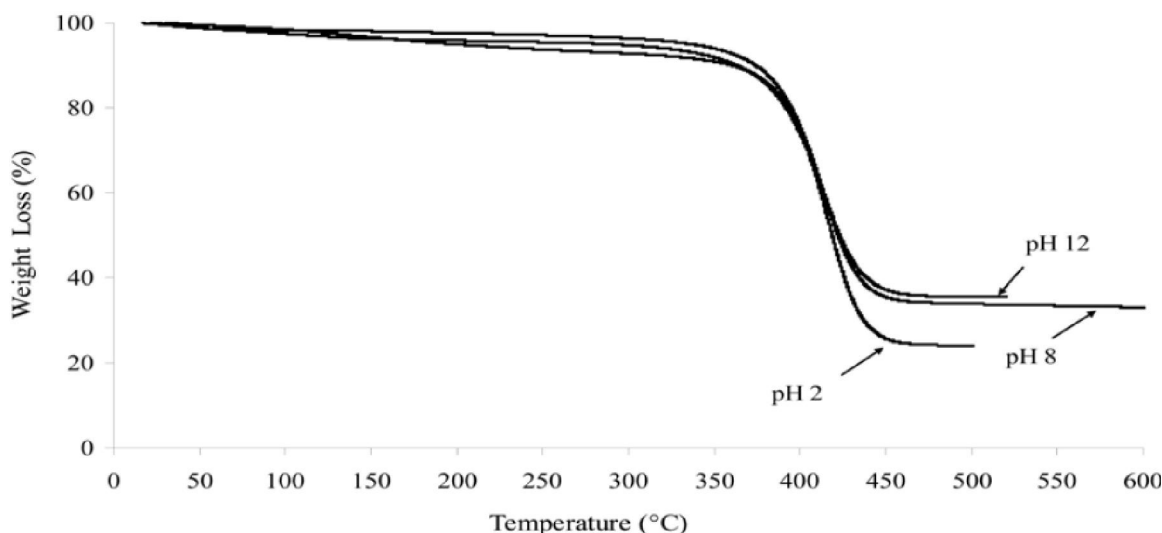
Figure 9 : TG traces of polystyrene/Ludox HS-30 composites prepared at different pH values
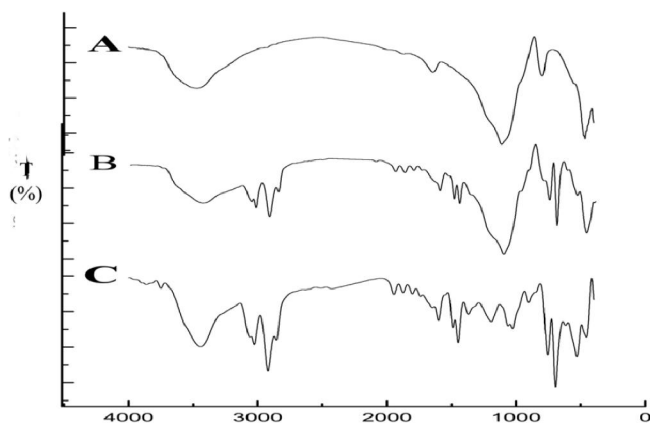

Figure 10 : FTIR spectra of Ludox HS-30 (A), polystyrene/ Ludox HS-30 composite (B) and polystyrene (C)

first stage from 100°C to 250°C due to the liberation of physically bound water, at the second stage a large rapid decrease of weight took place, about 98% and 61%, respectively, at (440-470°C) due to the decomposition of polystyrene.

It is obvious that the polystyrene/Ludox HS-30 composite exhibits enhanced thermal stability due to presence of the inorganic component. The degradation temperature of PS in PS/SiO$_2$ hybrid was a bit higher in the range 280-380°C which was originally resulting from the physical interaction between the SiO$_2$ nanoparticles and the styrene units during the polymerization process and after the polymerization in the form of a protective sheath surrounding the particles. This sheath may also have acted as an insulating layer against the heat transfer thus the thermal stability was elevated. This effect extended to some extent in the range 430-600°C and

represented by a residual weight about 38%.

Figure 9 shows the relevant TG thermograms of polystyrene/Ludox HS-30 composites prepared at different pH values at Ludox HS-30 concentration of 5 v% and styrene concentration of 0.435 mol/L.

The effect of the pH is initially trivial and becomes more obvious at the temperature range above 350ºC which reveals that the thermal stability and residual weight increase with more increase in the pH range up to pH 12. This is thought to be related to the compactness of the stabilizing protective layer on the surface, which formed during the polymerizationz

Figure 10A depicts the related FTIR spectra of Ludox HS-30. The peak at 1111 cm^{-1} refers to the Si–O asymmetric stretching and that at 798 cm^{-1} is ascribed to the Si–O symmetric stretching while the peak at 466 cm^{-1} is attributed to the Si–O asymmetric bending vibration[24]. The FTIR spectra of polystyrene is shown in Figure 10C. The bands at 755.9 and 695.2 cm^{-1} could be attributed to C–H vibrations of the benzene ring whereas the bands at 1600, 1489, and 1448 cm^{-1} could be assigned to benzene ring vibrations (C=C) of polystyrene and the bands at 3061, 3026, 2921 and 2855 cm^{-1} were referred to C-H aromatic and C-H aliphatic, respectively. Also, the band at 3443 cm^{-1} was related to O-H of absorbed water.

The spectra of polystyrene/Ludox HS-30 composite is additionally revealed in Figure 10B which shows that all the major characteristic bands of both polystyrene and Ludox HS-30 are present and that the spectra does not differ very much from that of pure polystyrene.

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TABLE 2 : Attributes of Pickering emulsion polymerization of styrene (0.435 mol/L) at 80ºC at different pH values in the presence of Ludox HS-30 (5 v%) as solid particles stabilizer

pH	Conversion, %												Rp (X10^{-5} mol/L.sec.)
	Time (min.)												
	5	10	15	30	45	60	90	120	150	180	210	240	
2	2.1	3.6	4.7	8.7	13.2	18.3	29.3	41.8	56.8	70.5	76.3	78	3.05
8	3	4.8	6.4	11.4	17.5	23.7	35.1	49.9	63.3	75.9	81	83.8	3.46
12	5	8.6	11.8	19	26.7	35.8	49.4	65.3	78.4	85.7	87.6	89.1	4.01

This combination of bands is pertaining to both components in the hybrid which indicates the participation of both in the formation of this hybrid. This further supports its formation via Pickering emulsification route especially that the intensity of the SiO$_2$ bands is more pronouncing as compared to pure polystyrene.

TABLE 2 reveals the effect of the pH on the rate of Pickering emulsion polymerization of styrene (0.435 mol/L) at 80°C in presence of the PPS (3.69 mmol/L) as initiator and Ludox HS-30 (5 v%) as solid particles stabilizer. It is obvious that the rate of Pickering emulsion polymerization as well as the conversion percent increase with increasing the pH. The promotion of the reaction with increasing the pH is thought to be caused by higher emulsification potency of the Ludox HS-30 at higher pH values despite the fact that the higher alkalinitry pH is likely to stop the action of the initiator. This may be explained by an efficient thermal initiation instead under the employed reaction conditions.

CONCLUSION

Silica nanoparticles proved to be effective solid stabilizers for emulsification of styrene in water, which is a necessary step before its polymerization. The emulsification potency of the silica nanoparticles can be optimized when the monomer is ultrasonicated in water under acidic pH (2 and 4) prior to polymerization. On the other hand, adjusting the pH after sonication was not of any importance as the silica nanoparticles were already set in the form of a protective sheath covering the monomer droplets in the aqueous phase and therefore can not be destroyed easily when changing the pH. The resulting composite latex particles acquire higher thermal stability as compared to the conventional emulsion prepared in absence of silica particles. The conversion %, average molecular weight and particle size

can be controlled as a function of the pH when adjusted before sonication of the monomer.

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