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The morphology study of polyacrylamide prepared by inverse emulsion polymerization

A.B.Mustafa*, M.E.Shaaban
Polymer and Pigment Department, National Research Center, Dokki, Giza, (EGYPT)
E-mail : abakr25@yahoo.com

ABSTRACT

A comprehensive experimental investigation of the inverse-emulsion polymerization of acrylamide was carried out using a water soluble initiator and a sorbitan monooleate as emulsifier. It was found that the increasing redox initiator (potassium persulfate/sodium bisulfite) and monomer concentration increases the volume average diameter ($\overline{D}_v$) and decreases the number of polymer particles per unit volume of oil (N_t) of the prepared polyacrylamide latex particles, while it is obvious that increasing the emulsifier concentration, stirring rate and oil content in water-oil mixture decreases the $\overline{D}_v$ and increases N_t of the prepared polyacrylamide latex particles.

KEYWORDS

Acrylamide;
Sorbitan monooleate;
Inverse-emulsion polymerization;
Particle size;
Morphology.

INTRODUCTION

Polyacrylamide and acrylamide based copolymers are important synthetic water soluble polymers which are used as coagulants and flocculants in waste water and potable water treatment applications. They are also employed as pushing fluids in enhanced oil recovery, as drag reduction agents and drilling fluids, as additives in paper making, and as thickening agents[1,2]. The high enthalpy of polymerization for acrylamide ($\Delta H_p = 19.5$ kCal/mol) along with extreme solution viscosities generated by the high molecular weights leads to problems in large scale reactor operation including non-uniform mixing and heat transfer limitations. These difficulties are generally overcome by polymerizing the acrylic monomer(s) in heterophase water-in-oil (w/o) polymerization process such as inverse-emulsion polymerization[3]. In this process, an aqueous solution of the monomer(s) is emulsified under agitation in a continuous aliphatic oil phase. Steric stabilizers are employed and the polymerization is initiated using, in general, oil soluble initiators at temperatures in the range of 35-50°C. This process allows for polymerizations at high solid concentrations, low viscosities and with good temperature control.

Ye, et. al. studied the inverse emulsion polymerization prepared by using poly(*N*-vinylpyrrolidone) as a steric stabilizer and 2,2'-azobisisobutyronitrile[4] as initiator and by radiation[5]. They found that the size of the resulting polyacrylamide particles increases with increasing initiator concentration as well as with increasing irradiation dose rate, monomer concentration, and polymerization temperature and decreases with increasing stabilizer concentration. In addition, the stability of the final emulsions is poor.

MATERIALS AND METHODS

Acrylamide monomer was purchased from Fluka Chemie packed in Switzerland and used without further purification. Potassium persulfate (PPS) and sodium bisulfite (SBS) were obtained from S.d. fine–chem. ltd. Sorbitan Monooleate as nonionic emulsifier (Span 80, Aldrich Chemical Company, Inc) was used as received. Mineral oil was purchased from Masr Co. for petroleum, and was used as received.

Preparation of polyacrylamide

Homopolymerization of acrylamide by semicontinuous technique

The mineral oil (60 ml) and the emulsifier were stirred for five minutes at 2000 rpm by using an emulsification mixer machine, acrylamide and potassium persulfate was dissolved in the water (40 ml) and then added to the dispersed media. The inverse emulsion was emulsified for 30 minutes at 2000 rpm by emulsification mixer machine.

This emulsion and the sodium bisulfite which is dissolved in a little amount of water both are then added drop wise to 10 ml of the emulsified mineral oil in a 500 ml three necked flask. All the experiments were carried out at room temperature 25°C for 180 minute.

Instrumental measurements

Polymer staining

Dilute solutions of the prepared latices were coated on a grate of transmission electron microscope and left to dry. Then 1% of lauryl acetate was added to the grate of polyacrylamide latices.

Morphological measurements

Transmission electron microscope (TEM) of Zesis model EM 10, Germany, was used to measure the average diameter (□$\overline{D}_v$) for different polymer latex particles. It works at 60 KV, magnification ranges between 2500 and $5x10^5$ and resolution until 0.5 nm.

Image analyzer

The image analyzer (Bild analyze, IBAS 1 and 2) was used to measure the average diameter $\overline{D}_i$ for the different polymer particles and the volume average diameter of the polymer particles ($\overline{D}_v$).

The polydispersity and the morphological characteristics

The volume average diameter of the polymer latex particles ($\overline{D}_v$), the number of polymer particles per unit volume of oil (N_t) and the other morphological characteristics of the prepared polymer particles were determined from the graphs of the prepared polymer particles, which were obtained by the aid of TEM.

The volume average diameter of the polymer particles (□$\overline{D}_v$) was determined from the following equation:

$$\overline{D}_v = [\Sigma N_i \overline{D}_i^3 / N_i]^{1/3}$$

Also the volume of the latex particles per cm^3 (υ) is calculated from the following equation:

$$\upsilon = \pi / 6(\overline{D}_v / 10^7)^3$$

Once the volume of the latex particles is known, the number of particles per unit volume of oil (N_t) can be calculated from the following equation:

$$N_t = (m/w)\ (\%conversion) / 100(\upsilon)\ d_p$$

Where (m/w) is the weight of monomer to oil and d_p is the density of polymer (g/cm^3). The number and weight average diameters were calculated from the following equation:

Number-average particle diameter:

$$(\overline{D}_n) = \Sigma N_i \overline{D}_i / \Sigma N_i$$

Weight-average particle diameter:

$$(\overline{D}_w) = [\Sigma N_i \overline{D}_i^6 / \Sigma N_i D_i^3]^{1/3}$$

RESULTS

The morphological studies of the prepared lattices

The effect of different redox initiator concentrations on the particle size of the prepared polyacrylamide latex particles

TABLE 1 and figure 1 illustrates the morphological data of prepared polyacrylamide latex particles using different concentrations of the potassium persulfate/sodium bisulfite redox system. Furthermore, Figure 2 shows the relationship between the volume average diameters□D_v of the prepared polyacrylamide latex particles versus the redox initiator system concentration. From figures (2,3) and TABLE 1, it is obvious that increasing redox initiator system concentration increases

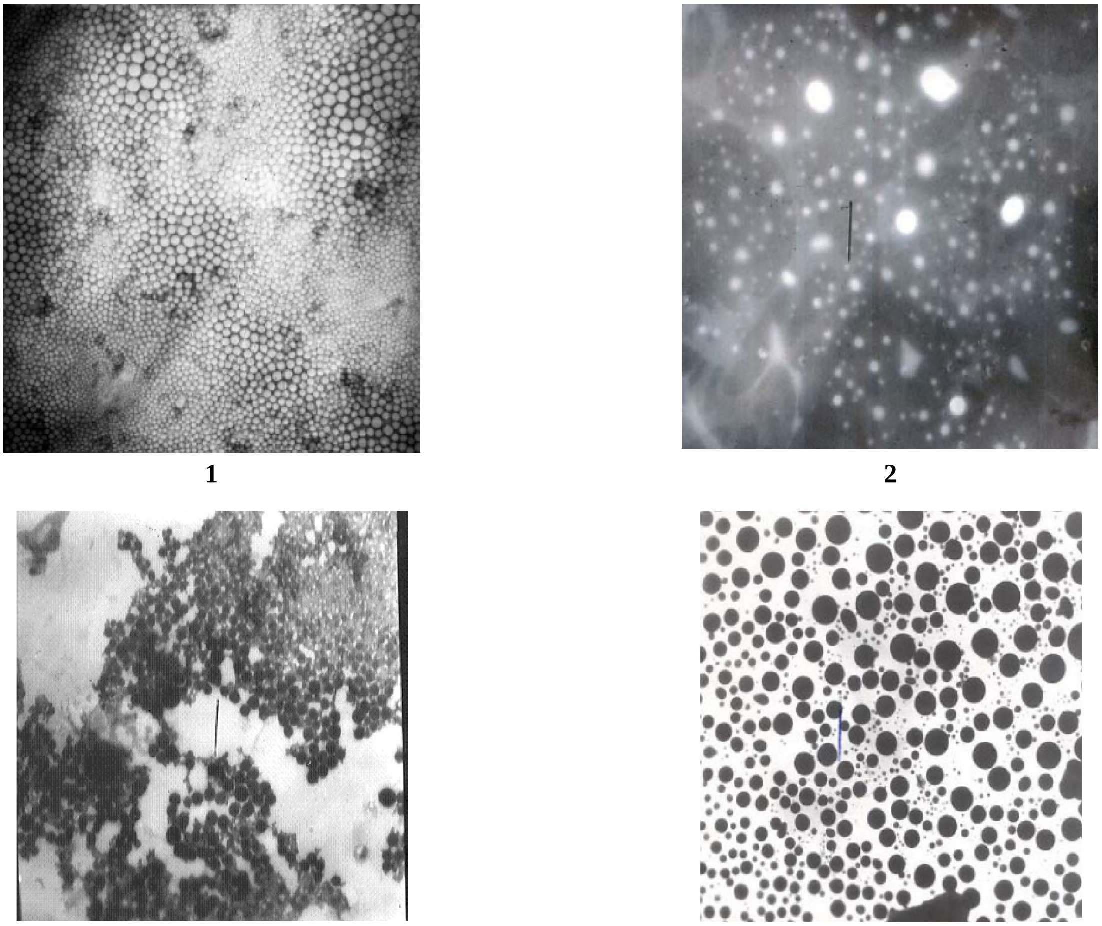

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Figure 1 : The TEM of polyacrylamide latex particles prepared by using span 80 (0.163 gmol/l) as emulsifier in presence of different PPS/ SBS redox initiator concentrations: 1- I=[0.37/0.74] x10^{-2}gmol/l (x=25000), 2- I=[0.55/1.05] gmol/l (x=25000), 3- I=[0.9/1.73] x10^{-2} gmol/l (x=31500), 4- I=[1.1/2.2] x10^{-2}gmol/l (x=40000), water/oil ratio (40/60), acrylamide concentration (3.52 gmol/l)

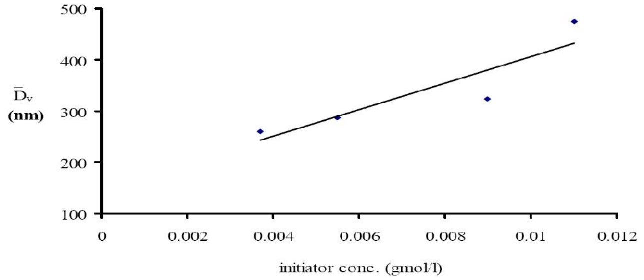

Figure 2 : The relationship between the $\overline{D}_v$ of the prepared polyacrylamide latex particles vs. the initiator concentration

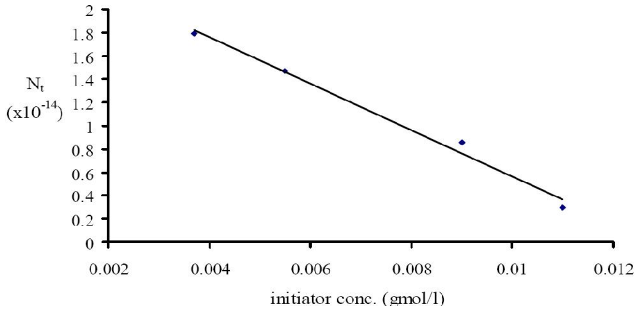

Figure 3 : The relationship between the N_t (10^{-14}) of the prepared polyacrylamide latex particles vs. the initiator concentration

the□$\overline{D}_v$ and decreases N_t of the prepared polyacrylamide latex particles.

This is in conformity with dispersion polymerization experiments[6,7]. where, Tseng et al.[6] as well as Shen et al.[7] believed that a greater initiator concentration leads to a greater rate of generation of unstable oligomeric radicals or dead polymer molecules, in turn leading to a greater rate of coagulation and resulting in larger but fewer particles. When the generation rate of the oligomeric radicals is much faster than the adsorption rate of the stabilizer, the oligomers would tend to aggregate and form larger particle nuclei of various sizes before enough stabilizers adsorbtion to stabilize them. In the same way, our result on the effect of the initiator concentration on the particle size is considered to support the view of Tseng et al.

TABLE 1 : The effect of different concentrations of redox system on $\bar{D}_v$, $\bar{D}_n$, $\bar{D}_w$ and $\bar{D}_w/\bar{D}_n$ for inverse emulsion polymerization of acrylamide (3.521 gmol/l) at room temperature in presence of span 80 (0.163 gmol/l) as nonionic emulsifier

[PPS/ SBS] concentration (x 10^{-2}gmol/l)	Sample number	$\bar{D}_v$ (nm)	$\bar{D}_n$ (nm)	$\bar{D}_w$ (nm)	$\bar{D}_w/\bar{D}_n$	N_t (x10^{-14})
0.37 / 0.74	1	261	252.7	280	1.108	1.79
0.55 / 1.105	2	286.9	281.5	336.2	1.19	1.47
0.92 / 1.84	3	323.9	319.8	399.2	1.24	0.85
1.11 / 2.22	4	474.8	426.6	572.3	1.34	0.30

The effect of different emulsifier concentrations on the particle size of the prepared polyacrylamide latex particles

The inverse emulsion polymerization of acrylamide (3.521 gmol/l.) was carried out at room temperature in presence of different span 80 concentrations as a nonionic emulsifier, using potassium persulfate/sodium bisulfite (0.37/0.74) x10^{-2} gmol/l redox system and water/oil ratio 40/60ml.

TABLE 2 and figure 4 illustrates the morphological data of the prepared polyacrylamide latex particles using different concentrations of the emulsifier. Figure 5 shows the relationship between the volume average diameters $\bar{D}_v$ of the prepared polyacrylamide latex particles versus the emulsifier concentration. From figures (5,6) and TABLE 2, it is obvious that increasing the emulsifier concentration decreases the□$\bar{D}_v$ and increases

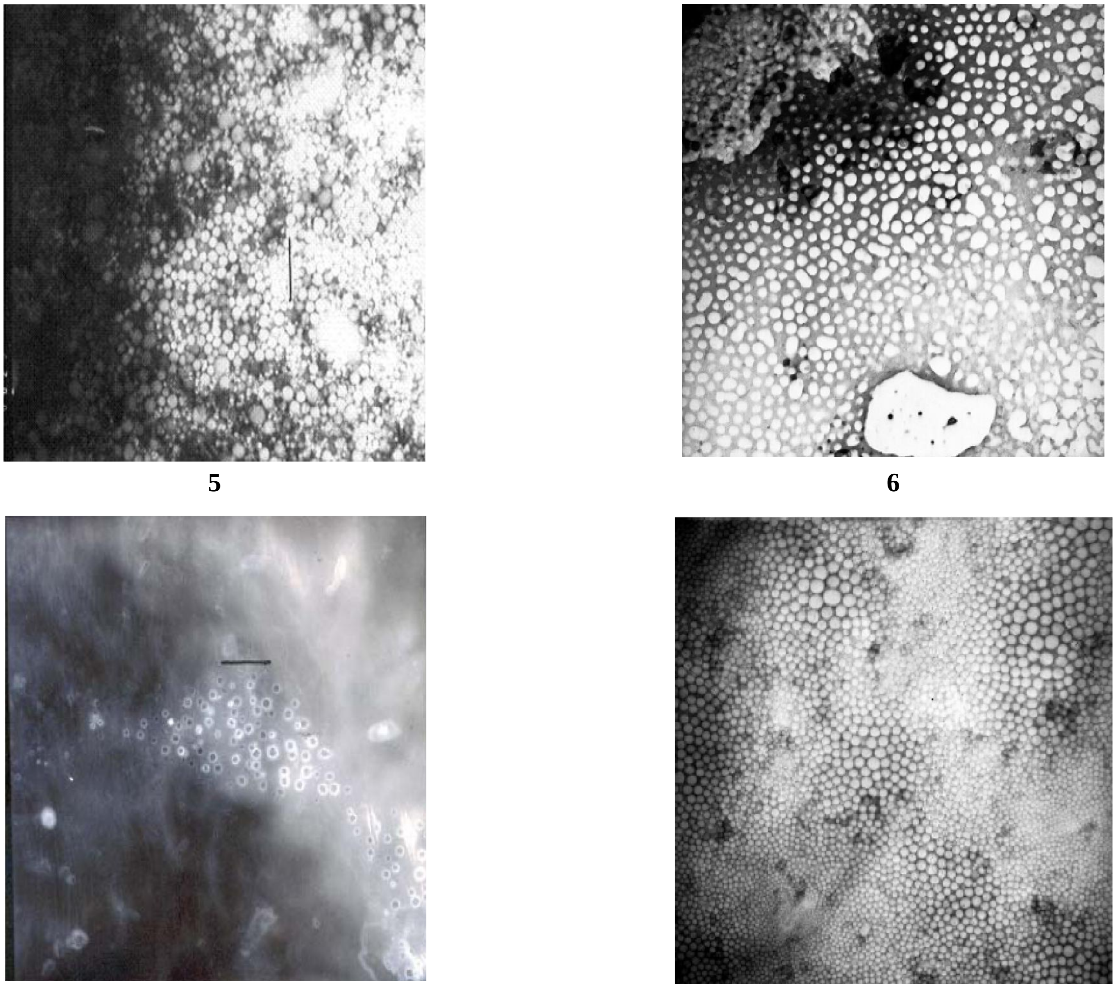

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Figure 4 : The TEM of polyacrylamide latex particles prepared by using PPS/SBS (0.37/0.74) x10^{-2} gmol/l as redox initiator in presence of different emulsifier (span 80) concentrations: 5- E= 0.069 gmol/l (x=40000), 6- E= 0.093 gmol/l (x=20000), 7- E= 0.139 gmol/l (x=25000), 1- E= 0.163 gmol/l (x=25000), water/oil ratio (40/60) and acrylamide concentration (3.521 gmol/l)

TABLE 2 : The effect of different concentrations of the emulsifier on $\overline{D}_v$, $\overline{D}_n$, $\overline{D}_w$ and $\overline{D}_w/\overline{D}_n$ for the inverse emulsion polymerization of acrylamide (3.521 gmol/l) at room temperature using potassium persulfate/sodium bisulfite (0.01/0.019 gmol/l) redox system

[Emulsifier] gmol/l	Sample number	$\overline{D}_v$ (nm)	$\overline{D}_n$ (nm)	$\overline{D}_w$ (nm)	$\overline{D}_w/\overline{D}_n$	N_t ($X10^{-14}$)
0.069	5	363	345	390	1.13	0.66
0.093	6	280.6	270	302.9	1.12	1.18
0.139	7	270.5	263.7	293.2	1.11	1.61
0.163	1	261	252.7	280	1.108	1.79

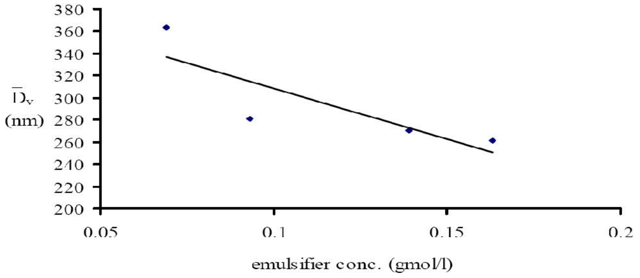

Figure 5 : The relationship between the $\overline{D}_v$ of the prepared polyacrylamide latex particles vs. the emulsifier concentration

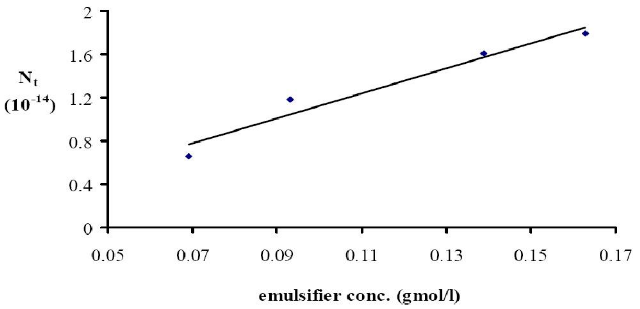

Figure 6 : the relationship between the N_t (10^{-14}) of the prepared polyacrylamide latex particles vs. the emulsifier concentration

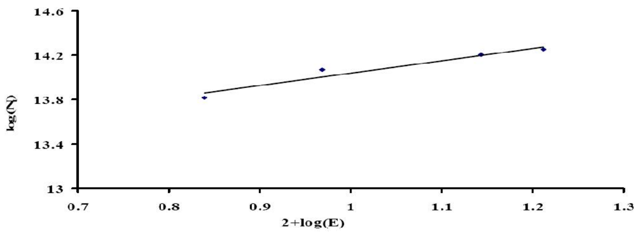

Figure 7 : The double logarithmic relationships between the N_t of the prepared polyacrylamide latex particles and Log (E)

N_t of the prepared polyacrylamide latex particles.

The decrease of particle size with an increase of stabilizer concentration is along the expected lines. With the fixed amounts of monomer and initiator, the rate of nucleation is given constant. Then, under the same rate of nucleation, particles of polyacrylamide will be adsorbed fast to the stabilizer and a greater number of particles of smaller size will be stabilized[9].

Figure 7 is the double logarithmic relationships between the N_t of the prepared polyacrylamide latex particles and the emulsifier concentration.

The relationships between the N_t of polyacrylamide latex particles and the emulsifier concentration can be written as follows: $N_t \, \alpha \, [\text{Emulsifier}]^x$

Where the value of x was calculated from the slope of the straight line of figure 7. This power with respect to the emulsifier concentrations is 1.11.

The effect of different monomer concentrations on the particle size of the prepared polyacrylamide latex particles

The inverse emulsion polymerization of acrylamide was carried out at room temperature 25°C, using potassium persulfate/sodium bisulfite (0.37/0.74) $x10^{-2}$ gmol/l as redox system in presence of span 80 (0.163 gmol/l) as emulsifier and water/oil ratio is 40/60ml.

TABLE 3 and figure 8 illustrate the morphological data of the prepared polyacrylamide latex particles using different concentrations of acrylamide monomer. Furthermore, Figure 9 shows the relationship between the volume average diameters□$\overline{D}_v$ of the prepared polyacrylamide latex particles versus the monomer concentration. From figures (9,10) and TABLE 3, it is obvious that increasing monomer concentration increases the□$\overline{D}_v$ and decreases N_t of the prepared polyacrylamide latex particles.

TABLE 3 : The effect of different concentrations of acrylamide monomer on $\overline{D}_v$, $\overline{D}_n$, $\overline{D}_w$ and $\overline{D}_w/\overline{D}_n$ for inverse emulsion polymerization of acrylamide at room temperature in presence of span 80 (0.163 gmol/l) as nonionic emulsifier using potassium persulfate/sodium bisulfite (0.01/0.019 gmol/l) as redox system

[monomer] gmol/l	Sample number	$\overline{D}_v$ (nm)	$\overline{D}_n$ (nm)	$\overline{D}_w$ (nm)	$\overline{D}_w/\overline{D}_n$	N_t ($X10^{-14}$)
3.521	1	261	252.7	280	1.108	1.79
3.873	8	304.2	297.7	333.5	1.12	1.13
4.225	9	489.9	462.1	587.7	1.27	0.48
4.577	10	544	494.1	664.5	1.34	0.19

The effect of different water/oil ratios on the particle size of the prepared polyacrylamide latex particles

The variation of the ratio of aqueous and organic

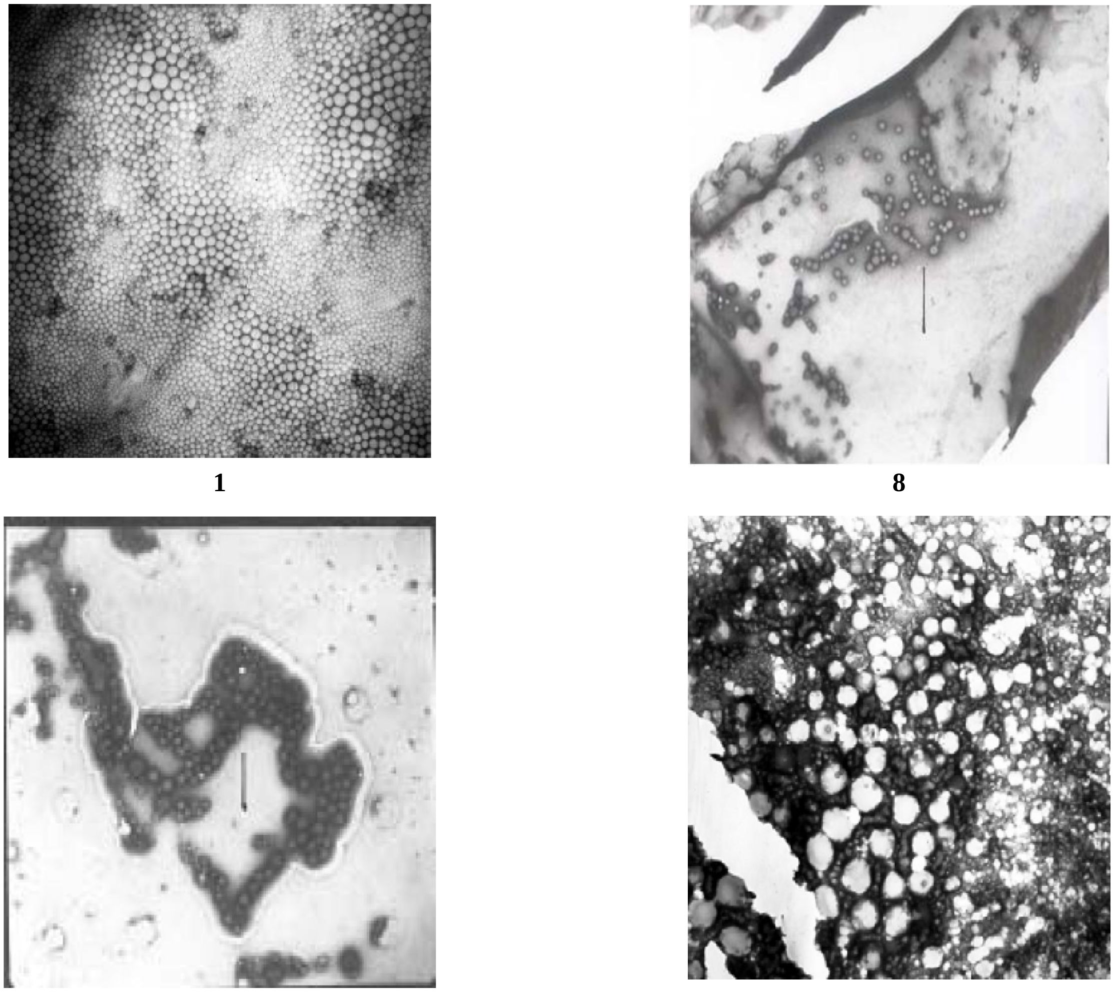
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Figure 8 : The TEM of polyacrylamide latex particles prepared by using PPS/SBS (0.37/0.74) x10^{-2} gmol/l as redox initiator and span 80 (0.163 gmol/l) as emulsifier, in presence of different acrylamide concentrations: 1- M= 3.521 gmol/l (x=25000), 8- M= 3.873 gmol/l (x=10000), 9- M= 4.225 gmol/l (x=10000), 10- M= 4.577 gmol/l (x=25000)

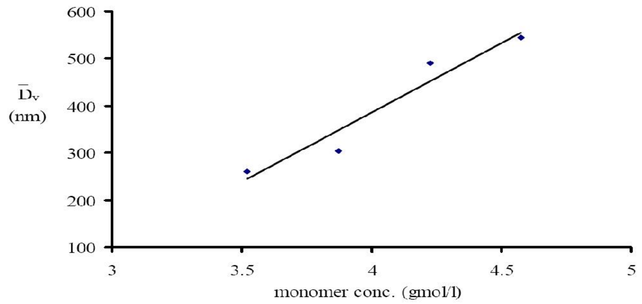

Figure 9 : The relationship between the $\overline{D}_v$ of the prepared polyacrylamide latex particles vs. the monomer concentration

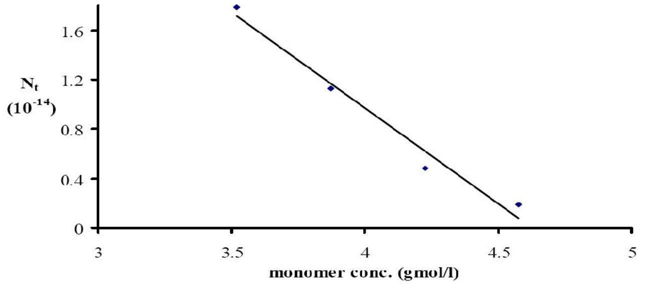

Figure 10 : The relationship between the N_t (10^{-14}) of the prepared polyacrylamide latex particles vs. the monomer concentration

phases also affects the polymerization reaction. As the toluene content in water-toluene mixture increases, the rate of polymerization, and the molecular weight of polymer decreases. This occurs due to an increase in the degree of dispersion of an aqueous phase in the dispersion medium which results in reduction of the emulsion particle size and in an increase of the total saturation of the emulsifier adsorption layers where the elementary polymerization events occur. For example, the inversion of latex obtained in inverse emulsions is easily obtained by adding excess water to facilitate solubility of

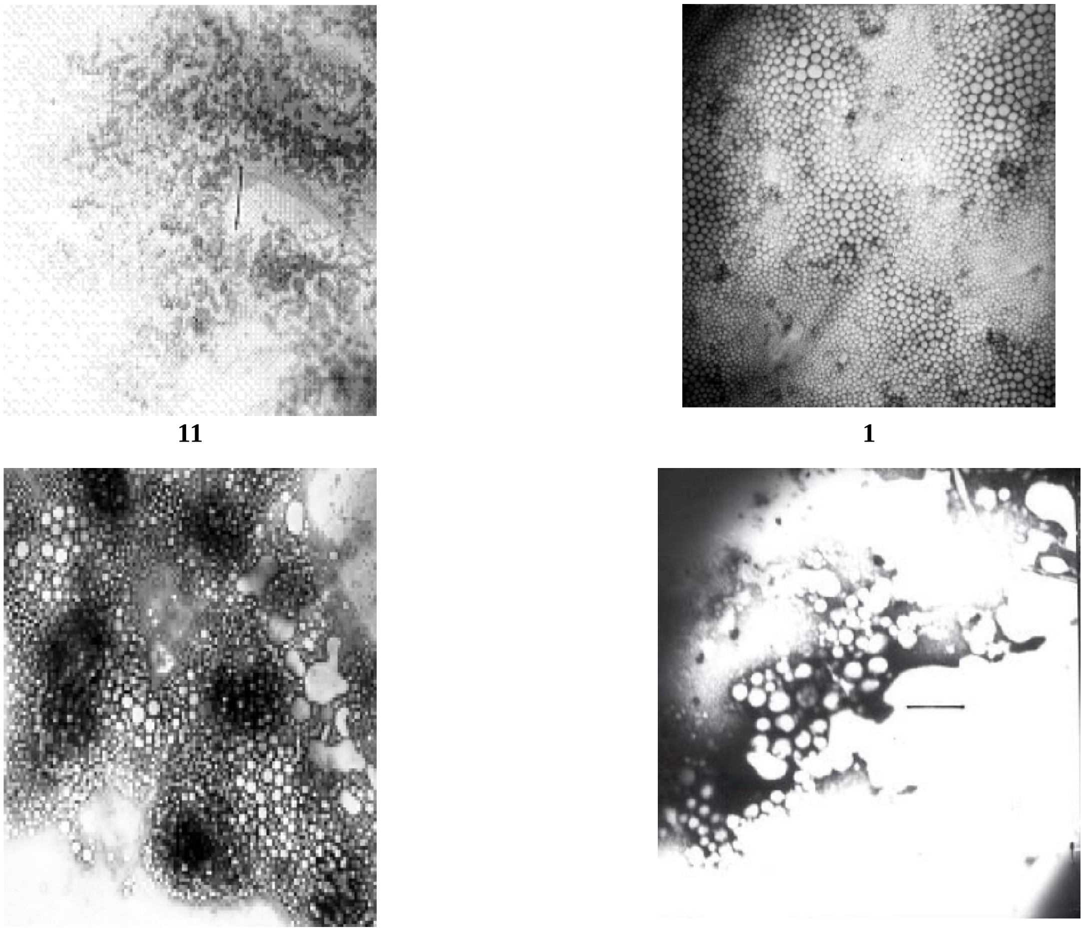

Figure 11 : The TEM of polyacrylamide latex particles prepared by using PPS/SBS (0.37/0.74) x10^{-2} gmol/l as redox initiator and span 80 (0.163 gmol/l) as emulsifier in presence of different water/oil ratios: 11- W/O =[30/70] ml (x=40000), 1- [40/60] ml (x=25000), 12- [50/50] ml (x=25000), 13- [60/40] ml (x=10000)

the polymer particles swelling in the water[10].

The inverse emulsion polymerization of acrylamide (3.521 gmol/l.) was carried out at room temperature 25°C, using potassium persulfate/sodium bisulfite (0.37/0.74) x10^{-2} gmol/l as redox system in presence of span 80 (0.163 gmol/l) as emulsifier.

TABLE 4 : The effect of different water/oil ratio on $\overline{D}_v$, $\overline{D}_n$, $\overline{D}_w$ and $\overline{D}_w/\overline{D}_n$ for inverse emulsion polymerization of acrylamide (3.521 gmol/l.) at room temperature in presence of span 80 (0.163 gmol/l) as nonionic emulsifier using potassium persulfate/sodium bisulfite (0.01/0.019 gmol/l) as redox system

Water/ oil ratio ml	Sample number	$\overline{D}_v$ (nm)	$\overline{D}_n$ (nm)	$\overline{D}_w$ (nm)	$\overline{D}_w/\overline{D}_n$	N_t (X10^{-14})
30/70	11	222.7	209.4	230.4	1.1	2.47
40/60	1	261	252.7	280	1.108	1.79
50/50	12	311.3	296.9	360	1.21	1.27
60/40	13	492.6	459	560	1.22	0.53

TABLE 4 and figure 11 illustrates the morphological data of the prepared polyacrylamide latex particles using different water/oil ratios. Furthermore, Figure 12 shows the relationship between the volume average diameters $\overline{D}_v$ of the prepared polyacrylamide latex particles versus the water\oil ratio. From figures (12, 13) and TABLE 4, it is obvious that increasing oil content in water-oil mixture the□$\overline{D}_v$ decrease of the prepared poly-

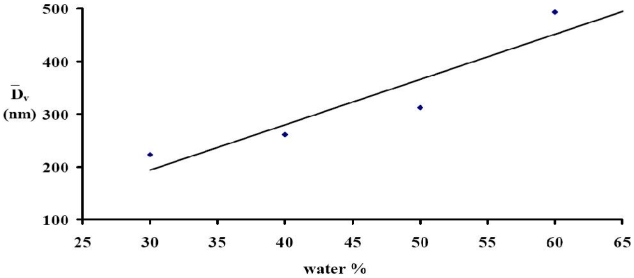

Figure 12 : The relationship between the $\overline{D}_v$ of the prepared polyacrylamide latex particles vs. the water/oil ratio

acrylamide latex particles occur.

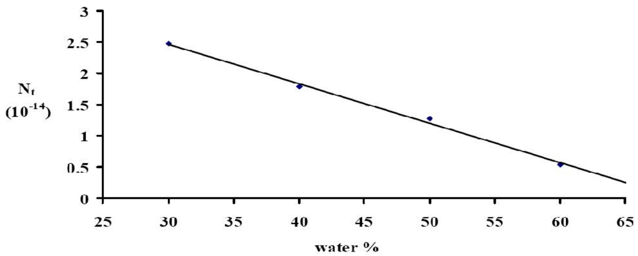

Figure 13 : The relationship between the N_t (10^{-14}) of the prepared polyacrylamide latex particles vs. the water/oil ratio

The effect of the stirring rate on the particle size of the prepared polyacrylamide latex particles

The inverse emulsion polymerization of acrylamide (3.521 gmol/l.) was carried out at room temperature 25°C, using potassium persulfate/sodium bisulfite (0.37/0.74) x10^{-2} gmol/l as redox system in presence of span 80 (0.163 gmol/l) as emulsifier and water/oil ratio is 40/60ml.

The stirring rate has been found to have a critical influence on the dispersion of the aqueous droplets which are usually believed to be the main reaction loci in inverse emulsion polymerization. As shown in the data of TABLE 5, partial coagulation takes place when the polymerization is carried out under agitation of 900 rpm. However a high stirring rate is necessary at the beginning of the polymerization in order to have a good dispersion of the monomer emulsion. Thus, a pre emulsification step at 2,000 rpm for 30 minutes has been carried out and then the stirring rate was reduced and fixed at the required rpm during the polymerization step.

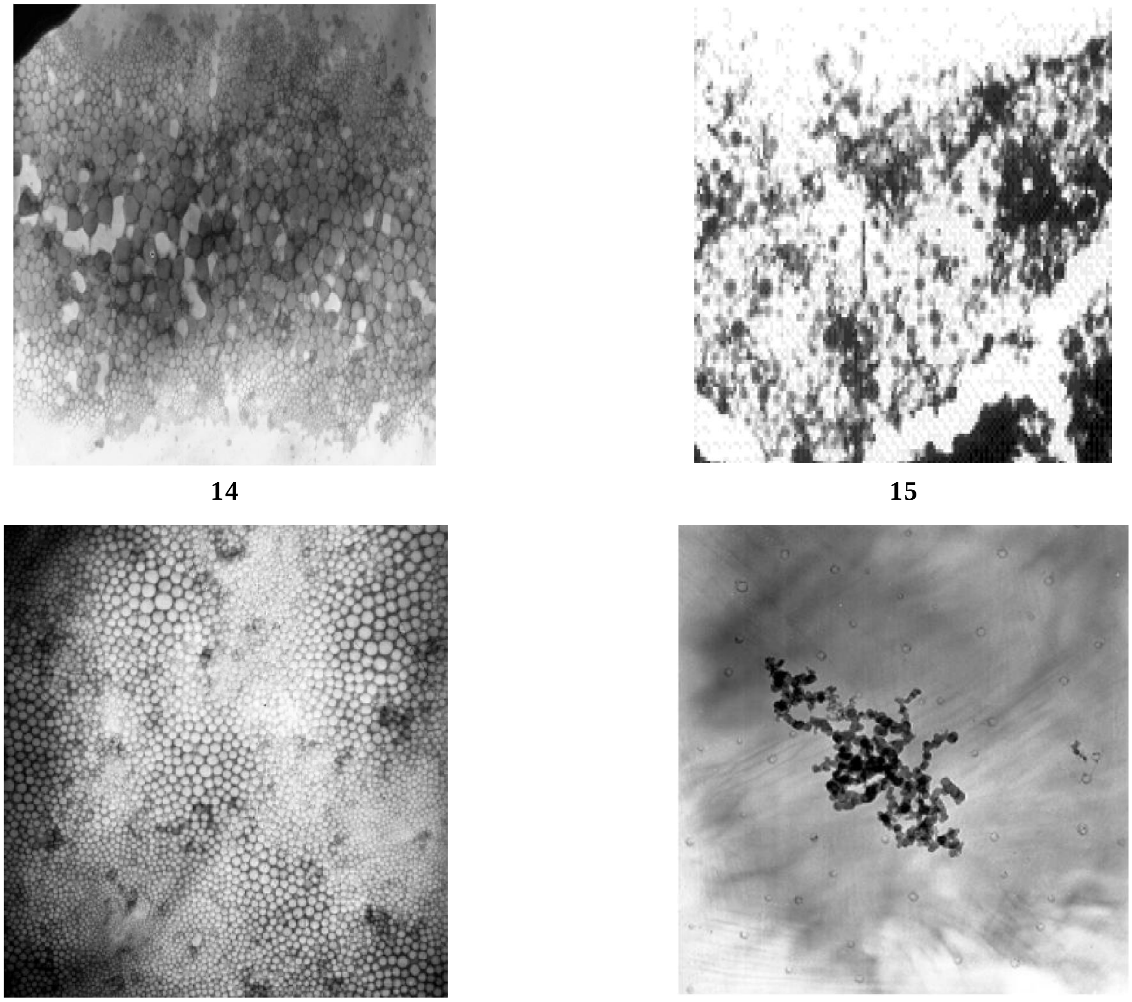
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Figure 14 : The TEM of polyacrylamide latex particles prepared by using PPS/SBS (0.37/0.74) x10^{-2} gmol/l redox system initiator and span 80 (0.163 gmol/l) as emulsifier in presence of different stirring rates: 14- S.R=[200] rpm (x=25000), 15- [350] rpm (x=40000), 1- [500] rpm (x=25000), 16- [700] rpm (x=40000)

TABLE 5 : The effect of stirring rate on $\overline{D}_v$, $\overline{D}_n$, $\overline{D}_w$ and $\overline{D}_w/\overline{D}_n$ for inverse emulsion polymerization of acrylamide (3.521 gmol/l.) at room temperature in presence of span 80 (0.163 gmol/l) as nonionic emulsifier using potassium persulfate/ sodium bisulfite (0.01/0.019 gmol/l) as redox system

Stirring rate S.R	Sample number	$\overline{D}_v$ (nm)	$\overline{D}_n$ (nm)	$\overline{D}_w$ (nm)	$\overline{D}_w/\overline{D}_n$	N_t ($X10^{-14}$)
200	14	313.9	299.4	344.3	1.15	1.03
350	15	301.7	296.2	333.8	1.12	1.16
500	1	261	252.7	280	1.108	1.79
700	16	188.6	191.7	204.5	1.06	2.65
900	coagulated					

TABLE 5 and figure 14 illustrate the morphological data of prepared polyacrylamide latex particles using different stirring rates. Furthermore, Figure 15 shows the relationship between the volume average diameters $\overline{D}_v$ of the prepared polyacrylamide latex particles versus the stirring rate. From figure (15,16) and TABLE 5, it is obvious that increasing the stirring rate decreases the $\overline{D}_v$ and increases N_t of the prepared polyacrylamide latex particles. While at the rate of stirring 900 rpm coagulation of particles took place. It was recognized that the increased coalescence of polymer particles due to the higher stirring speed, due to de-sorption of the stabilizer molecule from the particles surface and the particles become unstable and the coagulation occurs[11].

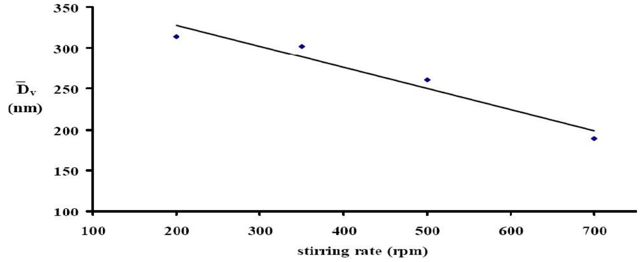

Figure 15 : The relationship between the $\overline{D}_v$ of the prepared polyacrylamide latex particles vs. the stirring rate

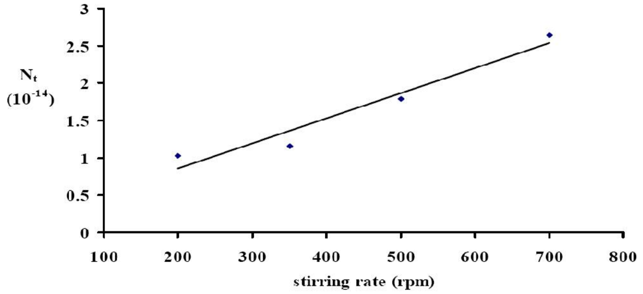

Figure 16 : The relationship between the N_t (10^{-14}) of the prepared polyacrylamide latex particles vs. the stirring rate

CONCLUSIONS

It was found that the increasing redox initiation system and monomer concentration increases the□$\overline{D}_v$ and decreases N_t of the prepared polyacrylamide latex particles, while it is obvious that increasing the emulsifier concentration, stirring rate and oil content in water-oil mixture decreases the□$\overline{D}_v$ and increases N_t of the prepared polyacrylamide latex particles

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