

Effect of Polyvinyl Alcohol of Different Molecular Weights as Protective Colloids on the Kinetics of the Emulsion Polymerization of Vinyl Acetate

K.A. Shaffie^{*1}, A.B. Moustafa², N.H. Saleh², H. E. Nasr²

¹Dept. of Chemistry, Faculty of Science, Helwan Univ, Helwan, Egypt.

²Dept. of Polymers & Pigments, National Research Center, Dokki, Cairo, Egypt

*Khaled.shaffei2006@yahoo.com

Abstract: The kinetics of emulsion polymerization of vinyl acetate in the presence of polyvinyl alcohol (PVA) of different molecular weights as protective colloid using potassium-persulphate / acetone sodium bisulphite as a redox initiation system was studied. The effect of polyvinyl alcohol on the rate of polymerization, maximum conversion as well as the morphological characteristics was investigated. The results showed that the rate of polymerization was found to be dependent on the initiator, protective colloid, and monomer concentrations to the powers 0.81, 0.65 and 0.60 respectively, for polyvinyl alcohol of lowest molecular weight and to the powers 0.90, 0.61 and 0.66 for the medium molecular weight, also to the powers 1.20, 0.51 and 0.63 for the highest one. The activation energies values for the emulsion polymerization of VAc using different molecular weights are as follows 0.946×10^4 , 1.0613×10^4 , and 0.932×10^4 J / mol for PVA of molecular weights (9000, 34000, 125000) respectively. The morphological studies of some prepared polyvinyl acetate latex particles reveal that increasing the initiator concentration decreases the volume average diameter (\bar{D}_v) of some prepared latex particles and increases the number of polymer particles per unit volume of water. Also the \bar{D}_v of some prepared latex particles increases with increasing the molecular weight of the protective colloid, while the number of polymer particles per unit volume of water decreases. The viscosity average molecular weights M_v of some prepared latices decreases with increasing the initiator concentration.

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Key words: Emulsion polymerization, kinetics, morphology, vinyl acetate, poly (vinyl alcohol), redox initiation system.

1. Introduction:

Emulsion polymerization is a free radical initiated chain polymerization in which a monomer or a mixture of monomers is polymerized in the presence of an aqueous solution of a surfactant to form a product known as latex. The latter is defined as a colloidal dispersion of polymer particles in an aqueous medium. Three types of processes are commonly used in emulsion polymerization, batch, semi continuous (or semibatch) and continuous. Semi-batch emulsion polymerization processes generate a large number of polymer particles compared with conventional batch processes^(1, 2). Semi batch processes produce more particles than batch processes only if monomer droplets are depleted earlier than surfactant micelles.

The chemical composition of the surfactant influences the compatibility with the polymer, if the surfactant is similar to the polymer, it will dissolve and plasticize the polymer^(3, 4) the amount of carboxylic groups in the shell of the particles can

modify the chemical compatibility with the surfactant^(5, 6). Polyvinyl alcohol PVA has been used industrially as a dispersant in the synthesis of the copolymer emulsions of vinyl acetate (VAc). There are several reasons to adopt PVA in the commercial co polymer emulsions of VAc⁽⁷⁾, the mechanical properties such as tensile strength and creep resistance are enhanced by PVA in the emulsion films. This is one of the most important points when the emulsion is utilized in the application field of adhesives.

The addition of alcohol⁽⁸⁾ to the emulsion polymerization of VAc using ammonium persulphate (APS) and PVA as a protective colloid remarkably affected the particle formation, especially grafting. This is thought to be attributed to competition between hydrogen abstraction from PVA and alcohol with a sulphate radical. The addition of acetone to the system decreased grafting to a great extent resulting in an increase in the particle size together with an increase in the number of polymer molecules in a

polymer particle. In the emulsion polymerization⁽⁹⁾ of VAc using PVA as a protective colloid where a small amount of VAc was employed, it is found that in the presence of large amounts of PVA, the number of new particles smaller than 80 nm continued to increase during the polymerization, while there was not much increase in the particle diameter. In contrast, in the absence of PVA, the particles formed at the very early stage continued to grow and the number of particles did not increase so many, the⁽¹⁰⁾ PVA blockiness did not influence greatly the polymerization kinetics in the emulsion polymerization of VAc using different types of PVA where three fractions of PVA are separated in the latex, free in the water phase, physically adsorbed onto the polymer particles and chemically grafted. The grafted fraction is relatively lower than the physically adsorbed fraction, and the grafted fraction is almost constant with different PVA types. Many authors studied the relation between the kinetics of emulsion polymerization of VAc and PVA molecular average molecular weight⁽¹¹⁻¹³⁾. Comparing the latexes⁽¹⁴⁾ obtained in the semi-continuous polymerization of VAc, butyl acrylate BA, Veova 10, and hexafluorobutyl methacrylate using an anionic polymerizable fumaric surfactant a new surfmer and that obtained using sodiumdodecyl sulphate SDS, it is found that the new surfmer behaved much better with respect to the stability of the latexes and the water sensitivity of the films. A nonlinear relationship⁽¹⁵⁾ was observed between the rate of polymerization R_p and the number of particles (N_p) and the final N_p was independent of the degrees of blockiness of PVA on studying the role of grafting in the particle nucleation during the emulsion polymerization of VAc with partially hydrolyzed PVA as a protective colloid and potassium persulphate KPS as an initiator. On studying⁽¹⁶⁾ the effect of the emulsion polymerization conditions of VAc on the viscosity fluctuation and the gelation behavior of the aqueous PVA solution at 40, 50 and 60°C, it is found that the viscosity is increased with increasing the molecular weight when other parameters are held constant. On emulsion polymerization⁽¹⁷⁾ of VAc in presence of APS as an initiator, an ethoxylated nonylphenol as a nonionic

surfactant and PVA as a protective colloid using semicontinuous process, the resultant latex viscosity decreased and the viscosity-average polymer molecular weight increased with increasing the ethoxylation degree of the nonionic surfactant. The increase in the ethoxylation degree did not seriously affect the surface tension of the resultant latex or the surface free energy of the dried PVAc films.

The aim of this work is to study the kinetics of emulsion polymerization of vinyl acetate using different molecular weights of polyvinyl alcohol as protective colloids and potassium persulphate – acetone sodium bisulphite as a redox initiation system. The morphological characteristics of the obtained polymer and the viscosity average molecular weights of some prepared polyvinyl acetate latexes are to be determined using different initiator concentrations and the different molecular weights of the protective colloid.

2. Experimental

Vinyl acetate monomer (stabilized with 14ppm hydroquinone) was provided by Sigma-Aldrich chemical company Ltd. England was redistilled before use and stored at -20°C. Potassium persulphate was recrystallized from water by methanol, and the final crystals were vacuum dried. Poly vinyl alcohol of molecular weights (9000, 34000 and 125000) are a product of Vinavil, Italy. All water used was purified by distillation.

Techniques

The following ingredients were mixed in a 250 ml three necked flask, the order of addition was as follows: water, initiator, PVA and VAc monomer according to the recipe in Table I. The polymerization reactions were carried out at the required temperature (± 2 °C) in an automatically controlled water bath. All the experiments were run with mechanical stirring at 250 rpm; this speed is in the range where the agitation has no noticeable effect on the rate of polymerization.

Table I: Recipe of emulsion polymerization of vinyl acetate

Ingredient	Function	Amount (Mol/l X10 ⁻³)
Vinyl acetate	Monomer	0.54-2.165
PVA with different Mw 9000, 34000 And 125000	Emulsifier	0.1389-0.5556 0.0184-0.1103 0.01-0.04
Potassium persulphate/ acetone sodium bisulphite	Oxidizing agent	2.5-15/5-30
Demineralized water	Dispersion medium	Variable

The rate of emulsion polymerization of vinyl acetate and the number of polymer particles per unit volume of water were calculated as mentioned previously⁽¹⁸⁾. The polydispersity of polymer particles were calculated by a computerized image analyzer equipment to find the particle size, the number of polymer particles per unit volume of water and the polydispersity. The viscosity average molecular weight of different emulsion latices were measured using Ostwald viscometer.

3. Results and Discussion:

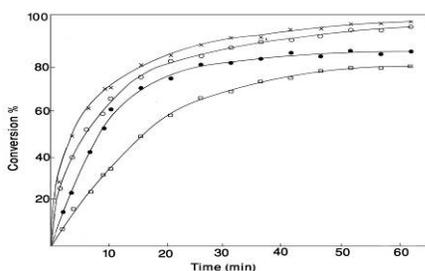
Effect of initiator concentration on the rate of polymerization

Figures (1-3) demonstrate the conversion-time relationships for emulsion polymerization of VAc at 50°C using different concentrations of potassium persulphate – acetone sodium bisulphite KPS /AcSBS in presence of PVA with different Mw (9000, 34000 and 125000). The monomer concentration was kept at 1.083 mol /l. It is obvious that the rate of polymerization as well as maximum conversion increased with increasing initiator concentration.

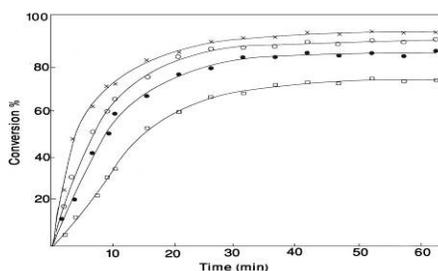
Moreover, the obtained conversion time curves show a sigmoidal shape similar to that revealed for the classical emulsion polymerization. From Figure (4) it is clear that the rate of polymerization (R_p) was found to be dependent on the initiator concentration to the power 0.81, 0.90, and 1.20 respectively for Mw 9000, 34000 and 125000 respectively due to the organic nature of the reducing agent of the initiation system which is more easily attracted to the high molecular weight of PVA micelles than the lower molecular weight. These results are agreement with that obtained by Badran et al⁽¹⁸⁾ which stated that the rate of polymerization was found to be 1.14 with respect to the initiator concentration. Another prove by this author that the emulsion polymerization of vinyl acetate was more efficiency in the presence of aliphatic adduct as reducing agent. The rate equation with respect to initiator concentration is as follow:

$$R_p \propto [I]^X$$

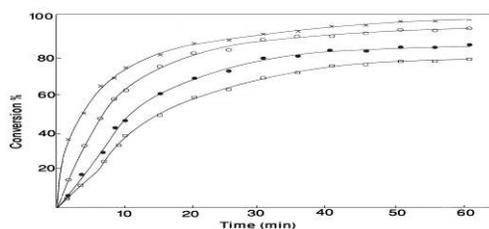
Where [I] is the initiator concentration and X was found to be equal 0.81, 0.90, and 1.20.



Figure(1): Conversion-time plot of the emulsion polymerization of VAc in presence of PVA (M.w 9000) using different concentrations of KPS/AcSBS
 □ - $2.5 \times 10^{-3} / 5 \times 10^{-3}$ mol / l ● - $5 \times 10^{-3} / 10 \times 10^{-3}$ mol / l
 ○ - $10 \times 10^{-3} / 20 \times 10^{-3}$ mol / l x - $15 \times 10^{-3} / 30 \times 10^{-3}$ mol / l



Figure(2): Conversion-time plot of the emulsion polymerization of VAc in presence of PVA (M.w 34000) using different concentrations of KPS/AcSBS
 □ - $2.5 \times 10^{-3} / 5 \times 10^{-3}$ mol / l ● - $5 \times 10^{-3} / 10 \times 10^{-3}$ mol / l
 ○ - $10 \times 10^{-3} / 20 \times 10^{-3}$ mol / l x - $15 \times 10^{-3} / 30 \times 10^{-3}$ mol / l



Figure(3): Conversion-time plot of the emulsion polymerization of VAc in presence of PVA (M.w 125000) using different concentrations of KPS/AcSBS
 □ - $2.5 \times 10^{-3} / 5 \times 10^{-3}$ mol / l ● - $5 \times 10^{-3} / 10 \times 10^{-3}$ mol / l
 ○ - $10 \times 10^{-3} / 20 \times 10^{-3}$ mol / l x - $15 \times 10^{-3} / 30 \times 10^{-3}$ mol / l

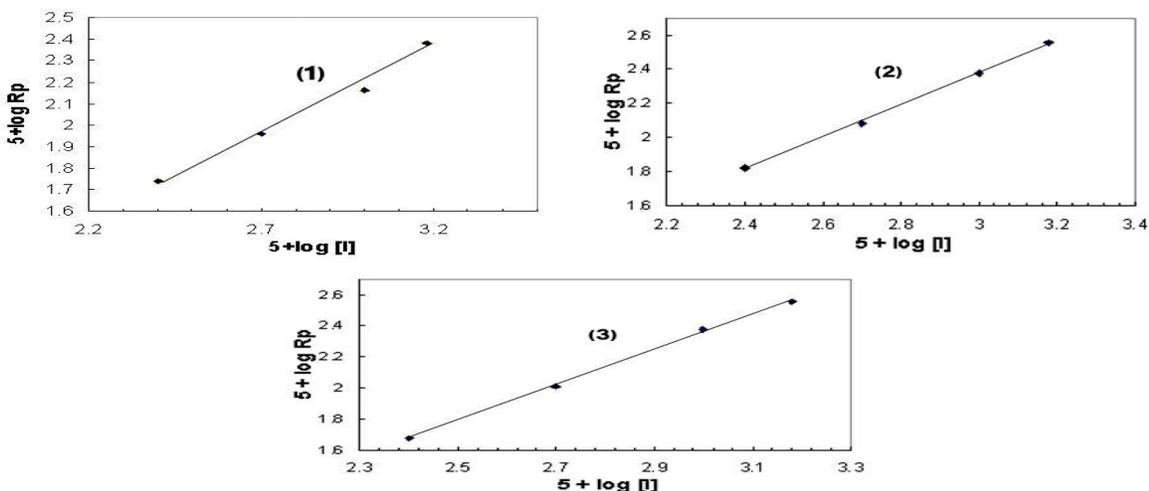


Figure (4): Double logarithmic plots of the R_p of VAc vs the concentrations of KPS/AcSBS using PVA of different molecular weights 1- (M.w 9000) 2 - (M.w 34000) 3- (M.w 125000)

Effect of Emulsifier concentration on the rate of polymerization

Figures (5-7) show the conversion-time relationships for emulsion polymerization of VAc at 50°C using different concentrations for all studied Mw of PVA in presence of developed redox initiation system KPS/AcSBS. The monomer concentration was 1.083 mol /l. The conversion time curves show a sigmoidal shape of a conventional emulsion polymerization. From Figure (8) it is clear that the

rate of polymerization (R_p) was found to be dependent on the concentration of PVA to the power 0.65, 0.61 and 0.51 respectively for Mw 9000, 34000 and 125000. This could be related to the grafting process which increases by increasing the molecular weight of PVA⁽¹²⁾. The polymerization rate equation with respect to emulsifier concentration is as follow:

$$R_p \propto [E]^Y$$

Where [E] is the emulsifier concentration and Y was found to be equal 0.65, 0.61 and 0.51.

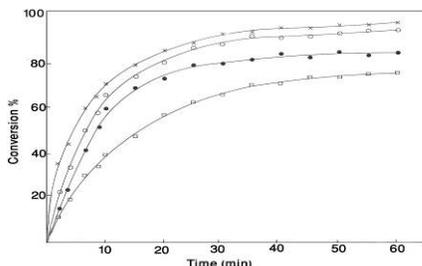
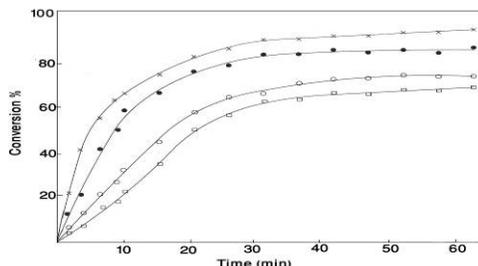
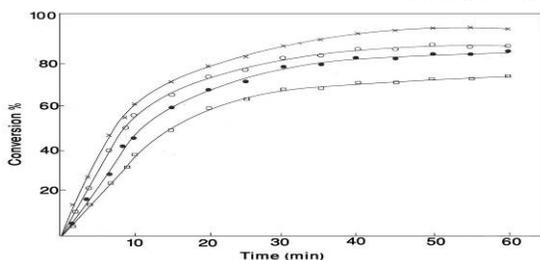


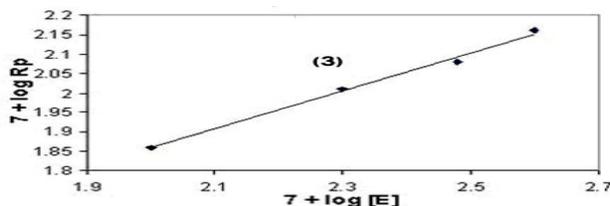
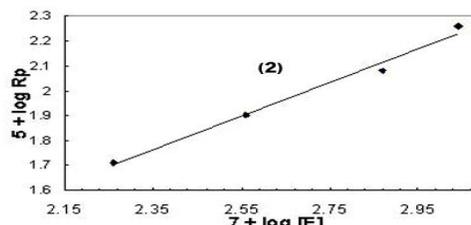
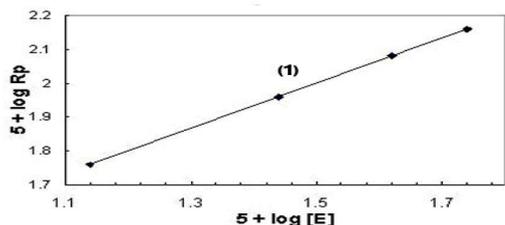
Figure (5) : Conversion – time plot of the emulsion polymerization of VAc in presence of KPS /AcSBS using different concentrations of PVA (Mw 9000)



Figure(6): Conversion – time plot of the emulsion polymerization of VAc in presence of KPS /AcSBS using different concentrations of PVA (Mw 34000)
 □ - 0.0184 x 10⁻³ mol/l o- 0.0368 x 10⁻³ mol/l
 ● - 0.0735 x 10⁻³ mol/l x - 0.1103 x 10⁻³ mol/l



Figure(7): Conversion – time plot of the emulsion polymerization of VAc in presence of KPS / AcSBS using different concentrations of PVA (M.w 125000)
 □ - 0.01 x 10⁻³ mol/l ● - 0.02 x 10⁻³ mol/l
 o - 0.03 x 10⁻³ mol/l x - 0.04 x 10⁻³ mol/l



Figure(8): Double logarithmic plots of the Rp of VAc vs the concentrations of PVA using KPS/AcSBS 1- (M.w 9000) 2 - (M.w 34000) 3 - (M.w 125000)

Effect of Monomer Concentration on the Rate of Polymerization

Figures (9-11) demonstrate the conversion–time relationships for emulsion polymerization of VAc at 50C° using different concentrations of VAc, in presence of KPS/AcSBS and PVA with molecular weights (9000, 34000, 125000). Obviously, the rate of polymerization increased with increasing monomer concentration. Figure (12) shows the relationship between the log rate of polymerization versus the log monomer concentration. The rate of polymerization (Rp) was found to be dependent on

the concentration of VAc to the power 0.60, 0.66 and 0.63 respectively for PVA with molecular weights (9000, 34000, 125000). The rate equation with respect to the monomer concentration is as follow:

$$R_p \propto [M]^z$$

Where [M] is the monomer concentration and Z equal 0.60, 0.66 and 0.63.

$$R_p \propto [I]^{0.81} [E]^{0.65} [M]^{0.60} \quad (\text{M.W 9000})$$

$$R_p \propto [I]^{0.90} [E]^{0.61} [M]^{0.66} \quad (\text{M.W 34000})$$

$$R_p \propto [I]^{1.20} [E]^{0.51} [M]^{0.63} \quad (\text{M.W 125000})$$

In our studies the proposed rate equations for the emulsion polymerization of vinyl acetate in presence of three different molecular weights of PVA are as follows

Where $[I]$, $[E]$, $[M]$ are initiator, protective colloid, and monomer concentration respectively.

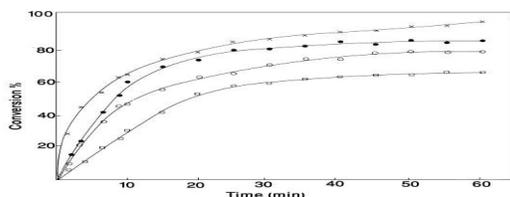
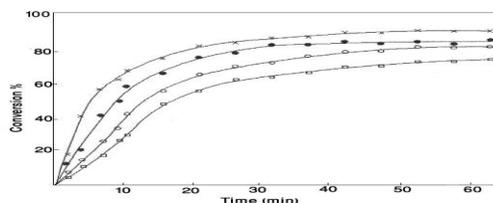


Figure (9): conversion – time plot of the emulsion polymerization of VAc in presence of KPS /AcSBS and PVA (Mw 9000) using different concentrations of VAc
 \square - 2.165 mol/l \circ -1.624 mol/l \bullet - 1.083 mol/l \times - 0.54 mol/l



Figure(10): Conversion – time plot of the emulsion polymerization of VAc in presence of KPS / AcSBS and PVA (M.w 34000) using different concentrations of VAc
 \square - 2.165 mol/l \circ -1.624 mol/l \bullet - 1.083 mol/l \times - 0.54 mol/l

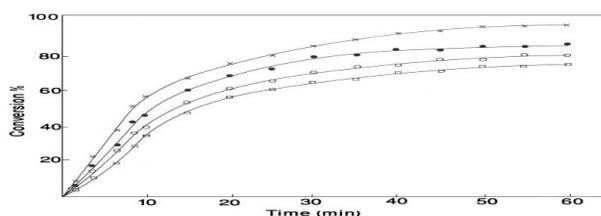


Figure (11): Conversion – time plot of the emulsion polymerization of VAc in presence of KPS /AcSBS and PVA (Mw 125000) using different concentrations of VAc
 \square - 2.165 mol/l \circ -1.624 mol/l \bullet - 1.083 mol/l \times - 0.54 mol/l

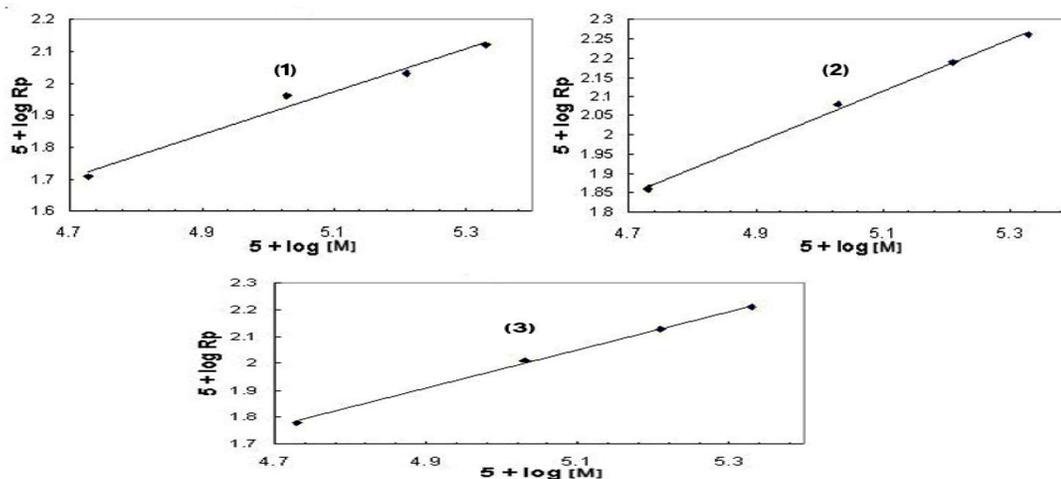
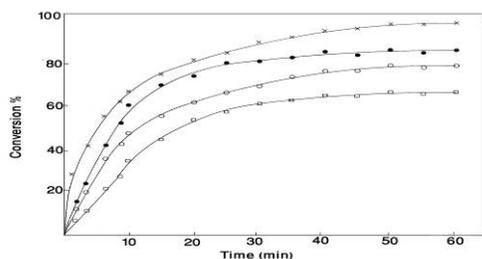


Figure (12) Double logarithmic plots of the R_p of VAc vs the VAc concentrations in presence of KPS /AcSBS using PVA with different molecular weights
 1- (Mw 9000) 2 – (Mw 34000) 3- (Mw 125000).

Calculation of the activation energy

The activation energies (E_a) for the emulsion polymerization of VAc using KPS/AcSBS and PVA with different molecular weights are determined. Figures (13-15) represented the conversion–time relationships for the previous

system. Also the log rate vs $1/T$ is represented in Figure (16). The values of E_a obtained for the different molecular weights of PVA were 0.946×10^4 , 1.0613×10^4 , and 0.932×10^4 J/mol for PVA (9000, 34000, 125000) respectively.



Figure(13): Conversion – time plot of the emulsion polymerization of VAc in presence of PVA (M.w 9000) using KPS / AcSBS at different temperatures
 □ - 30 C° ○ - 40 C° ● - 50 C° x - 60 C°

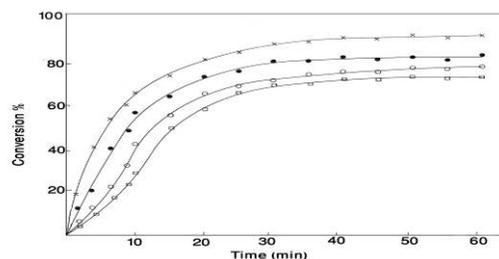
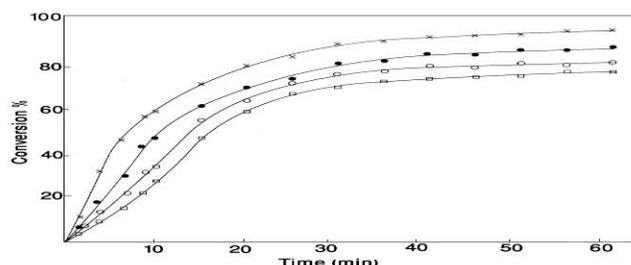


Figure (14): Conversion – time plot of the emulsion polymerization of VAc in presence of PVA (M.w 34000) using KPS / AcSBS at different temperatures
 □ - 30 C° ○ - 40 C° ● - 50 C° x - 60 C°



Figure(15): conversion – time plot of the emulsion polymerization of VAc in presence of PVA (M.w 125000) using KPS / AcSBS at different temperatures
 □ - 30 C° ○ - 40 C° ● - 50 C° x - 60 C°

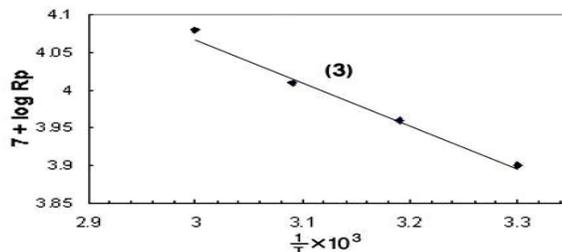
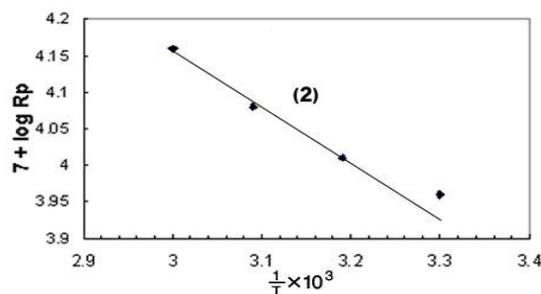
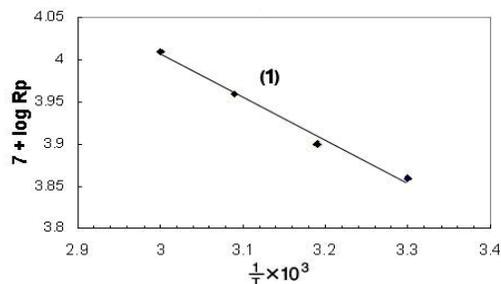


Figure (16): Arrhenius plots of log Rp of VAc in presence of KPS/AcSBS and PVA with different molecular weights 1- (Mw 9000) 2 - (Mw 34000) 3 - (Mw 125000)

Effect of concentration of developed redox initiation system on the morphological of the obtained latices

Graph (17) shows the morphology of the obtained latex particles for the emulsion

polymerization of VAc prepared using different concentration of the KPS/AcSBS and PVA (Mw 9000). Table (2) shows the particle size \bar{D}_v ; the

number of polymer particle per unit volume of water N_t , and the polydispersity \bar{D}_w/\bar{D}_n , it is obvious that increasing the concentrations of the KPS/AcSBS decreasing the size of the polymer particles values and the number of polymer particles per unit volume of water increasing. The greater the number of N_t the better the film forming properties of the obtained

latexes which means good application in surface coatings. Also the polydispersity values for the emulsion prepared were founded to be closely equal to 1. i.e monodisperse emulsion latexes. The graph obtained from TEM for such latexes reveal that the used redox initiation system produced more spherical emulsion latexes particles.

Table (2): Morphology of particles prepared in presence of different concentrations of KPS/AcSBS in presence of PVA (Mw 9000).

[Redox system]	[I] x 10 ³ (mol/l)	\bar{D}_v (nm)	\bar{D}_n (nm)	\bar{D}_w (nm)	\bar{D}_w/\bar{D}_n	N_t (x10 ⁻¹⁴)
KPS/AcSBS	2.5 / 5	31.61	32.72	31.65	0.97	36.4
	5 / 10	25.41	26.25	25.41	0.97	76.6
	10 / 20	21.21	21.87	21.24	0.96	152
	15 / 30	19.46	20.031	19.533	0.98	198.7

Effect of Different Molecular Weights of the Protective Colloid on the Morphological Characteristics of the Obtained Latexes.

Graph (18) shows the morphology of the obtained latex particles for the emulsion polymerization of VAc prepared using different molecular weights of PVA (9000, 34000, 125000) in presence of KPS/AcSBS. Table (3) shows the particle size \bar{D}_v , the number of polymer particle per unit volume of water N_t , and the polydispersity \bar{D}_w/\bar{D}_n , it is obvious that increasing the molecular weights of PVA increasing the size of the polymer particles values and the number of polymer particles per unit volume of water decreasing. Also the polydispersity values for the emulsion prepared were founded to be

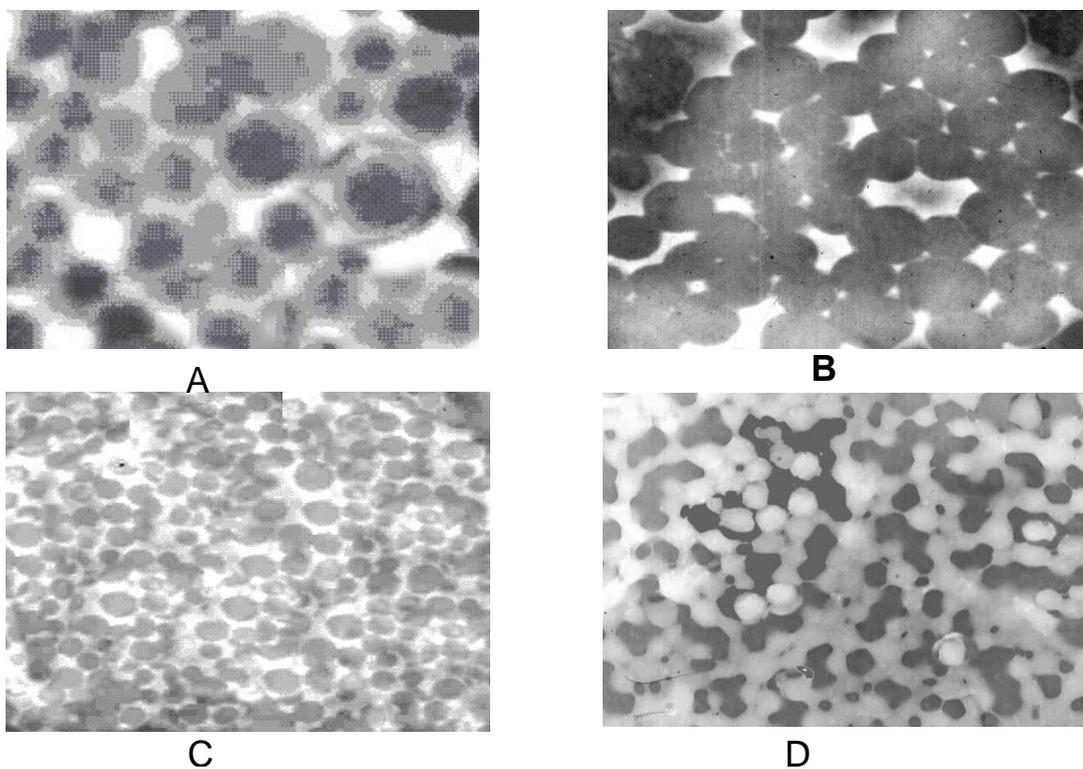
closely equal to 1. i.e monodisperse emulsion latexes. The graph obtained from TEM for such latexes reveal that the used molecular weight of PVA produced more spherical emulsion latexes particles.

Effect of Different Polymerization Conditions on the Viscosity Average Molecular Weight

The effect variation of the concentration of the redox initiation system on the viscosity average molecular weight of some prepared PVAc latex is represented in Table (4) it is clear that the molecular weight of PVAc decreases as the concentration of the initiator increases but it increases as the molecular weights of PVA increases.

Table (3): Morphology of particles prepared in presence of different molecular different molecular weights of PVA

Type	[I] x 10 ³ (mol/l)	M.w of PVA	\bar{D}_v (nm)	\bar{D}_n (nm)	\bar{D}_w (nm)	\bar{D}_w/\bar{D}_n	N_t (x10 ⁻¹⁴)
KPS/AcSBS	10/20.	9000	21.21	21.87	21.24	0.97	152.0
		34000	43.29	44.97	43.28	0.96	16.20
		125000	59.77	62.25	59.89	0.96	6.79



Figure(17): Effect of different concentration of KPS/AcSBS on the morphological characteristic of PVAc latex using PVA (M.w.9000) (a) $2.5 \cdot 10^{-3} / 5 \cdot 10^{-3}$ mol / l (b) $5 \cdot 10^{-3} / 10 \cdot 10^{-3}$ mol / l, (c) $10 \cdot 10^{-3} / 20 \cdot 10^{-3}$ mol / l (d) $15 \cdot 10^{-3} / 30 \cdot 10^{-3}$ mol / l (magnification 40000)

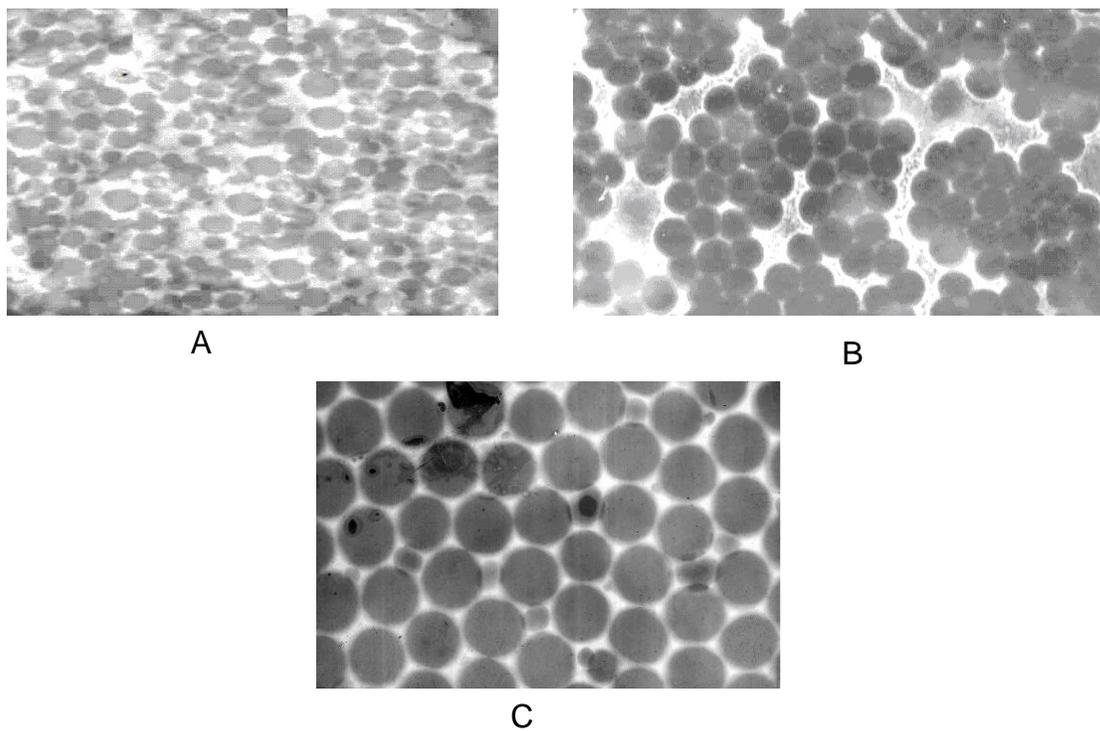
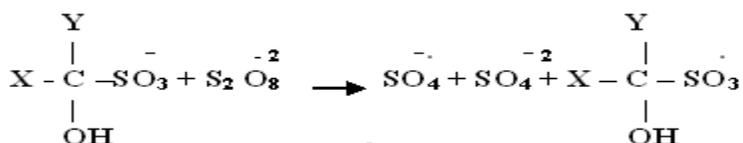


Figure (18): Effect of different molecular weight of PVA using KPS/AcSBS on the morphological characteristic of PVAc latex (a) (M.w 9000) (b) (M.w 34000) (c) (M.w 125000) (magnification40000)

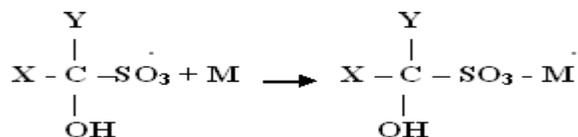
Table (4): Effect of polymerization conditions on the viscosity average molecular weight

Mw of PVA	[I] x 10 ³ (mol / l)	Mv of PVAc x10 ⁻⁵
9000	2.5 / 5	4.4
	10 / 20	2.39
	15 / 30	1.73
34000	5 / 10	5.43
	10 / 20	3.03
	15 / 30	2.93
125000	2.5 / 5	6.84
	10 / 20	4.87
	15 / 30	3.13

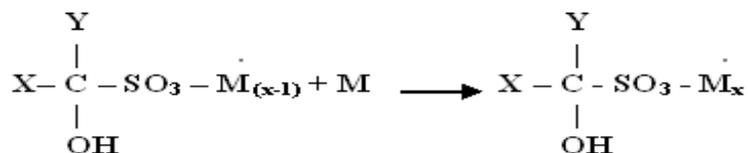
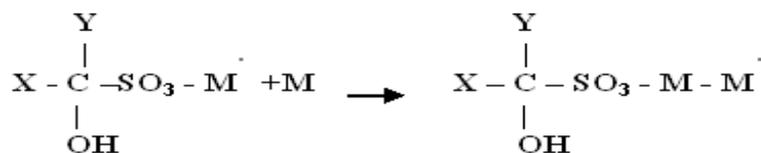
Mechanism of the reaction



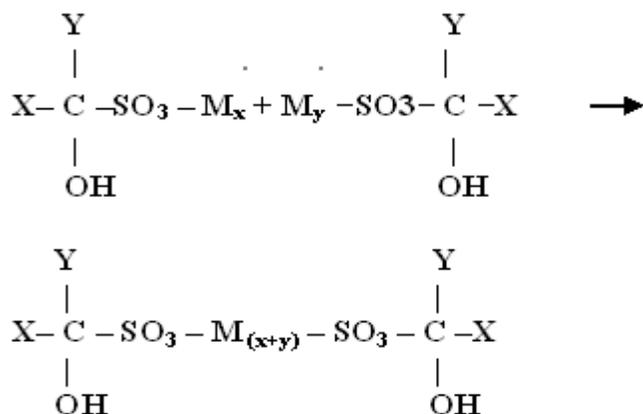
Initiation



Propagation



Termination



Scheme 1

Corresponding author

K.A. Shaffie

Dept. of Chemistry, Faculty of Science, Helwan Univ, Helwan, Egypt.

*Khaled.shaffie2006@yahoo.com**4. References:**

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