Amphiphatic Copolymer as Surfactant for Emulsion Polymerization of Styrene

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ABSTRACT

The emulsion polymerization of styrene (St) using sodium persulfate ($Na_2S_2O_8$) as an initiator has been kinetically investigated in the presence of amphiphatic copolymer as surfactant. Amphiphatic copolymer of three different composition types from vinyl acetate, monomer, and methoxy polyoxyethylene (PVAc-b-MPOE) (35:65, 27:73, 19:81 wt%:wt%) were prepared in the presence of benzoyl peroxide using a macroradical initiator technique. Fourier Transform Infrared Spectroscopy (FTIR) and ^{1}H NMR were carried out to confirm the structure of the obtained copolymer.

The rate of emulsion polymerization of styrene was found to be proportional to the 0.33^{rd}, 0.375^{rd} and, 0.385^{rd} power of the (amphiphatic) surfactant concentration [E] and to the 0.67^{th}, 0.71^{th}, and 0.8^{th} power of the initiator concentrations [I]. The apparent activation energy was found to be 91.7, 81.9, and 71.6 kJ/mol for 65, 73, and 81 wt% POE, respectively. It is seen that the number of the average particle diameter (Dn) decreases with increasing surfactant [E], while it increases with [I]. The number of polymer particles (N_t) increased with surfactant concentration but decreased with initiator concentration. The reaction order of N_t with respect to [E], was determined. Polydispersity index (D_w/D_n) (particle size distribution) of the prepared latices was found in the range from 1.05-1.20 with changing POE wt% and from 0.8 to 1.23 with varying initiator concentration.

INTRODUCTION

In emulsion polymerization, nonionic surfactants alone are not widely used as stabilizing agents [1], So stabilization by oligomeric or polymeric surface active materials have been applied because of their advantages such as less sensitivity to fluctuations and an increase in electrolyte concentrations [2]. Polymeric surface active material can be prepared as amphiphatic block copolymer [3, 4] or amphiphatic graft copolymer [5, 6]. Accordingly, many authors [7-10] have investigated the preparation and characterization of polymerizable surfactants to be used in emulsion polymerization. Berger *et al*. [11] studied the poly(styrene)-block-poly-(ethylene oxide) as a polymerizable surfactant in emulsion polymerization of styrene and methyl methacrylate at $60\text{-}80°C$. They found that particle size varied between 50 and 300 nm and decreased with increasing copolymer concentration. The particle size was larger at higher temperature, and size distribution was narrower. Also, Jean-Lue and Gerard [12] carried out the emulsion polymerization of styrene and styrene-butyl acrylate for the preparation of hairy latexes in the presence of polystyrene-poly(ethylene oxide) PS-PEO-di and tri-block copolymers as stabilizers. They concluded that the efficiency of these polymeric surfactants decreased with increasing molecular weight and PS content of the block copolymer. Moreover, Cartney and Piirma [13] prepared di-Me-5-sulfa isophthalate Na-salt-phthalic anhydride polyoxyethylene copolymer and used as a stabilizer in emulsion polymerization of styrene. They found that the rate of polymerization was independent on initiator concentration and the molecular weight of polystyrene was low. Furthermore, Piirma and Lenzotti [14] prepared poly(p-methyl styrene)-graft-poly(oxyethylene) copolymers and studied the stabilizing efficiency of these copolymers in the emulsion polymerization of styrene. They found that the rate of polymerization and number of polymer particles increased with increasing emulsifier concentration using the same copolymer, also the polymerization temperature had quite effect on the rate of reaction; it tripled for a 15°C change in temperatures. Meanwhile, Jialanella *et al.* [15] prepared polystyrene-block-polyoxyethylene copolymers for use as stabilizers in the emulsion polymerization of styrene.They concluded that as the concentration of the block copolymer was increased; there was an increase in the rate of polymerization and the number of particles but a decrease in the particle size.

A goal of this paper is to study the synthesis of amphiphatic copolymer polyvinyl acetate-block-methoxy polyoxyethylene for use as polymeric surfactant in emulsion polymerization of styrene monomer, and to study the effect of varying the amounts of POE on the reaction kinetics, particle size and number of polymer particles formed.

EXPERIMENTAL

Materials

Styrene (St) and vinyl acetate (VAc) monomers were redistilled and stored at -20°C before use. Sodium persulfate (Na_2S_2Og) and benzoyl peroxide (BP) were provided by Merck-Schuchardt (Germany). Sodium bicarbonate ($NaHCO_3$) was used to adjust the pH of the medium and hydroquinone was used to stop the polymerization reaction from ADWIC (Egypt). Methoxy polyoxyethylene (MPOE) M.Wt 2000 was supplied by Union Carbide Company (USA). Hexane and toluene were supplied by E1-Naser Pharmaceutical Chemical Company (Egypt). Ammonium molybdate, for particle staining, was supplied from Merck-Schuchardt (Germany).

Preparation of Amphiphatic (PVAc-b-MPOE) Copolymers

Methoxy polyoxyethylene (M.wt. 2000) 65%, 73%, and 81% wt%, benzoyl peroxide 0.5 g and (100 ml) distilled toluene were heated under reflux at 115-120°C for 2 hours. After cooling at room temperature, vinyl acetate monomer (required amount) was added dropwise for 30 minutes. After that, the reaction was allowed to proceed for another 4 hours at 65°C with stirring. The resultant solution was concentrated using a rotary evaporator, and then precipitated into distilled hexane. The crude products were dried in a vacuum oven at 40°C overnight.

Characterization of Amphiphatic Copolymers

Copolymers of (PVAc-b-MPOE) were characterized by Fourier Transform Infrared Spectroscopy (FTIR) 300E, JASCO type-Japan), and by ^{1}H NMR spectroscopy (JEOL type EX 270 MH, Japan).

Polymerization Procedure

Batch emulsion polymerization of styrene monomer were carried out at 60-70°C. In all ratios, the recipe containing 90 g water, 9.09 g styrene, 0.125g sodium bicarbonate, 0.125- 0.350 g initiator, the PVAc-b-POE as surfactant with different compositions, varied from 0.25 to 0.75 g (35:65 and 27:73 wt%/wt%) and from 0.125 to 0.75g (19:81 wt%/wt%). All experiments were run with mechanical stirring at 500 rpm. This speed is in the range where the agitation has no noticeable effect on the rate of polymerization [16]. Samples of the reaction mixture were taken at various time intervals. These samples were very small so that the overall composition in the reaction vessel was not seriously affected. Once a sample was removed and put in a watch glass, the reaction was stopped with 1 ppm hydroquinone solution, and the sample was evaporated at room temperature, then dried in
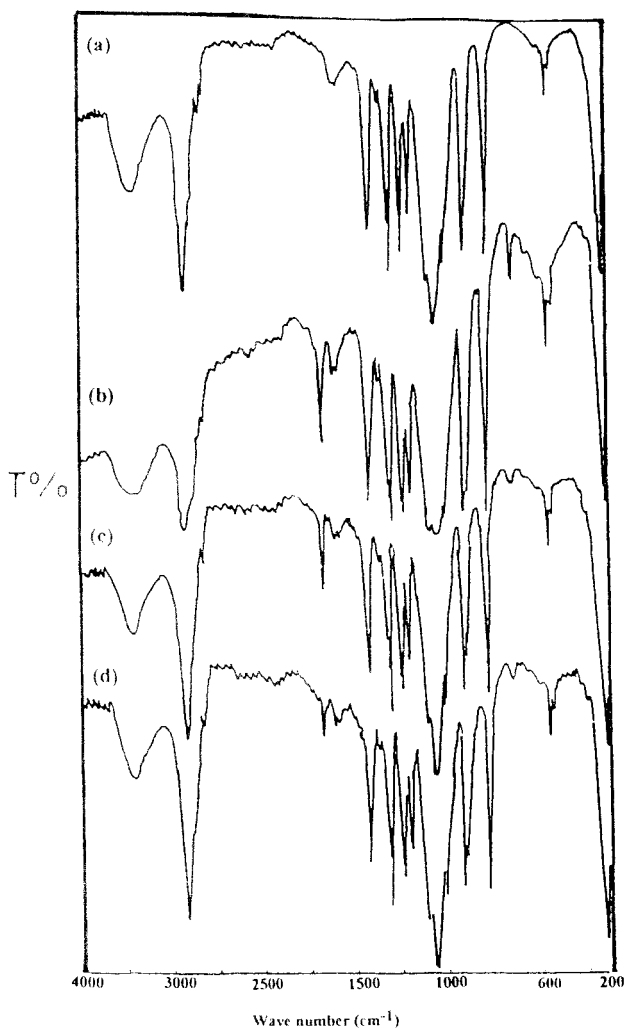
Figure 1.   FTIR spectra of MPOE and different ratios of PVAc-b-MPOE
(a) MPOE, (b) 35.65 wt%, (c) 27:73 wt% and (d) 19:81 wt%.

an electric oven to constant weight. Conversion of monomer was determined gravimetrically.

Morphological Characteristics of Polymer Latices

Ammonium molybdate was used for staining the particles of polystyrene emulsion latices using Transmission Electron Microscope (TEM), JEOL type JEM 100S (Japan). It works at 60-100 KV, magnification 1000-140000, and the reso-

lution until 4A°. The number average particle diameter (D_n), number of polymer particles (N_t), and the polydispersity index $(PDI)(D_w/D_n)$ of polystyrene emulsion latices were determined
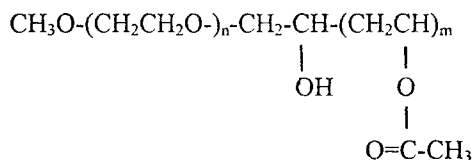
RESULTS AND DISCUSSION

Characterization of Amphiphatic Copolymers

FTIR spectra of methoxy polyoxyethylene (MPOE) and polyvinyl acetate block-methoxy polyoxyethylene copolymers with three different compositions (35:65, 27:73, and 19:81 wt%), are shown in Figures l(a,b,c and d). The repeating unit of the copolymer is -CH_2-CH_2O- having strong ether vibrations at 1110 cm^{-1} and OH stretching at 3200-3500 cm^{-1}, while the three ratios of PVAc-b-POE have carbonyl groups at 1700 cm cm^{-1}, C-O stretching at 1250 and 1170 cm cm^{-1}. At any even CH_2- groups have stretch at 713 cm cm^{-1}.

The ^{1}H NMR spectra gives more support for the structure of the prepared amphiphatic copolymers. The chemical shifts at δ = 3.2 to δ = 3.8 ppm for the proton in POE (-OCH_2-CH_2-) and protons in PVAc appear at δ = 2.5 ppm. The typical ^{1}H NMR spectrum for PVAc-b-POE copolymers is shown in Figure 2.

The amphiphatic copolymer is expected to have the following structure:

$$CH_3O\text{-}(CH_2CH_2O\text{-})_n\text{-}CH_2\text{-}CH\text{-}(CH_2CH)_m$$
$$\quad\quad\quad\quad\quad\quad\quad\quad | \quad\quad |$$
$$\quad\quad\quad\quad\quad\quad\quad\quad OH \quad\quad O$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O\text{=}C\text{-}CH_3$$

Rate of Polymerization

Effect of Concentrations of Amphiphatic Compositions as Surfactant on the Emulsion Polymerization of Styrene

The prepared polyvinyl acetate-block-methoxy polyoxyethylene was used as a surfactant in the emulsion polymerization of styrene.

The conversion-time data for the emulsion polymerization of styrene initiated by $Na_2S_2O_8$ in the presence of PVAc-b-POE as a surfactant at 70°C are shown in Figure 3 (a, b and c). These conversion- time curves give the effect of surfactant composition PVAc-b-POE on the polymerization process. It is seen that a slow rate of polymerization was obtained below 40% conversion, whereas the rate increases greatly after 40% conversion, with increasing the surfactant concentration,
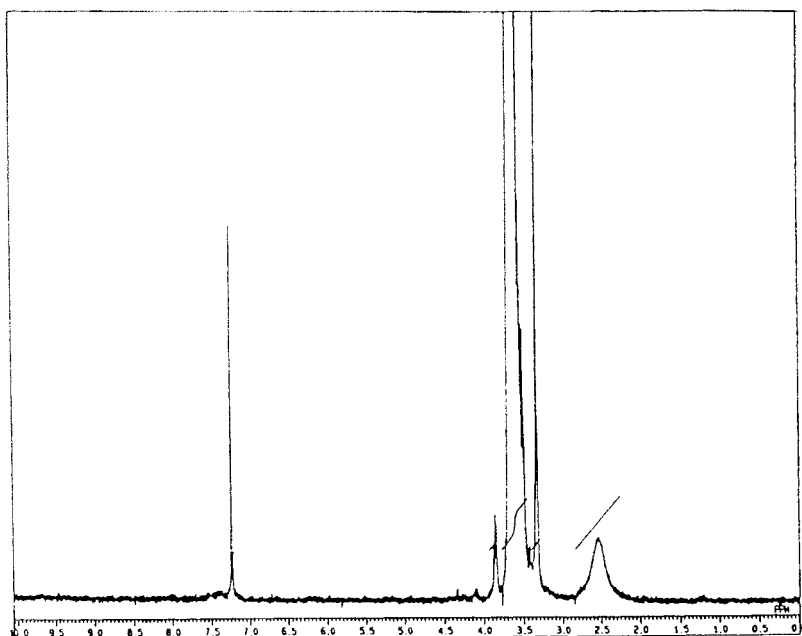
Figure 2.   ¹H NMR of PVAc-b-MPOE.

the final conversion increases. These results are in agreement with those obtained by Piirma *et al.* [14]. The rate of polymerization calculated from interval II (20-60% conversion) are summarized in Table 1.

Increasing the polyoxyethylene content from 65 to 73 wt% resulted in a decrease in the rate of polymerization. At high polyoxyethylene content 81 wt%, the surfactant, may be more inclined to remain in the aqueous phase than to absorb at the particle/water interface, this is due to increased hydrophilicity. The surfactant would tend to become more like homo-polyoxyethylene and therefore, less surface active.

These results show that the rate of polymerization increases with increasing the surfactant concentration until the block copolymer contained 73 wt% POE, while block copolymer with 81 wt% POE exhibits the same stabilizing effectiveness in the emulsion polymerization of styrene which can be shown from the following relationship and obtained from Figure 4.

Similar results were observed in the emulsion copolymerization of alkyl acrylate in the presence of POE type of emulsifier [17], but these deviate from
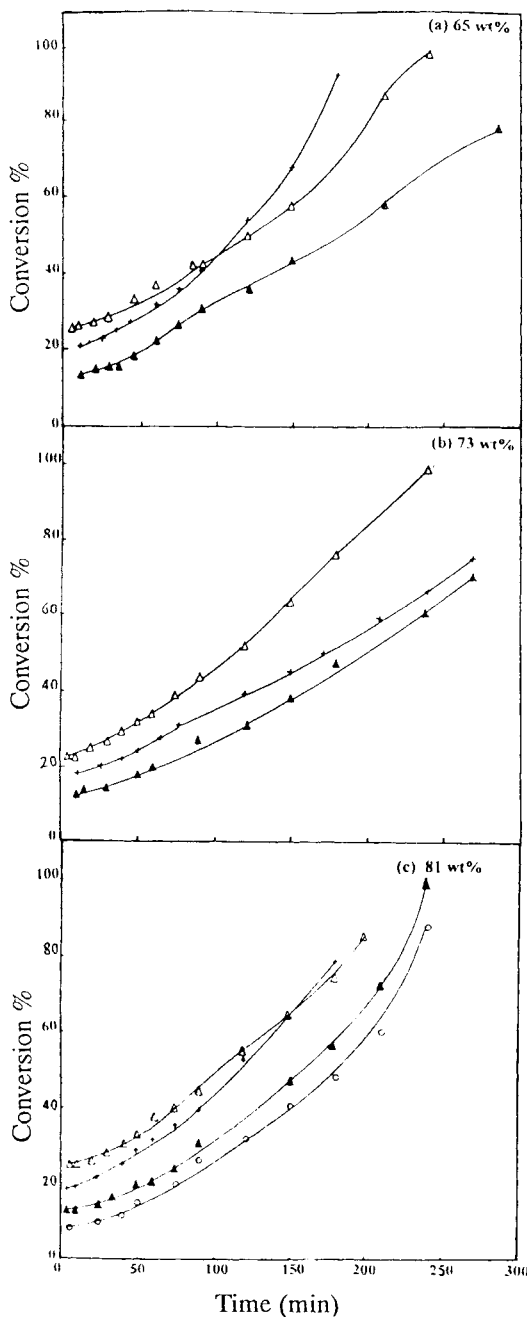
Figure 3. Rate dependence of emulsifier concentration in different compositions: (a) wt% POE, (b) 73 wt% POE and (c) 81 wt% POE on emulsion polymerization of styrene monomer, Initiator = 0.25 gm, Monomer = 9.09 gm and Temperature = 70°C.
Emulsifier = (O) 0.125 gm, (▲) 0.25 gm, (+) 0.5 gm and (Δ) 0.35 gm.

TABLE 1. Effect of Varying Surfactant Concentration in Emulsion Polymerization of Styrene using Different Compositions of POE.

| wt% POE	[E] gm.	$R_p x10^{-5}$ mol.l$^-$.sec^{-1}	D_n nm.	D_w nm.	D_w/D_n	N_t x10^{-12}
	0.25	3.4	389	437	1.12	2.2
65	0.50	4.5	212	236	1.11	6.8
	0.75	5.09	200	243	1.20	22.4
	0.250	2.3	291	348	1.19	4.78
73	0.500	2.9	249	292	1.17	6.99
	0.750	3.5	178	199	1.12	28.7
	0.125	3.37	512	556	1.08	1.15
81	0.250	3.97	361	386	1.05	4.19
	0.500	5.45	204	225	1.105	15.5

D_n = Number -average diameter of particles.

D_w = Weight- average diameter of particles.

D_w/D_n = Polydispersity.

N_t = Number of particles per cm^3 aqueous. phase.

micellar model which may be ascribed to the type of interaction between the surfact-ant and polymer particle surface. Thus, increasing hydrophilicity of the polymer particle surface increases the exponent of the emulsifier concentration up to 73% POE and a higher percentage of POE in the copolymer has no effect on the exponent of emulsifier which agrees with that obtained by Jialanella et al. [15] .
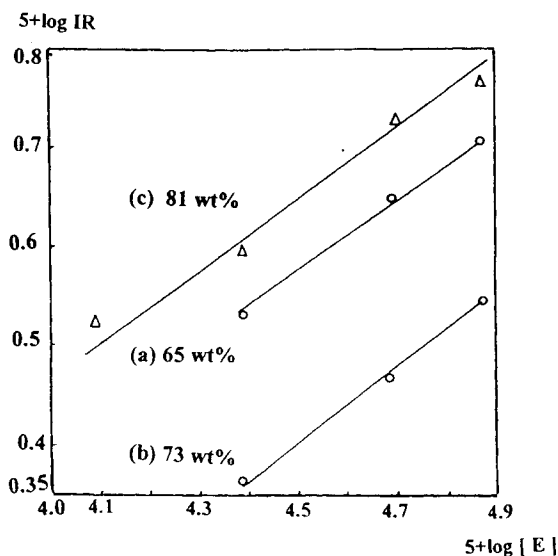
Figure 4. Double logarithmic plot of the initial rate of polymerization versus emulsifier concentration.

Effect of Initiator Concentration

Figure 5 (a, b and c) and Table 2 show the effect of initiator concentration on the kinetics of the emulsion polymerization of styrene. It is obvious that the initial rate of polymerization, as well as maximum conversion, increases with increasing the initiator concentration. This can be attributed to the formation of the new monomer/polymer phase which leads to the increase of initiator concentration in the continuos phase, while the total volume of the continuous phase decreases due to transfer of the monomer to polymer phase. Thus, this variation in the initiator concentration should lead to an increase in the rate with conversion. Figure 6 shows log-log plots of polymerization rate versus initiator concentration. The order of reaction (X) with respect to the initiator concentration is given as follows

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

Where X is equal to 0.67 (65%), 0.71 (73 %), and 0.8 (81%) respectively. This deviates from that obtained by ideal kinetic model [18] and homogeneous nucleation model [19] which give the relationship $Rp \propto [I] 0 5$ and $Rp \propto [I]^{0.4}$

TABLE 2. Effect of Initiator Concentration in Emulsion Polymerization of Styrene.

| wt% POE	[I] gm.	$\bullet R_p x10^{-5}$ mol./l.sec.	D_n nm.	D_w nm.	D_w/D_n	N_t $x10^{-12}$
	0.125	2.9	172	219	1.2	27.9
65	0.250	4.5	212	236	1.11	6.8
	0.35	5.8	373	431	1.153	3.2
	0.125	2.0	190	234	1.23	13.4
73	0.250	2.9	249	292	1.17	6.99
	0.35	4.0	438	484	1.106	1.87
	0.125	3.05	184	188	1.02	17.0
81	0.250	5.45	204	225	1.105	15.5
	0.350	6.38	278	224	0.806	12.6

D_n = Number -average diameter of particles.

D_w = Weight- average diameter of particles.

D_w/D_n = Polydispersity.

N_t = Number of particles per cm^3 aqueous. phase.

respectively. The higher exponent of initiator concentration indicates that bimolecular termination between the growing radicals is strongly suppressed in both phases (the continuos phase and the polymer particle interior). This can be discussed as follows: bulky substituents (PEO units) around the propagation end increase the lifetime of a radical [20] and suppress the mutual penetration between growing radicals and macromonomer [21]. Besides, the chain transfer to POE macro-
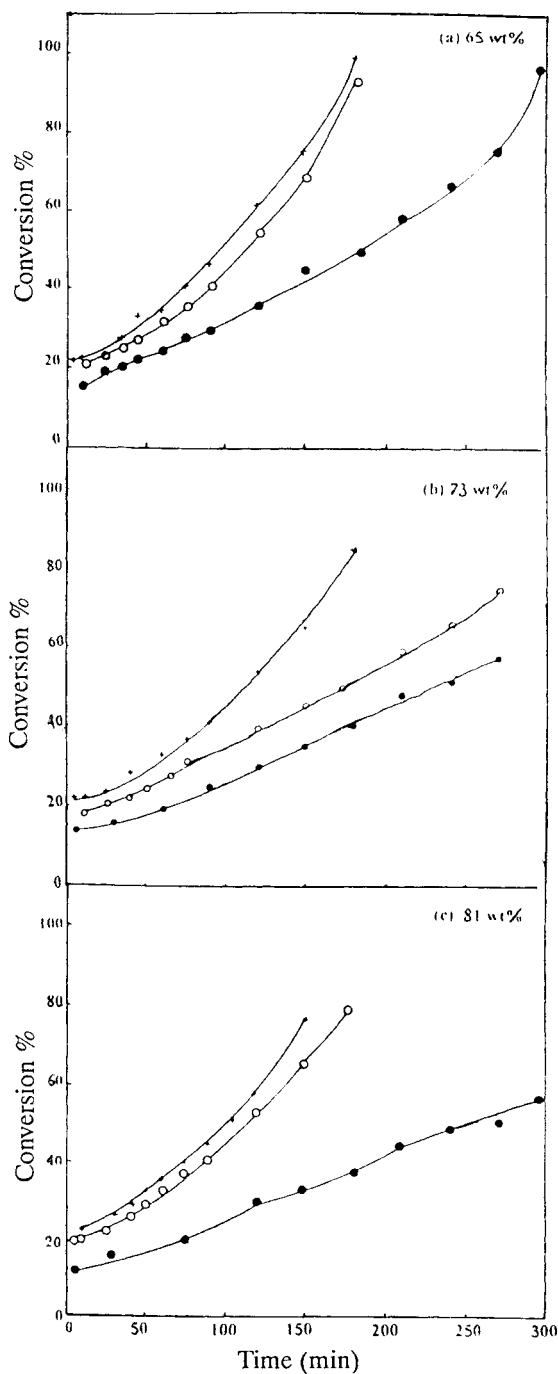
Figure 5. Rate dependence of initiator concentration using PVAc-bMPOE of different composition: (a) 65 wt% POE, (b) 73 wt% POE and (c) 81 wt% POE as emulsifier, Emulsifier = 0.5 gm, Monomer = 9.09 gm and Temperature 70°C. Initiator = (●) 0.125 gm, (○) 0.125 gm and (+) 0.35 gm.
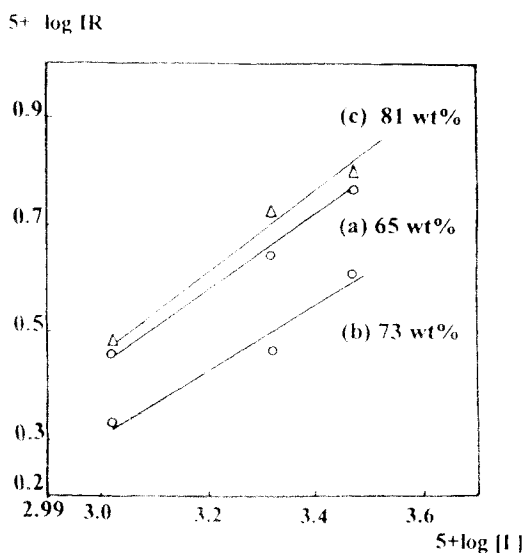
Figure 6.   Double logarithmic plot of the initial rate of polymerization versus initiator concentration.

monomer [22] and the multibranched structure of the propagation radicals [23] favors the increase of the exponent X above 0.5. Similar value of reaction order X reported by Capek *et al.* [9].

Effect of Temperature

Figure 7(a, b and c) show the conversion-time data for the emulsion polym-erization of styrene at different temperatures (60-70°C).The polymerization temper-ature had quite an effect on the rate of reaction. Apparently, an increased in temperature resulted in an increase in the efficiency of the initiator then increase limiting conversion and the rate of polymerization.

The apparent activation energy (E_a) was estimated from the relationship between the initial rate of polymerization and $1/T$ (an Arrhenius plot Figure 8). The E_a of the polymerization process of styrene was calculated according to Arrhenius equation and was found to equal 91.7, 81.9 and 71.6 K J/ mol for the 65%, 73% and 81% POE, respectively. These values are in agreement with those obtained in the dispersion copolymerization of POE macromonomer [24]. As a result of these data, increasing POE fraction in surfactant decreases the activation energy .
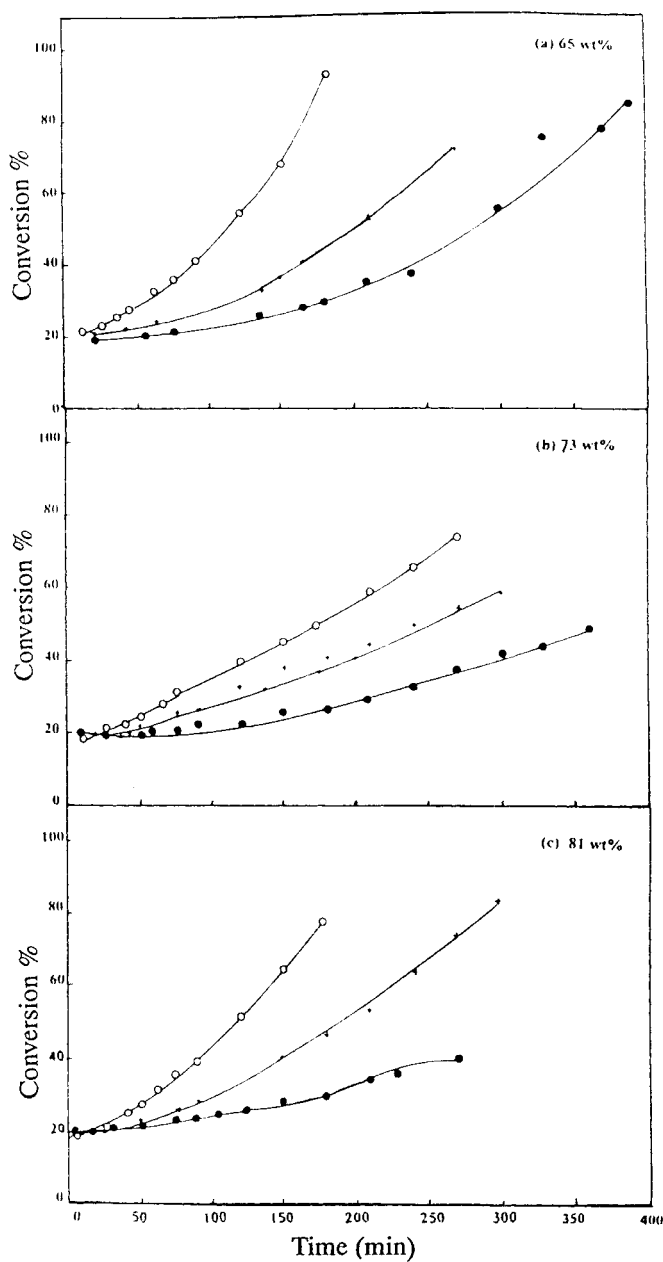
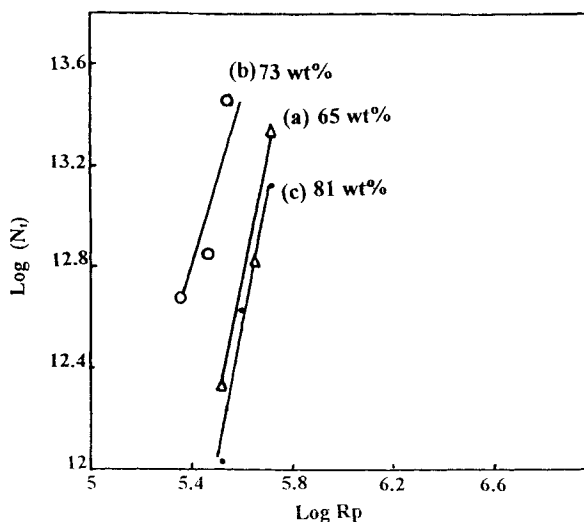**Figure 7.** Rate dependence of temperature using PVAc-b-MPOE of different compositions: (a) 65 wt% POE, (b) 73 wt% POE and (c) 81 wt% POE as an emulsifier, at temperature (●) 60°C, (+) 65°C and (O) 70°C.
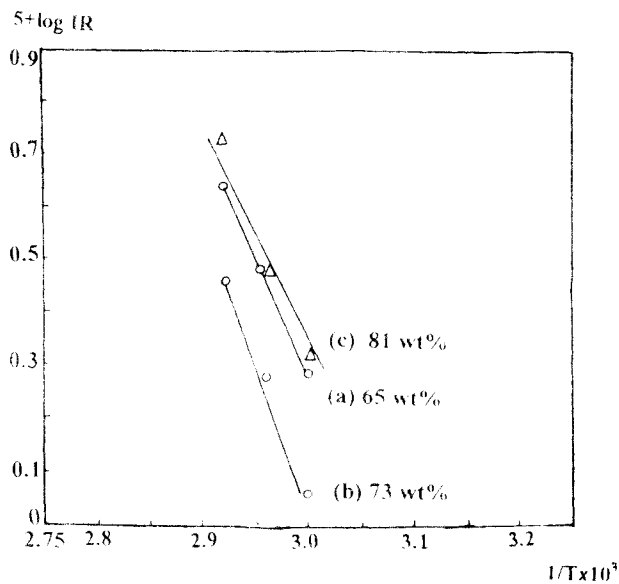
Figure 8. Arrenhenius plot of the initial rate of polymerization versus $1/T_r$ (a) 65 wt% POE, (b) 73 wt% POE and (c) 81 wt% POE.
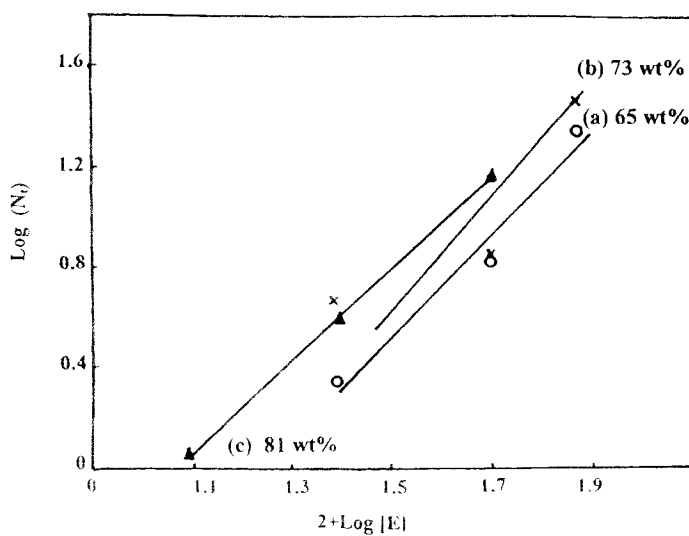
Figure 9. Log number of polymer particles (N_t) versus log [Emulsifier].

Figure 10.   Log number of polymer particles (N_t) versus log rate of polymerization.

Morphological Characteristics

The dependence of the particle size, number of polymer particle and poly-dispersity index on the concentration of amphiphatic copolymer with different com-positions are summarized in Table 1. From these data, it can be concluded that the average number particle size (D_n) decreases with an increasing concentration of amphiphatic copolymer while the number of polymer particles (N_t) increases abruptly with increasing methoxyoxyethylene weight percent.

According to the Smith-Ewart micellar theory [25], the relationship between the number of polymer particles and the emulsifier concentration can be expressed mathematically as

$$N_t \propto [\text{emulsifier}]^{0.6}$$

The experimental results in Table 1, and Figure 9 show that the relationship between [emulsifier] and N_t is as follows:

$$N_t \propto [E]^{1.82} \ (65\%), \ N_t \propto [E]^{2.1} \ (73\%) \ \text{and} \ N_t \propto [E]^{1.66} \ (81\%)$$

Similar results were obtained in the emulsion polymerization of styrene using poly(styrene)-block-poly(ethylene oxide) as an emulsifier [26]. But our

results are higher, especially with the ratio 73 wt% of POE. This may be due to the effectiveness of amphiphatic copolymer with composition up to 73 wt% POE as surfactant in emulsion polymerization of styrene. Also, these results are higher than those obtained by other authors [27, 28].

Figure 10 gives the relationship between the rate of polymerization Rp end the number of polymer particles N_t which can be summarized as follows:

$$Rp \propto N_t^{4.66} (65\%), Rp \propto N_t^{3.0} (73\%) \text{ end } Rp \propto N_t^{5.9} (81\%)$$

These powers are higher than those obtained by [8, 25]. This deviation probably results from the nucleation of particles throughout the polymerization. The lower value of the power in ratio 73% of POE may be due to the configuration of POE and VAc which have loops extending into the continuous phase [29]. The data in Table 1 shows that the polydispersity index (D_w/D_n) have the value between 1.05 - 1.20. Table 2 gives the effect of initiator concentration on the particle size, number of polymer particle and polydispersity index (D_w/D_n). From this Table, it is seen that increasing the initiator concentration led to a decrease number of polymer particles and increase particle size. This may be due to further nucleation of small particles, followed by their rapid homoassociation and it can be ascribed to propagate within polymer particles. Also, increasing initiator concentration decreases polydispersity.

CONCLUSION

The amphiphatic copolymers synthesized in this study provided some insight into the stabilization mechanism when these amphiphatic surfactants are used as surfactants in the emulsion polymerization of styrene. The results showed that increasing polyoxyethylene content from 65 to 73 wt% resulted in decreasing the rate of polymerization and a corresponding decrease in the average number particle size. Increasing hydrophilicity of polymer particle surfaces increase exponent of the emulsifier concentration up to 73% POE, and a higher percentage of POE in the copolymer has no effect on the exponent of emulsifier. Also, increasing POE fraction in surfactant decreases the activation energy and increases the power of initiator with respect to the rate of polymerization .

From the foregoing discussion results, it is seen that the rate of emulsion polymerization of styrene in the presence of POE type surfactants increased with increasing the initiator and surfactant concentration.

The apparent activation energy varies in the wide range showing the contribution of both the homogeneous and heterogeneous polymerization kinetics.

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