Microemulsion Polymerization of Styrene Using Developed Redox Initiation System and Study of Rheological Properties of Obtained Latices

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ABSTRACT: Microemulsion polymerization of styrene was kinetically studied using a potassium persulfate (KPS)/*P*-methyl benzaldehyde sodium bisulfite (MeBSBS) adduct as the developed redox pair initiation system. The rate of microemulsion polymerization of styrene was found to be dependent on the initiator, emulsifier, and monomer to the powers of 1.4, -0.77, and 0.83, respectively. The apparent Arrhenius activation energy (E_a) estimated for the microemulsion polymerization system was 6.5×10^4 J/mol. Also, the morphological parameters were studied at different initiator concentrations. The rheological measurements for the prepared microemulsions were carried out to investigate the effect of the preparation parameters on the rheological behavior of the polystyrene microemulsions. The rheological flow curves of the polystyrene microemulsion latices prepared at different temperatures were carried out, and we found that the plastic viscosity and Bingham yield values of the flow curves increased with an increasing reaction temperature. That may be due to the cage effect of the prepared polymer particles, which trapped the medium molecules. The plastic viscosity increased with increasing emulsifier concentration while the Bingham yield value decreased. For the polystyrene microemulsion prepared in the presence of different initiator concentrations, the plastic viscosity and Bingham yield increased with increasing initiator concentration. This trend was found to be the same for the microemulsion latices prepared in the presence of different monomer concentrations. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1240–1249, 2000

Key words: microemulsion polymerization; styrene; redox initiation system

INTRODUCTION

Emulsion polymerization of most vinyl monomers has been extensively studied using different initiation systems, emulsifiers, and other reaction conditions.[1,2] The characterization and applica-tion of the obtained emulsion latices have also been discussed.[3,4] So, a modern extension of macroemulsion polymerization is the microemulsion polymerization technique in which the obtained microemulsion latices are optically isotropic, transparent, or translucent and thermodynamically stable when using the appropriate emulsifier and long-chain alcohols or amines.[5] Oil in water type (O/W) homomicropolymerization of some unsaturated vinyl monomers have been in-

vestigated by many authors.[6-8] Microemulsion polymerization of vinyl acetate using ammonium persulfate has been studied[9] in the presence of sodium dodecyl sulfate, n-propanol, and water. It was found that the polymerization rates of microemulsion polymerization were smaller than those in emulsion, and the reaction order versus the initiator concentration was 0.9. Moreover, the polymerization rate was decreased by increasing the surfactant and cosurfactant concentration. Candau et al.[10] studied the polymerization of acrylamide in inverse microemulsions stabilized by Aerosol TO emulsifier and initiated by azobisisobutyronitrile (AIBN) or potassium persulfate ($K_2S_2O_8$). They found that the rate of polymerization is first order with respect to the initial monomer concentration in the presence of AIBN and 1.5 order with $K_2S_2O_8$. The obtained polyacrylamide latices were clear and highly stable. This suggests kinetics that do not follow the Smith and Ewart theory but are characterized by continuous particle nucleation. Guo et al.[11] studied the kinetics and mechanism of microemulsion polymerization of styrene in the presence of water soluble $K_2S_2O_8$ and oil soluble AIBN initiators. They found that the conversion–time curves showed only two intervals with neither a constant rate region nor a gel effect. The particle nucleation stage continued to 20–50% conversion for $K_2S_2O_8$ and 15–20% conversion for AIBN; this long nucleation stage was attributed to the slow rate of radical entry into the microemulsion droplets. Also, the obtained microemulsion latices had 20–30 nm particles. The maximum polymerization rate and the number of particles varied with 0.49 and 0.39 powers of the $K_2S_2O_8$ concentrations, respectively, and with 0.40 and 0.38 powers of the AIBN concentration, respectively. They also reported that the polymerization mechanism involved nucleation in the microemulsion droplets by radical entry from the aqueous phase.[11] Both O/W and W/O polystyrene stable microemulsions with average droplet diameters of 50–70 nm were prepared[12] using $K_2S_2O_8$ as the initiator. Also, microemulsion polymerization of styrene was carried out[13] in water, hexadecyltrimethyl ammonium bromide, or sodium dodecyl sulfate and butyl carbitol using water soluble $K_2S_2O_8$ or oil soluble AIBN as the initiator. The latices obtained were stable for 1 year. The polymerization rate showed two stages. A longer nucleation period was found in the polymerization initiated by $K_2S_2O_8$ as compared to AIBN. The polymerization rate varied with the 0.47 power of the $K_2S_2O_8$

concentration and with the 0.39 power of the AIBN concentration. The apparent activation energy of the polymerization was $\sim$ 50 kJ/mol for the systems initiated with AIBN and $\sim$ 90 kJ/mol for the $K_2S_2O_8$ initiated system. The latex particles were nearly spherical with an average particle diameter of $\sim$ 25 nm. The rheology of the emulsion latices is a subject of considerable importance from fundamental and applied points of view. At the fundamental level the rheology of emulsion is a direct manifestation of the various interaction forces that occur in the system. At an applied level the study of the rheology of the emulsion is vital in many industrial applications such as food emulsion, paints, inks, adhesives, and many others.[14] Huoming et al.[15] studied the effect of the component structure, morphology, model diameter, and distribution of the latex particles on the rheological properties of the obtained acrylate emulsion latices. They found that the viscosity of the emulsion latices increased as the model diameter of the emulsion particles decreased and the behavior of the emulsion latices is pseudoplastic. Moreover, Pal[16] studied the rheological behavior of an O/W emulsion prepared from concentrated emulsifier solutions using a coaxial cylinder. The emulsions produced at higher emulsifier concentrations were highly flocculated in nature, non-Newtonian type, and indicated the presence of yield stress.

The aim of this article was to study the kinetics of the microemulsion polymerization of styrene using a developed redox initiation system that consists of $K_2S_2O_8$ as the oxidizing agent and MeBSBS adduct as the reducing agent. We also studied the effect of different polymerization conditions on the rheological properties of the obtained microemulsion latices.

EXPERIMENTAL

Chemicals

The styrene was (Merck) redistilled before use and stored at $-20°C$. The potassium persulfate and P-methyl benzaldehyde were supplied by Merck. Sodium dodecyl sulfate, methanol, ethanol, 2-butanol, and toluene were products of Prolabo Company (France). The sodium bisulfite was a product of El-Naser Pharmaceutical Chemical Company (Egypt). All of the water used was purified by distillation. The MeBSBS adduct was prepared as described previously.[3]

Table I   Recipe of Microemulsion Polymerization of Styrene

Ingredients	Function	Amount (g)
Styrene	Monomer	Variable
Sodium dodecyl sulfate	Emulsifying agent	Variable
Redox initiation system		
Potassium persulfate/methyl benzaldehyde	Oxidizing agent	Variable
Sodium bisulfite adduct	Reducing agent	Variable
Demineralized water	Dispersion medium	82.35
2-Butanol	Cosurfactant	3.79
Toluene	Comedium	2.34

Microemulsion Polymerization of Styrene

The styrene monomer, 2-butanol, and toluene were added to the solution of emulsifier (sodium dodecyl sulfate) in water using the recipe given in Table I. These experiments were run with mechanical stirring at 500 rpm for 1 h to obtain a clear solution at room temperature. When the hazy cast of the solution disappeared, the solution was heated at the required temperature with an automatically controlled water bath. The microemulsion polymerization was started at once by adding the redox pair initiation system (KPS/MeBSBS).

To determine the conversion of monomer to polymer during the polymerization process it is necessary to withdraw the samples at different intervals. These samples were relatively small so that the overall composition in this reaction vessel was not seriously affected. Once a sample was removed and put in a watch glass, the reaction was stopped with 7 ppm hydroquinone solution, a small amount of ethanol was added as coagulant, and the content of the watch glass was evaporated at room temperature and then dried in an electric oven till constant weight. Because the composition of the materials in the reaction vessel at sampling time is known, the conversion percentage of monomer to polymer is easily calculated.

Transmission Electron Microscope

A Zeiss type transmission electron microscope (model EM. 10, Germany) was used that works at 60 kV and has a magnification range between

Table II   Microemulsion Polymerization of Styrene Using KPS/MeBSBS as Redox Initiation System and Rheological Properties of Obtained Latices

Temp. (°C)	[Emulsifier] (mol/L)	[KPS/MeBSBS] (mol/L)		[Monomer] (mol/L)	Plastic Viscosity (P)	Yield Value (dyn/cm^2)	Rate $\times 10^4$ (mol/L s)	$E_a \times 10^{-4}$ (J/mol)
30	0.38	0.018	0.036	0.029	0.038	0.022	0.23	
40	0.38	0.018	0.036	0.029	0.046	0.030	0.36	
50	0.38	0.018	0.036	0.029	0.057	0.036	0.96	6.5
60	0.38	0.018	0.036	0.029	—	—	2.39	
70	0.38	0.018	0.036	0.029	—	—	4.78	
50	0.26	0.018	0.036	0.029	0.0235	0.039	4.80	
50	0.30	0.018	0.036	0.029	0.0380	0.037	4.50	
50	0.34	0.018	0.036	0.029	0.0490	0.046	1.50	
50	0.38	0.018	0.036	0.029	0.0570	0.036	0.96	
50	0.38	0.009	0.018	0.029	0.036	0.030	0.93	
50	0.38	0.018	0.036	0.029	0.057	0.036	0.96	
50	0.38	0.027	0.054	0.029	0.060	0.037	4.40	
50	0.38	0.036	0.072	0.029	0.069	0.040	6.70	
50	0.38	0.018	0.036	0.029	0.057	0.036	0.96	
50	0.38	0.018	0.036	0.57	0.028	0.024	1.81	
50	0.38	0.018	0.036	0.86	0.031	0.034	2.36	
50	0.38	0.018	0.036	1.16	0.037	0.054	—	
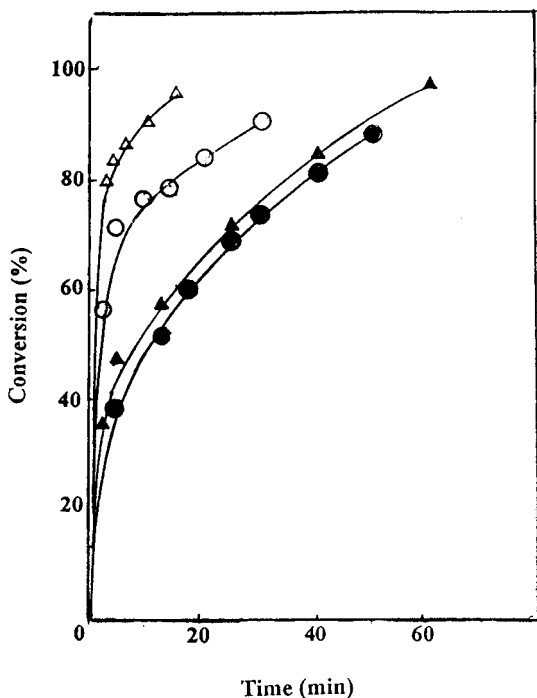
Figure 1 The rate dependence of the initiator concentration: [KPS/MeBSBS] = (○) 0.009/0.018, (▲) 0.018/0.036, (●) 0.027/0.054, and (△) 0.036/0.072 mol/L using [emulsifier] = 0.38 mol/L and [monomer] = 0.29 mol/L at 50°C.

2500 and 5×10^5 and a resolution of 0.5 nm. An image analyzer (Bild analyze, 1BAS 1 and 2) was used to measure the average diameter (D_i) for different polymer particles. The volume average diameter of polymer particles (D_V), the number of particles per unit volume of water (N_t), and the polydispersity were determined as described earlier.[3]

## Rheological Measurements

Flow Curves

Every rheological instrument has a defined range of shear rates and there is no rheological instrument that allows the determination of the complete flow curve in the entire range of shear rates. Therefore, we studied the flow curves for different polymer emulsions and solutions at a definite range of shear rates from 10^{-2} to 10 s^{-1}. Measurements were made with increasing and decreasing rates of shear in the same stages and with the same time intervals to determine whether the type of flow involves thixotropy or not.

RESULTS AND DISCUSSION

Kinetics of Microemulsion Polymerization of Styrene

Rate Dependence of Initiator Concentration

Microemulsion polymerization of styrene was carried out in the presence of sodium dodecyl sulfate as an emulsifier, MeBSBS with KPS as the redox pair initiation system, 2-butanol, toluene, and water. The obtained microemulsion was stable and transparent. The data recorded in Table II and illustrated in Figure 1 show the conversion time values for the microemulsion polymerization of styrene using different concentrations of the our redox initiation system.[17] It is obvious that the initial rate of microemulsion polymerization, as well as the maximum conversion, increased with increasing initiator concentration. Moreover, the obtained conversion–time curves did not show a sigmoidal shape similar to that revealed
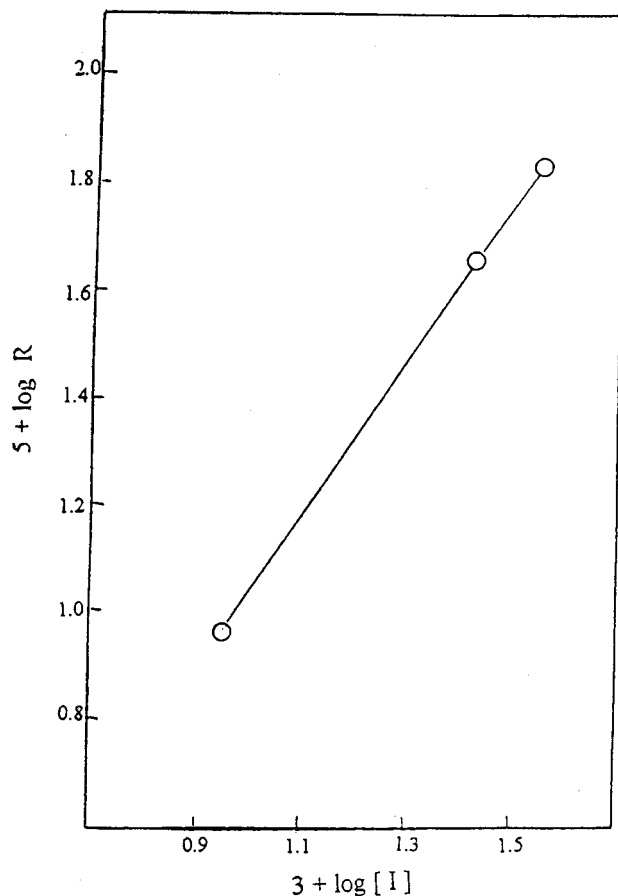
Figure 2 The double logarithmic plot of the rate of microemulsion polymerization, R (mol/L s) vs. initiator concentrations.
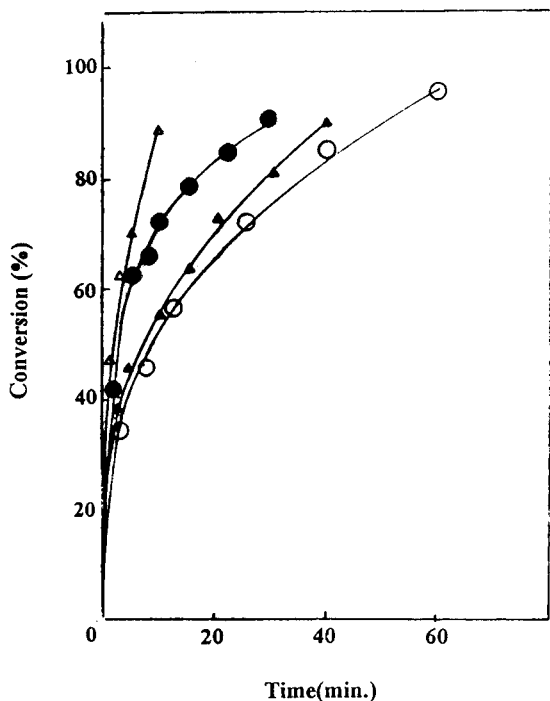
Figure 3 The rate dependence of the emulsifier concentration: [Emulsifier] = ($\triangle$) 0.26, ($\bullet$) 0.30, ($\blacktriangle$) 0.34, and ($\bigcirc$) 0.38 mol/L using [monomer] = 0.29 mol/L and [KPS/MeBSBS] = 0.018/0.036 mol/L at 50°C.

for the classical emulsion polymerization.[17] In other words, these curves gave only two intervals with no constant rate region. The long particle nucleation stage was due to the low rate of radical absorption by microemulsion droplets.[11] Another probable explanation[18] could be related to the free micelles of the emulsifier being present after the total consumption of the monomer.

On the other hand, we found that the microemulsion polymerization reaches the limiting conversion calculated at 85–95%. Probably most of the limiting conversion can be explained by the interaction between the initiator molecules and the growing radicals, as well as the strong cage effect.[19] Figure 2 shows the double logarithmic plot of the microemulsion polymerization rate versus the initiator concentration. Figure 2 shows the calculated power of the developed redox pair initiation system with respect to the rate of microemulsion polymerization of styrene to be 1.4. This power was found to be higher than that obtained by others.[11,20] This is attributed to the developed redox initiation system used.

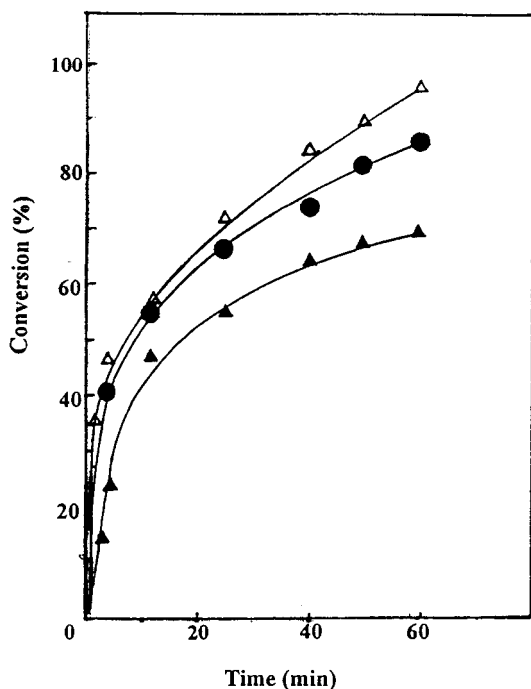### Rate Dependence of Emulsifier Concentration

Figure 3 and Table II show the effect of emulsifier concentration on the rate of microemulsion poly-

merization of styrene. These data show that the rate of microemulsion polymerization and the maximum conversion decreased with increasing emulsifier concentration. This may be attributed to the large amount of emulsifier required for the preparation of the microemulsion, which in this case retards the polymerization reaction of styrene.

Figure 4 shows the relationship between log rate of microemulsion polymerization against log emulsifier concentration. The power of the emulsifier with respect to the rate of microemulsion polymerization was found to be −0.77. This may be attributed to the shell structure formed by adsorption of the surfactant on the microemulsion droplets that may slightly retard the entry of oligomeric radicals and lead to a lower radical capture efficiency.[21] Others[22] attributed the negative reaction order to the so-called diluation effect (i.e., monomer is diluted by the hydrophobic chains of the emulsifier or to the strong transfer of the growing radical to the emulsifier).[9] However, the formation of polymer particles via homogeneous nucleation allows oligomeric radicals to readily react with monomers in the aqueous phase and then adsorb surfactant molecules for stabilization.
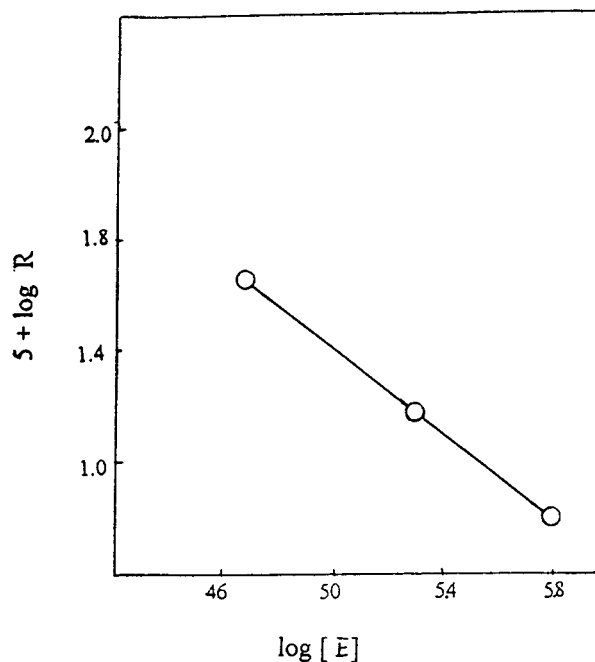
Figure 4 The double logarithmic plot of the rate of microemulsion polymerization, R (mol/L s) vs. emulsifier concentrations.
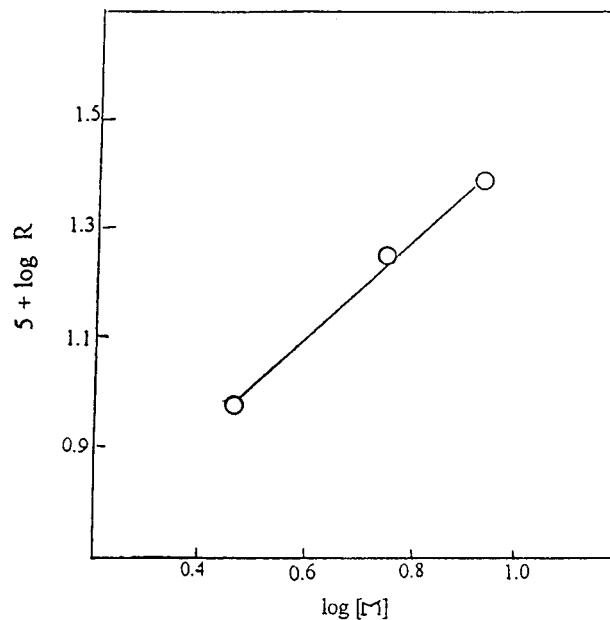
Figure 5 The rate dependence of the monomer concentration. [Monomer] = (▲) 0.29, (●) 0.57, and (△) 0.86 mol/L using [KPS/MeBSBS] = 0.018/0.036 mol/L and [emulsifier] = 0.38 mol/L at 50°C.

Rate Dependence of Monomer Concentration

The data recorded in Table II show the effect of the initial monomer concentration on the rate of microemulsion polymerization of styrene performed at 50°C using fixed concentrations for the initiator and emulsifier. The conversion–time plots of these data are illustrated in Figure 5. Obviously, the rate of microemulsion polymerization increased with increasing monomer concentration. Figure 6 shows the relationship between the log rate of microemulsion polymerization versus the log monomer concentration. The rate of polymerization is proportional to the power of 0.83 with respect to the monomer concentration. The higher power of the monomer concentration may be due to the presence of the large amount of emulsifier used in microemulsion polymerization.
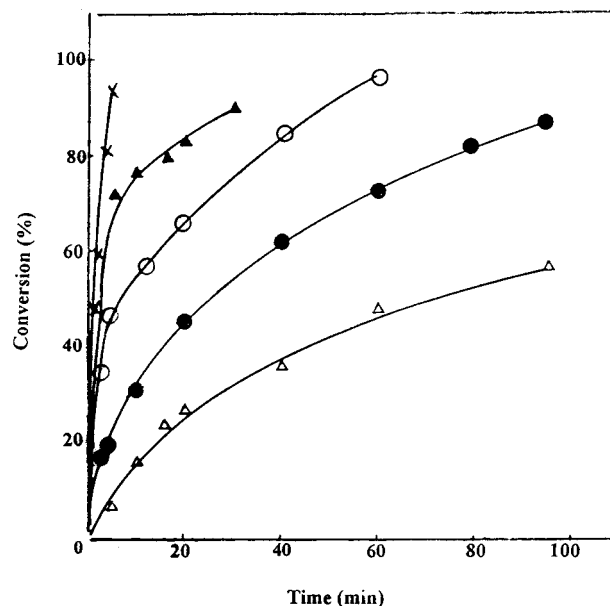
Effect of Temperatures on Rate of Microemulsion Polymerization of Styrene

The effect of different temperatures on maximum conversion and the rate of microemulsion polymerization of styrene at constant concentrations of initiator, emulsifier, and monomer was studied. The data of the initial rate of microemulsion
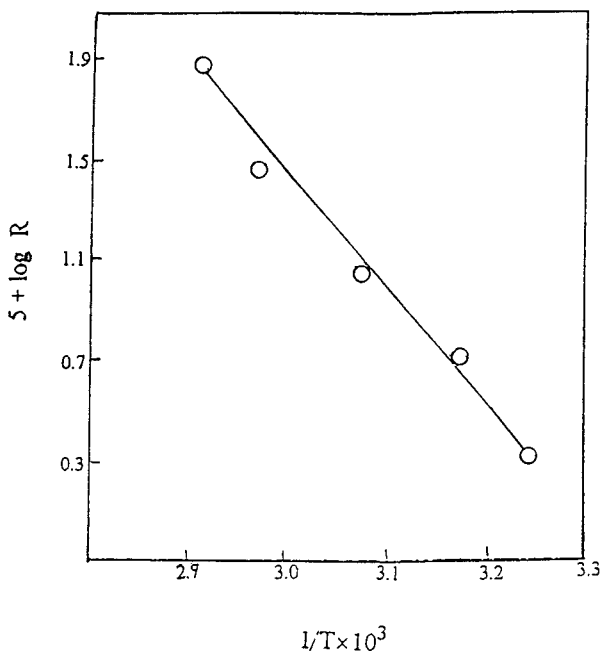

Figure 6 The double logarithmic plot of the rate of microemulsion polymerization, R (mol/L s) vs. monomer concentrations.

polymerization obtained at different temperatures (30–70°C) are present in Table II. The conversion–time curves for the microemulsion poly-

Figure 7 The rate dependence of the microemulsion polymerization temperature. Temperature = (△) 30, (●) 40, (○) 50, (▲) 60, and (×) 70°C using [monomer] = 0.29 mol/L, [KPS/MeBSBS] = 0.018/0.036 mol/L, and [emulsifier] = 0.38 mol/L.

Figure 8 The Arrhenius plot of the rate of microemulsion polymerization, R (mol/L s).

merization obtained at different temperatures are represented in Figure 7. The conversion curves take on a shape similar to that for emulsion polymerization, especially for runs performed at low temperatures. It is clear that maximum conversion and initial rate values increased with increasing temperature. The rate values of microemulsion polymerization present in Table II were used to draw the Arrhenius plot ($\log R$ vs. $1/T$). The Arrhenius apparent activation energy (E_a) for this system was calculated from the slope of the obtained straight line of Figure 8 and was found to be 6.5×10^4 J/mol. This value is less than that obtained by Gan et al.[13] (9×10^4 J/mol). This is attributed to the higher activity of the developed redox pair initiation system (KPS/MeBSBS) toward microemulsion polymerization of styrene.

In our studies the proposed rate equation for the microemulsion polymerization of styrene is as follows:

$$R_P \propto [I]^x [E]^y [M]^z$$

where I, E, and M are the initiator, emulsifier, and monomer concentration, respectively. The calculated values of x, y, and z were found to be 1.4, -0.77, and 0.83.
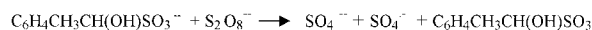
Reaction Mechanism

The suggested mechanism for the microemulsion polymerization reaction is shown in Scheme 1.

Morphological Characterization

The morphology of some obtained polystyrene microemulsion latex particles prepared by KPS coupled with MeBSBS was studied using different concentrations of the redox initiation system. Table III shows the values of D_V that range from 66 to 81 nm, and these values are near to that obtained by Yu and Guo[12] (50–70 nm). Also, this table indicates that N_t increased with the increasing concentration of the redox initiator. The polydispersity index values were nearly equal to 1.3.

Rheological Studies of Prepared Polystyrene Microemulsion Latices

The flow characteristics (rheology) of an emulsion are the subject of considerable importance from the fundamental and applied points of view. At a fundamental level the rheology of an emulsion is a direct manifestation of the various interaction forces that occur in the system. At an applied level the study of the rheology of an emulsion is vital in many industrial applications: food emulsions, cosmetics, paints, agrochemical, pharma-
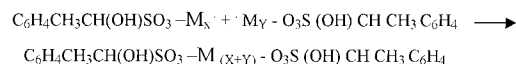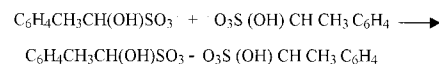
$C_6H_4CH_3CH(OH)SO_3^{--} + S_2O_8^{--} \longrightarrow SO_4^{--} + SO_4^{--} + C_6H_4CH_3CH(OH)SO_3$

Initiation:

$C_6H_4CH_3CH(OH)SO_3^{\cdot} + M \longrightarrow C_6H_4CH_3CH(OH)SO_3\text{-}M^{\cdot}$

Propagation:

$C_6H_4CH_3CH(OH)SO_3\text{-}M^{\cdot} + M \longrightarrow C_6H_4CH_3CH(OH)SO_3\text{-}M\text{-}M^{\cdot}$

$C_6H_4CH_3CH(OH)SO_3-M^{\cdot}_{(x-1)} + M \longrightarrow C_6H_4CH_3CH(OH)SO_3-M_X^{\cdot}$

Termination:

$C_6H_4CH_3CH(OH)SO_3-M_X^{\cdot} + {}^{\cdot}M_Y\text{-}O_3S(OH)CHCH_3C_6H_4 \longrightarrow$

$C_6H_4CH_3CH(OH)SO_3-M_{(X+Y)}\text{-}O_3S(OH)CHCH_3C_6H_4$

Dimerization:

$C_6H_4CH_3CH(OH)SO_3^{\cdot} + {}^{\cdot}O_3S(OH)CHCH_3C_6H_4 \longrightarrow$

$C_6H_4CH_3CH(OH)SO_3\text{-}O_3S(OH)CHCH_3C_6H_4$

Scheme 1 The reaction mechanism.

Table III   Average Particle Size of Polystyrene Microemulsion Latex Particles as Function of Concentrations of Redox Initiation at 50°C

[Redox Initiator] $\times 10^2$ mol/L		D_V (nm)	N_t ($\times 10^{-14}$)	PDI
KPS	MeBSBS			
0.9	1.8	81	0.03	1.34
1.8	3.6	71	1.16	1.22
2.7	5.4	68	1.14	1.3

PDI, polydispersity index.

ceuticals, bitumen emulsions, inks, paper coatings, adhesives, and many other applications.[14]

This study deals with the rheological properties of polystyrene microemulsion latices that were prepared by our developed initiation system at different polymerization conditions (i.e., different concentrations of initiator, monomer, and emulsifier, as well as temperature). To investigate the rheological properties of the prepared polystyrene microemulsion latices, the effect of shear rate on the stress was determined and plotted as characteristic flow curves.

### Rheological Study at Different Polymerization Temperatures

The measured values of shear stress for polystyrene microemulsion latices prepared using different temperatures are represented in Figure 9. From this figure it is clear that at a small shear rate the shear stress is too small; by increasing the shear rate the shear stress, which is negligible up to a certain shear rate, causes the emulsion to flow, the shear stress increases linearly as the shear rate increases and it obeys Newton's law. This type of flow is a non-Newtonian flow called a plastic flow, which is characterized by its yield value (yield stress). This means that at first they behave as solids and flow will only take place after a certain shear stress (the yield value) is surpassed. Bingham described such systems. The yield value is mostly obtained by plotting the shear stress (τ) as a function of the shear rate (γ) and extrapolating to a zero shear rate.

From the curves shown in Figure 9, the derived values of plastic viscosity (the slope of the straight part of the flow curve) and yield value (the intercept of the straight part of the flow curve with the shear stress axis) for each polystyrene microemulsion latex are listed in Table II. As shown in the table, increasing the polymerization temperature gave an increase in the plastic viscosity and yield value.

Increasing the temperature of the medium will increase the caging of polymer particles within the medium and it will behave as one structure, and the viscosity of emulsifier in the medium (in the microemulsion latex emulsifier always used by large amount) is responsible for trapping the free radical in the medium. Thus, the number of radicals decreases and the molecular weight of the obtained polymer increases with increasing temperature. For these reasons the plastic viscosity of the system increases with increasing polymerization temperature.

Rheological Study at Different Emulsifier Concentrations

Some polystyrene microemulsion latices were prepared using different emulsifier concentrations. The measured values of shear stress for these latices at different shear rates and 30°C are plotted in Figure 10. From this figure it is clear that the emulsion systems exhibit a plastic flow character. The values of the plastic viscosity and yield value were determined from the flow curves (Fig. 10) for each microemulsion latex and are listed in Table II. This table shows that the in-
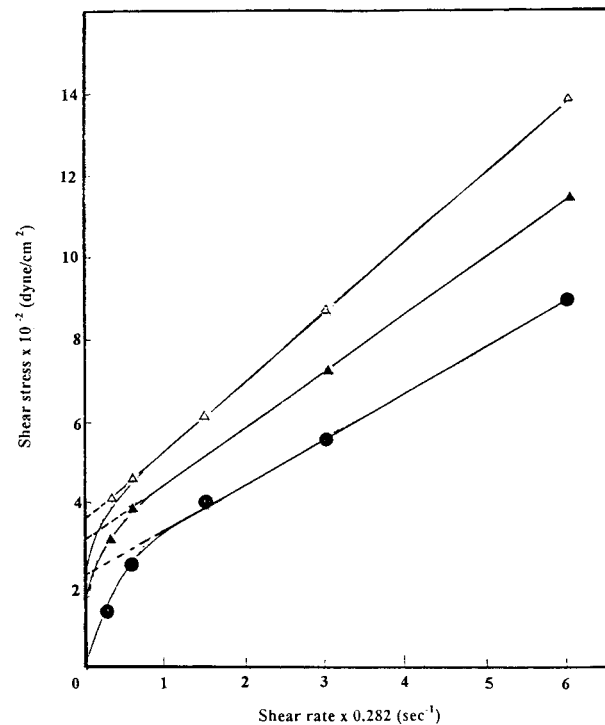
Figure 9   The flow curves of the polystyrene microemulsion at (●) 30, (▲) 40, and (△) 50°C using [monomer] = 0.29 mol/L, [emulsifier] = 0.38 mol/L, and [KPS/MeBSBS] = 0.018/0.036 mol/L.
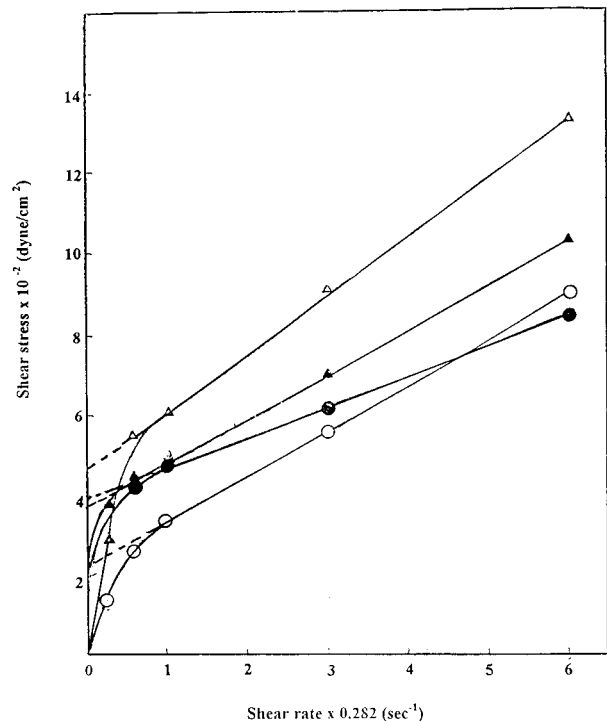
Figure 10 The flow curves of the polystyrene microemulsion with different emulsifier concentrations. [Emulsifier] = (●) 0.26, (▲) 0.30, (△) 0.34, and (○) 0.38 mol/L using [KPS/MeBSBS] = 0.018/0.036 mol/L and [monomer] = 0.29 mol/L at 50°C.

crease of the emulsifier concentration gives an increase in the plastic viscosity from 0.0265 to 0.057 P and a small decrease in the yield value of the system with the emulsifier concentration.

Pal[16] reported that at high emulsifier concentrations the rheological behavior of these emulsions was non-Newtonian. In addition, the rheological data clearly indicated the presence of a yield stress that is in a good accord with the results obtained in this work. The increasing[23–26] of the viscosity of the emulsion systems as the emulsifier concentration increased, which may be due to the association of the emulsifier molecules when their concentration exceeds the critical micelle concentration (CMC). Therefore, the number of globules (beyond CMC) increases, and thus the smooth flow of the solvent is disturbed by globules and an increase in viscosity occurs as showed in Table II.

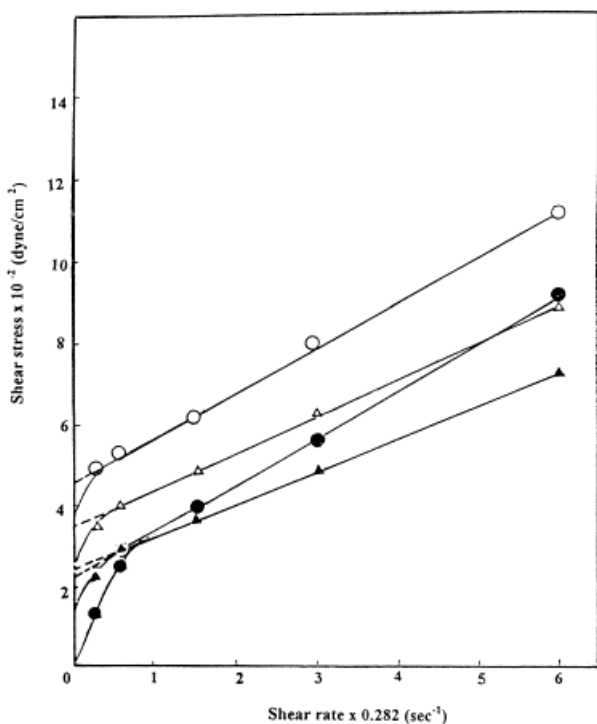## Rheological Study at Different Initiator Concentrations

The values of shear stress for polystyrene microemulsion latices prepared at different initiator concentrations measured at different shear rates and

30°C are represented in Figure 11. The flow curves show that these microemulsion systems exhibit a plastic type flow. As shown in Table II, the increase of initiator concentration gives an increase in the plastic viscosity and yield value. As the initiator concentration increases the number of particles increase, the particle sizes decrease (as shown in Table III), and the adsorbed layer on the particle increases, because small spheres have more surface area. For this reason the smooth flow of the solvent is disturbed by particles, and with increasing the surface area and volume of particles in the adsorbent the disturbance of flow increases and so an increase in viscosity occurs that is due to the flow occurring as one structure is formed from the medium and polymer particles.

This result is in accordance with that given by Sweeny and Geckler.[27] They observed that the viscosity increases as the particle size decreases and suggested that this behavior may be due to adsorbed layers of the medium, where small spheres have more surface area for a given concentration and more adsorbed layer.
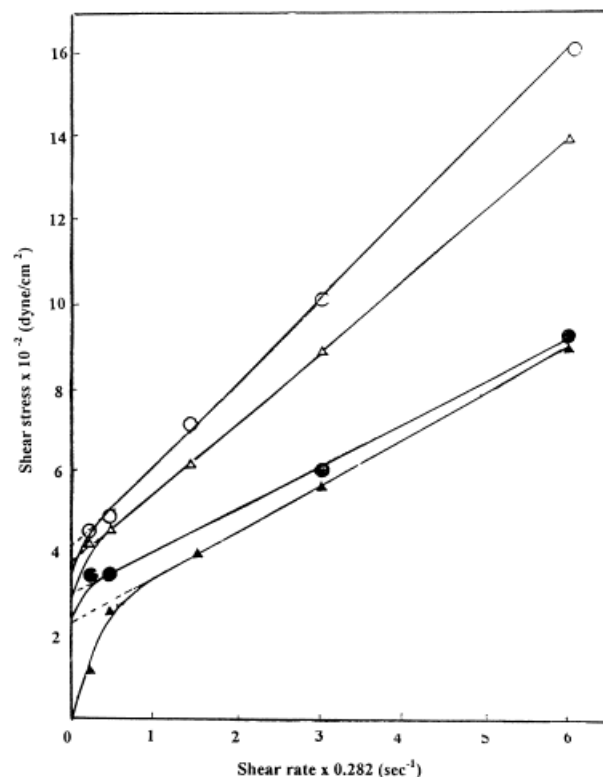
Figure 11 The flow curves of the polystyrene microemulsion with different initiator concentrations. [KPS/MeBSBS] = (●) 0.009/0.018, (▲) 0.018/0.036, (△) 0.027/0.054, and (○) 0.036/0.072 mol/L using [monomer] = 0.29 mol/L and [emulsifier] = 0.38 mol/L at 50°C.

Figure 12 The flow curves of the polystyrene microemulsion with different monomer concentrations. [Monomer] = (●) 0.29, (▲) 0.57, (△) 0.86, and (○) 1.16 mol/L using [KPS/MeBSBS] = 0.018/0.036 mol/L and [emulsifier] = 0.38 mol/L at 50°C.

Rheological Studies at Different Monomer Concentrations

The measured values of shear stress for polystyrene microemulsion latices prepared using different monomer concentrations at different shear rates at 30°C are plotted in Figure 12. From the flow curves these emulsions systems exhibit a plastic flow character. The values of the plastic viscosity and yield value are derived from flow curves for each polystyrene microemulsion latex and are listed in Table II. Observe in Table II that the increase of the monomer concentration increases the plastic viscosity and yield values. Increasing the monomer concentration leads to an increase in the molecular weight of the obtained polymer and that leads to an increase in the viscosity of the microemulsion latex. The other reason for increasing the viscosity of such a microemulsion is the increase of the globule size by increasing the monomer concentration, so the disturbance of the flow increases and hence the plastic viscosity increases.

REFERENCES

1. Badran, A. S.; Yehia, A. A.; Moustafa, A. B.; Shendy, S. M. M. Acta Polym Ber 1990, 41, 187.
2. Badran, A. S.; Moustafa, A. B.; Yehia, A. A.; Shendy, S. M. M. J Polym Sci Part A Polym Chem 1990, 28, 411.
3. Badran, A. S.; Ayoub, M. M. H.; Abd El-Ghaffar, M. A.; Nasr, H. E.; Abd El-Hakim, A. A. Eur Polym J 1997, 33, 537.
4. Mohsen, R. M.; Nasr, H. E.; Badran, A. S. Pigment Resin Technol 1995, 24(3), 9.
5. Piirma, I. Polymeric Surfactant; Marcel Dekker, Inc.: New York, 1992; p 267.
6. Jaga Krishanan, J.; Shah, D. O. J Polym Sci Polym Lett Ed 1984, 22, 31.
7. Antonietti, M.; Lohmann, S.; Niel, C. V. Macromolecules 1992, 25, 1139.
8. Full, A. P.; Puig, J. E.; Gron, L. U.; Kaler, E. W.; Minter, J. R.; Mourey, T. H.; Texter, J. Macromolecules 1992, 25, 5157.
9. Donescu, D.; Anghel, D.; Gosa, K.; Balcan, M. Angew Makromol Chem 1991, 188, 1.
10. Candau, F.; Leong, Y. S.; Fitch, R. M. J Polym Sci Part A Polym Chem 1985, 23, 193.
11. Guo, J. S.; El-Asser, M. S.; Vanderhoff, J. W. ACS Symposium Series 384, Polymer Assoc Stract American Chemical Society: Washington, D.C., 1989; p 86.
12. (a) Yu, D.; Guo, X. Shigou Huagong 1991, 20(1), 55; (b) C.A., 115,137,092. 1991.
13. Gan, L. M.; Chew, C. H.; Lye, I. Makromol Chem 1992, 193, 1249.
14. Tadros, T. F. Colloids Surfaces 1994, 91, 39.
15. (a) He, H.; Li, J.; Chen, S.; Li, X. Polym Mater Sci Eng 1993, 9, 92; (b) C.A., 121,301,995, 1994.
16. Pal, R. J Colloids Surfaces 1992, 64, 207.
17. Badran, A. S.; Abd El-Hakim, A. A.; Nasr, H. E.; Abd El-Ghaffar, M. A. In Proceedings of the 2nd Arab International Conference on Advances in Material Science and Engineering (Polymeric Materials); 1993; p 163.
18. Guo, J. S.; Sudol, E. D.; Vanderhoff, J. W.; El-Assar, M. S. J Polym Sci Part A Polym Chem 1992, 30, 69.
19. Capek, I.; Riza, M.; Akashi, M. Polymer 1992, 24, 959.
20. Guo, J. S.; David, E.; Vanderhoff, J. W.; El-Asser, M. S. ACS Symposium Series 492, Polymer Latexes; American Chemical Society: Washington, D.C., 1992; p 99.
21. Guo, J. S.; El-Asser, M. S.; Vanderhoff, J. W. J Polym Sci Part A Polym Chem 1989, 27, 691.
22. Capek, I.; Potisk, P. J Polym Sci Part A Polym Chem 1995, 33, 1675.
23. Sherman, P. J Soc Chem Ind 1950, 2(Suppl.), 570.
24. Sherman, P. Kolloid Z 1959, 165, 156.
25. Sherman, P. Proc Thried Int Congr Surface Activity 1960, II, 596.
26. Sherman, P. Food Technol 1961, 15, 394.
27. Sweeny, K. H.; Geekler, R. D. J Appl Phys 1954, 25, 1135.