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Styrene polymerization in ternary microemulsions: effects of water-soluble and oil-soluble initiators

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Abstract: The polymerization of styrene in ternary microemulsions stabilized by the cationic surfactant tetradecyltrimethylammonium bromide was studied as a function of concentrations of water-soluble (potassium persulfate, KPS) and oil-soluble (AIBN) initiators. At a particular molar ratio of the initiators, similar maximum rates of polymerization can be achieved from using both types of the initiators. In addition, both initiated systems produced microlatexes with similar hydrodynamic radius, number of polymer particles, molecular weight of polystyrene and number of polymer chain per latex particle. But the dependencies of these latex parameters on concentrations of KPS and AIBN may not be the same. The polymerization mechanism appears to be similar, irrespective of using KPS or AIBN. It is discussed in terms of "effective radicals" produced for the polymerization. While the different dependencies of some latex parameters on concentrations of the initiators are attributed to the different efficiencies of the initiators in producing "effective radicals".

Key words: Styrene Polymerization – microemulsions – microlatexes

Introduction

During the past decade, most of microemulsion polymerization of styrene and methyl methacrylate have been carried out in four-component (o/w) microemulsions [1–11] consisting of water, monomer, surfactant and cosurfactant which is often a short-chain alcohol. Since 1989, polymerization of oil-soluble monomers have also been successfully conducted in three-component (o/w) microemulsions [12–20] without a cosurfactant.

The microemulsion polymerization of styrene in a four-component system [3, 4] exhibits only two rate intervals: an interval of increasing rate of polymerization due to the nucleation of polymer particles followed by an interval of decreasing rate due to polymer growth. A thermodynamic model [21] has recently been used to predict the depletion of oil cores of microemulsion droplets at about 4% of monomer conversion during polymerization. In addition, the average size of the monomer-swollen polymer particles at that level of monomer conversion will be at its maximum and then it decreases on further polymerization. This prediction has been experimentally verified by our study on styrene polymerization in ternary (o/w) microemulsions [22] which are stabilized by stearyltrimethylammonium chloride (STAC) or tetradecyltrimethylammonium bromide (TTAB).

The recent paper by Puig et al. [23] on styrene polymerization in a three-component microemulsion suggests that particle size and molecular weight of polymers correlate with initiator concentration, but are independent of whether oil-soluble (AIBN) or water-soluble ($K_2S_2O_8$) initiators are used. This interesting observation is further discussed in this paper. We also attempt to analyze the effects of AIBN and KPS on styrene polymerization in ternary microemulsions in terms of different "efficiencies" of the initiators in producing "effective radicals" for the polymerization.

Experimental section

Materials

Tetradecyltrimethylammonium bromide (TTAB) from Tokyo Chemical Industry (TCI) was recrystallized from a mixture of ethanol-acetone (1:3 by volume). Styrene (Fluka) was vacuum distilled to remove the inhibitor. Potassium persulphate ($K_2S_2O_8$, KPS) from Fluka and 2,2′-azobisisobutyronitrile (AIBN) from TCI were recrystallized from distilled water and methanol respectively.

Polymerization

The polymerization of styrene in a transparent ternary microemulsion was carried out in a glass dilatometer which was immersed in a 60 ± 0.1 °C water bath. After degassing at 10 Torr for one freeze-thaw cycle, the microemulsion was directly introduced into a dilatometer attached to a vacuum line. The change of liquid level in the capillary of the dilatometer as a function of time was monitored using a cathetometer. The fractional conversion of styrene was determined from the volume change which was calculated from the liquid-height change in the capillary. After polymerization, polystyrene was precipitated in a large quantity of distilled methanol. The polymer was repeatedly washed with methanol and water respectively, and dried under reduced pressure at 60 °C.

Molecular weight

Molecular weights of polystyrene were determined by gel permeation chromatography (GPC) using a Varian 5500 liquid chromatography system equipped with a RI-3 detector. The columns used were Varian micropale TSK 7000 H and GMH6 in series and eluent was the degassed tetrahydrofuran (THF). Polystyrene standards (0.2 mg/mL in THF) from Polyscience were used for the calibration.

Particle size

Particle sizes (hydrodynamic radius, R_h) of microlatexes were determined by photon correlation spectroscopy (PCS) using Malvern 4700 light scattering spectrophotometer. Prior to measurements, the latexes were diluted with distilled water until the volume fractions of particles were in the range of 0.01 to 0.1. An average R_h was calculated from the intrinsic diffusion coefficient (D_0) via the well-known Stokes–Einstein equation: $R_h = kT/6\pi\eta D_0$, where η is the viscosity of the dispersion medium.

The latexes were also examined by a JEOL JEM-100CX electron microscope. One drop of the latex was thoroughly mixed with 2 mL of 0.2% phosphotungstic acid (PTA). A drop of the mixture was then put on a copper grid coated with a thin layer of Formvar.®

Results

Kinetics of styrene polymerization

The compositions of ternary microemulsions selected for the detailed study are listed in Table 1. The latexes initiated by KPS and AIBN are coded by symbols K and A respectively. The numbers after K or A denote the concentration (mM) of KPS or AIBN based on water content used in each microemulsion. For example, K24 represents the system in which 0.24 mM KPS was used. Figs. 1a and 1b show the conversion-time plots with the increasing concentrations of KPS and AIBN respectively. The variations of the rate of polymerization (R_p) as a function of polymer conversions are depicted in the insets of Fig. 1. For both series K and A, all rates of polymerization first increase to their respective maxima at about 15% polymer conversion and then decrease on further polymerization. The plots of $\log R_p$

Table 1. Compositions of microemulsions

Microemulsion*)	Latex code	KPS (mM)	AIBN (mM)
7 wt% Styrene 9 wt% TTAB 84 wt% Water	K24	0.24	–
	K31	0.31	–
	K42	0.42	–
	A33	–	0.33
	A58	–	0.58
	A86	–	0.86

*) The concentrations of KPS and AIBN are all based on the water content used in microemulsions which were polymerized at 60 °C.

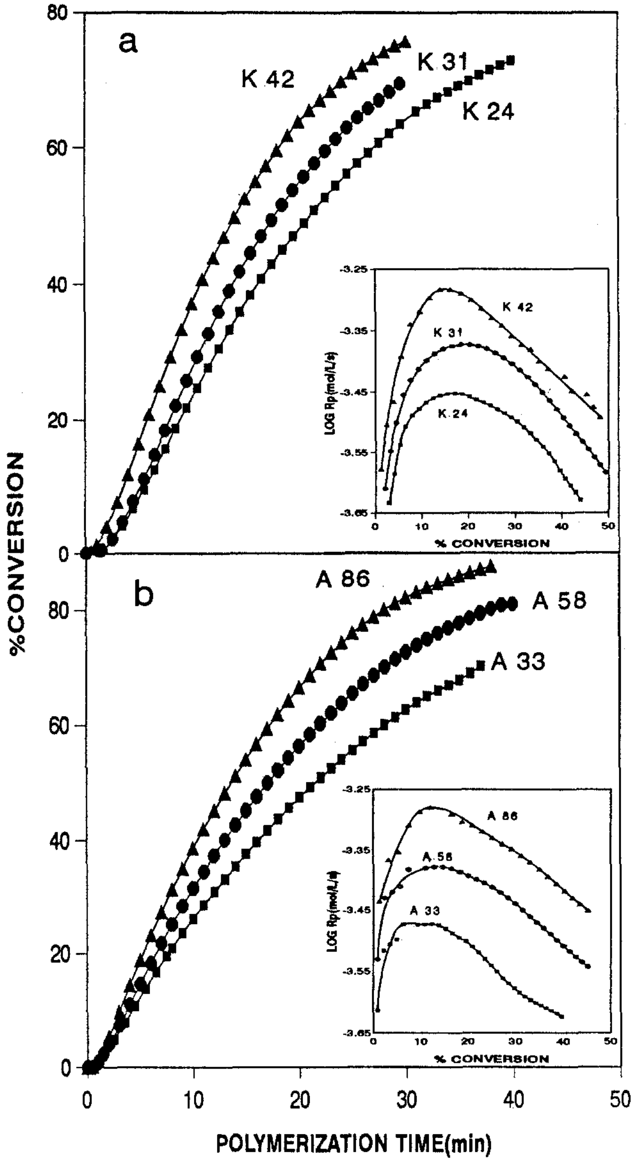

Fig. 1. The styrene polymerization curves at 60 °C for microemulsions containing 7 wt% styrene, 9 wt% TTAB and 84 wt% water: (a) Variation with KPS concentration, (b) Variation with AIBN concentration

against % conversion are very similar between series K and A. At lower concentrations of initiators, especially for sample A33, there seems to be a rather constant R_p around 10% conversion. But the rather constant R_p regions become maximum peaks at higher concentrations of both initiators. Three pairs of similar maximum R_p (R_{pm}) were obtained for samples K24 and A33, K31 and A58 or K42 and A86 as listed in Table 2. This shows that R_{pm} of about 3.5×10^{-4} mol/L/s for microemulsion polymerization of styrene at 60 °C can be achieved using either 0.24 mM KPS or 0.33 mM AIBN. Similarly, R_{pm} of approximately 4.2×10^{-4} mol/L/s can also be obtained from using 0.31 mM KPS or 0.58 mM AIBN, while the use of 0.42 mM KPS or 0.86 mM AIBN can yield R_{pm} of about 5.1×10^{-4} mol/L/s.

The effect of concentrations of both initiators on the maximum rate of polymerization (R_{pm}) is shown in Fig. 2. It is found that the initial rate of polymerization at about 5% conversion (R_{pi}) is proportional to the 0.48 power of [KPS] and to the 0.40 power of [AIBN]. From the Arrhenius plots, the overall activation energies of 95 and 48 kJ/mol were obtained for the polymerizations initiated by KPS and AIBN respectively. Similar results on the activation energy of polymerization and the dependence of R_p on the initiator concentration have also been reported [4, 11] for styrene polymerization in four-component microemulsions containing a short-chain alcohol as a cosurfactant.

Features of the microlatexes

Based on the similar maximum rates of styrene polymerization (R_{pm}) obtained from KPS- and AIBN-initiated systems (Fig. 2), the features of three similar pairs (K24/A33, K31/A58 and K42/A86) are analyzed. Table 2 shows the average hydrodynamic radius (R_h) of latex particles, number of polymer particles per mL latex (N_d), molecular weight of polystyrene ($\bar{M}_w$), number of polymer chain per latex particle (N_p) and R_{pm}. There are striking similarities in R_h, N_d, $\bar{M}_w$, $\bar{M}_w/\bar{M}_n$, N_p and R_{pm} among three pairs of latexes, i.e., K24 vs A33, K31 vs A58 and K42 vs A86. It implies that these features are independent of the type of initiator used, but only dependent on the specific molar ratios of AIBN and KPS used as shown in Table 4.

Fig. 3 shows that R_h, $\bar{M}_w$ and N_p decrease, whereas R_{pm}, N_d and $\bar{M}_w/\bar{M}_n$ increase with the increase of initiator concentration. For the plots, the concentrations of initiators are expressed in mole per mole of styrene. The dependencies of $\bar{M}_w$ and R_h on both initiator concentrations (Table 3) are in close agreement with that reported by Puig

Table 2. Some features of polystyrene microlatexes

Features	Latex Code					
	K24	A33	K31	A58	K42	A86
R_h (nm)	33.4	34.3	30.9	31.0	29.7	29.7
N_d (10^{14}/mL)	9.4	8.6	12.0	12.0	15.1	15.1
$\bar{M}_w$ (10^7)	3.35	3.39	2.88	2.80	2.71	2.57
$\bar{M}_w/\bar{M}_n$	3.36	3.43	4.23	4.13	4.91	4.82
N_p^*)	1.40	1.46	1.23	1.29	1.05	1.09
R_{pm} (10^{-4} mol/L/s)	3.53	3.42	4.23	4.19	5.06	5.16

*) N_p: number of polymer chain per latex particle

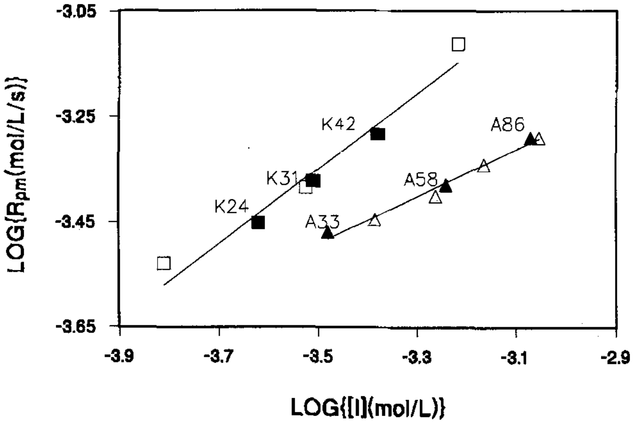

Fig. 2. Effects of initiator concentrations on rates of styrene polymerization

et al. [23], but $\bar{M}_w$ is inconsistent with that ($\bar{M}_w \propto [I]^{-0.07}$) obtained from the four-component microemulsion polymerization of styrene [4]. The effect of initiator concentration on R_h and $\bar{M}_w$ appears to be less dependent on the type of initiator used, but N_d, N_p and R_{pi} are rather strongly dependent on the type of initiator.

The TEMs (Fig. 4) show spherical latex particles of various sizes for all samples. The particle sizes range from about 20 to 60 nm in diameter with a majority at about 40 nm. There is no conclusive evidence to show the effects of type and concentration of initiators on particle sizes.

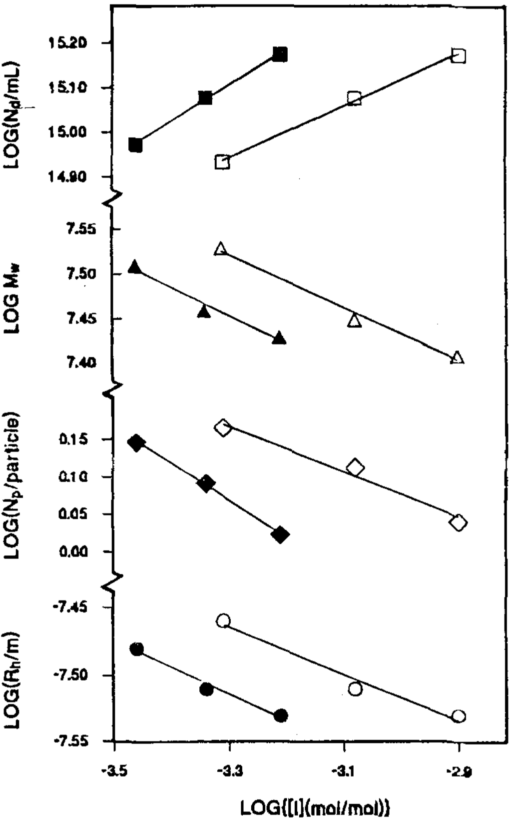

Fig. 3. Effects of KPS (black symbols) and AIBN concentration (in moles per mole of styrene) on various properties of polystyrene latexes

Discussion

The rates of styrene polymerization in ternary microemulsions are much higher for KPS-initiated systems than those of AIBN at several equal concentrations of initiators as revealed in Fig. 2. Similar observations have also been reported for KPS- and AIBN-initiated polymerization of styrene and methyl methacrylate in four-component microemulsions [7, 11] and ternary

Table 3. Relationships of some properties of microlatexes and concentrations of initiators

Properties	Relationships	
	Present results	Ref. 23
R_h	$\propto [\mathrm{KPS}]^{-0.20}$ $\propto [\mathrm{AIBN}]^{-0.17}$	$\propto [\mathrm{I}]^{-0.20}$
N_d	$\propto [\mathrm{KPS}]^{0.81}$ $\propto [\mathrm{AIBN}]^{0.59}$	–
$\bar{M}_w$	$\propto [\mathrm{KPS}]^{-0.32}$ $\propto [\mathrm{AIBN}]^{-0.30}$	$M_p \propto [\mathrm{I}]^{-0.40}$
N_p	$\propto [\mathrm{KPS}]^{-0.50}$ $\propto [\mathrm{AIBN}]^{-0.31}$	–
R_{pi}	$\propto [\mathrm{KPS}]^{0.48}$ $\propto [\mathrm{AIBN}]^{0.40}$	–

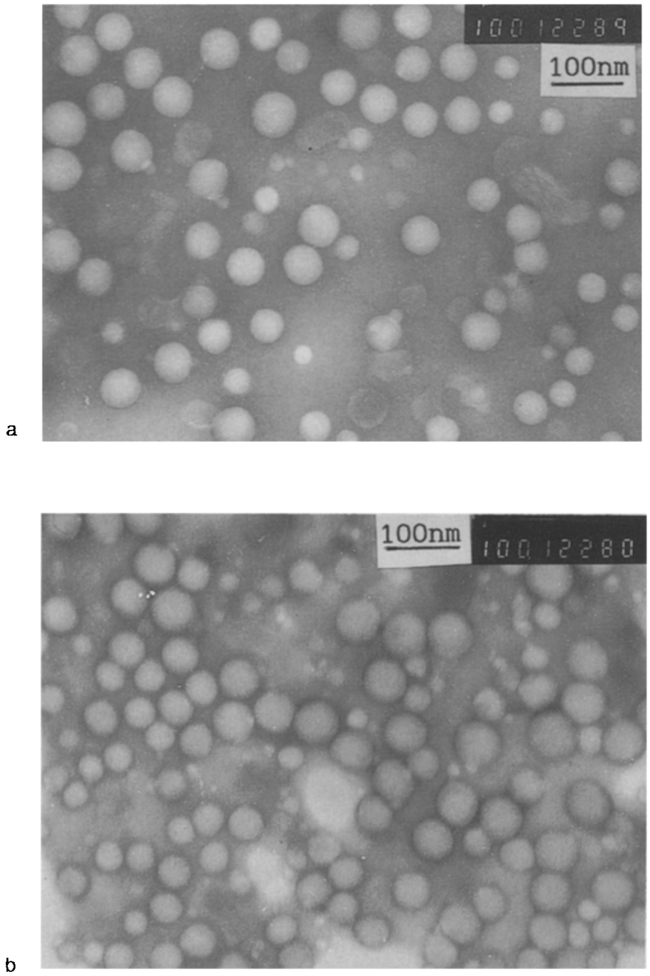

Fig. 4. TEM of microemulsion polystyrene latexes with phosphotungstic acid negative staining: (a) A33 and (b) K42

microemulsions [16]. However, Puig et al. [23] observed faster polymerization rates with AIBN than with KPS in a ternary microemulsion containing 6 wt% styrene, 14.1 wt% dodecyltrimethylammonium bromide (DTAB) and 79.9 wt% water. The only difference is that they used a much higher concentration of DTAB which is also more water-soluble than TTAB and CTAB.

The following discussion may provide some explanation for the similar latex features obtained from using KPS- and AIBN-initiated polymerization of styrene in ternary microemulsions. The decomposition rate constants (k_d) for KPS in water and AIBN in styrene at 60 °C are not readily available for calculation of the rate of radical generation. Based on k_d obtained at other temperatures [24], it is estimated that k_d for AIBN in styrene at 60 °C is $1.2 \times 10^{-5}\,\mathrm{s}^{-1}$ and $3.2 \times 10^{-6}\,\mathrm{s}^{-1}$ for KPS in water at 60 °C. These two k_d values are subsequently used for calculations. The estimation of these k_d values is based on an approximately linear relationship between k_d and temperature as it is true for AIBN in toluene (37 to 70 °C) and KPS in 0.1 M NaOH solution (50 to 70 °C).

Table 4 shows the calculated rates of radicals generated by various concentrations of KPS in water and AIBN in styrene for the microemulsions. Latexes of similar features could be prepared from the microemulsions using certain molar ratios of AIBN to KPS. The molar ratio increases nonlinearly from 1.38, 1.87 to 2.05 for similar pairs of A33/K24, A58/K31 and A86/K42 respectively. In terms of radical generation, the respective pairs would produce 5.2, 7.1 and 7.8 times more AIBN radicals than those of KPS. Based on the similar R_{pm} (Table 2), this may be interpreted in terms of effective polymerization that each KPS radical being equivalent to 5.2 AIBN radicals at 0.33 mM AIBN concentration, 7.1 at 0.58 mM AIBN and 7.8 at 0.86 mM AIBN. In other words, only about 19, 14 and 13% of AIBN radicals generated by the respective 0.33, 0.58 and 0.86 mM AIBN are as effective as KPS radicals for the polymerization. The efficiency of AIBN for the polymerization is also decreasing with the increase of the initiator concentration.

Since AIBN is soluble in oil, it dissolves mainly in the microemulsion droplets and only about 9×10^{-3} mM AIBN is found to be solubilized in

Table 4. Calculated ratios of free radicals generated by similar pairs of KPS and AIBN in microemulsions at 60 °C

System	Rate of free radical generation (10^{-9} mol/L/s)	Calculated ratio of radical produced by AIBN and KPS	Actual molar ratio of AIBN and KPS added
K24	1.29	–	–
A33	6.75	–	–
A33/K24	–	5.20	1.38
K31	1.67	–	–
A58	11.8	–	–
A58/K31	–	7.10	1.87
K42	2.26	–	–
A86	17.6	–	–
A86/K42	–	7.78	2.05

the aqueous phase. From quasielastic light scattering measurements, the average size of unpolymerized microemulsion droplets is estimated to be 16.2 nm in hydrodynamic radius (R_h) and the calculated number of microemulsion droplets per mL is 8×10^{15}. Hence a microemulsion droplet may contain as many as 22, 38 and 59 AIBN molecules in systems A33, A58 and A86 respectively. However, the efficiency of AIBN for effective polymerization (R_p) is low as compared with that of KPS. This is attributed to its high rate of autotermination of radical pairs generated in such small microemulsion droplets populated with AIBN molecules.

It is also believed that some AIBN molecules are preferably located at microemulsion droplet-water interfaces due to the polar nature of AIBN. Hence a small fraction of AIBN radicals generated near the interfaces of microemulsion droplets may diffuse out the droplets into the aqueous phase. Some of the exiled radicals may re-enter the droplets for polymerization. It is also possible that only one of two radicals (generated in pair) diffuses out a droplet, while the other single radical remains in the droplet to initiate the polymerization.

Total concentration of "effective AIBN radicals" available for the polymerization may be from three sources: (i) those generated in the aqueous phase (dissolved AIBN) and entered the droplets [25], (ii) those exiled from and re-entered the droplets, and (iii) those single radicals still remained in the droplets. The formation of radicals from the first source depends only on the solubility of AIBN in the aqueous phase, while radicals from the other two sources are deemed to be dependent on the concentration of AIBN. In contrast to AIBN initiated microemulsion polymerization of styrene, KPS radicals generated in the vast aqueous medium of a microemulsion are less likely to be autoterminated. They could therefore effectively enter the microemulsion droplets for the polymerization.

It is generally believed that the loci of styrene polymerization initiated by either water-or oil-soluble initiators are in the microemulsion droplets [23]. The polymerization rate is thus mainly dependent on the concentration of "effective radicals" available for polymerization, irrespective of the type of initiators used. In the case of radicals (either AIBN or KPS) available in the aqueous phase, the dissolved styrene in the aqueous phase (ca. 0.012 M) may first be reacted with the radicals to form oligomeric radicals of higher hydrophobicities [26, 27]. It is these oligomeric radicals that diffuse more favourably to the microemulsion droplet-water interfaces where more styrene molecules are available for further polymerization. On the other hand, the direct initiation of styrene polymerization by radicals of both initiators may be equally important at the microemulsion droplet-water interfaces. This is especially so for anionic KPS radicals which may be electrostatically attracted by cationic surfactant ions at the interfaces. In addition, the direct polymerization by radicals which are produced by a fraction of AIBN solubilized inside the microemulsion droplets also cannot be ruled out [28].

The features of three similar pairs of latexes prepared by KPS- and AIBN-initiated microemulsions strongly suggest that the mechanisms of initiation and polymer particle growth for both systems are similar at an equivalent concentration of the "effective radicals" generated by either KPS or AIBN. Once microemulsion droplets are being initiated by either KPS- or AIBN-derived radicals, the polymer particles grow by recruiting monomer and surfactant from uninitiated swollen droplets. The only difference is that KPS is more efficient in producing "effective radicals" than that of AIBN at an equimolar concentration of the initiators. In emulsion polymerization of styrene at 60 °C, it has been found [29] that only 3 to 5% of the radicals produced by AIBN are effective for particle nucleation.

The different dependencies of some latex features (Table 3) on concentrations of KPS and AIBN are due to different efficiencies of the initiators in producing "effective radicals" for polymerization. It shows that N_d, N_p and R_{pi} exhibit stronger dependencies on the concentration of KPS than that of AIBN.

Although KPS is more efficient than AIBN in producing "effective radicals" for polymerization, the overall activation energy of polymerization for KPS-system is much higher (95 kJ/mol) than that of AIBN (48 kJ/mol). Since the decomposition energies for both initiators are about the same (130 kJ/mol), the significant difference in activation energy of polymerization may be due to the electrostatic interactions between anionic-oligomeric free radicals of $SO_4^{\bar{\cdot}}$ and positively charged surfactant ions at the interfaces of microemulsion droplets. This would result in a higher energy barrier at the interfaces for anionic-oligomeric radicals to enter the microemulsion droplets or latex particles, allowing propagation to ensue therein. For styrene emulsion polymerization initiated by persulfate, the critical oligomer size for entry to latex particles is reported to be dimeric [26]. On the other hand, the uncharged radicals and oligomeric radicals of AIBN would experience a lower energy barrier at the positively charged interfaces.

Conclusions

Styrene polymerization in transparent microemulsions of TTAB/water/styrene using either KPS or AIBN produces stable, bluish-translucent microlatexes. Three similar pairs of microlatexes (K24/A33, K33/A58 and K42/A86) were obtained from using different molar ratios of KPS and AIBN. The microlatexes of similar pairs show striking similarities in R_{pm}, R_h, N_d, $\bar{M}_w$, $\bar{M}_w/\bar{M}_n$ and N_p. These results suggest that the mechanism of styrene polymerization is similar in the ternary microemulsions initiated either by KPS or AIBN. The only difference is that KPS produces more "effective radicals" for polymerization than that of AIBN at an equimolar concentration of the hinitiators. However, it is due to the different efficiencies of the initiators in producing "effective radicals" for polymerization, so that N_d, N_p and R_{pi} show stronger dependencies on the concentration of KPS than that of AIBN.

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