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Microemulsion polymerization of styrene in the presence of macroinimer

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Abstract

The kinetics of o/w electrostatically and sterically-stabilized microemulsion polymerization of styrene with and without macromonomeric azoinitiator (macroinimer; MIM) have been investigated. The microemulsion polymerization stabilized by the ionic emulsifier sodium dodecyl sulfate (SDS) or the non-ionic emulsifier Tween 20 (Tw 20) was initiated by ammonium peroxodisulfate (APS)/sodium thiosulfate (STS) redox system. The rate of polymerization vs. conversion curve shows the two non-stationary rate intervals. This behavior is a result of two opposing effects, the continuous particle nucleation and the decrease of monomer concentration at the reaction loci. The addition of MIM favors the additional particle nucleation. The sterically (Tw 20)-stabilized microemulsion polymerization is much faster than that of the electrostatically (SDS)-stabilized microemulsion polymerization. This was attributed to the higher Tw 20 concentration and increased solubilization of MIM and comonomer concentration in the polymer particles. The formation of initial large polymer particles is attributed to the intensive agglomeration polymer particles with monomer droplets. The continuous decrease in the average size is mainly attributed to the additional particle nucleation.

Keywords: Macromonomeric azoinitiator; Macroinimer; Microemulsion polymerization

1. Introduction

Microemulsions are at least ternary mixtures of two immiscible liquids stabilized with a surfactant or a mixture of surface active agents. They are isotropic, transparent or translucent, and thermodynamically stable [1]. Unique properties of microemulsions such as lower viscosity, greater stability, and transparency due to uniformly dispersed smaller droplets have made them attractive media for polymerization [2,3].

A major difference between emulsions and microemulsions comes from the amount of surfactant needed to stabilize the systems. This amount is much larger for microemulsion (~10% of the total mass). This is a drawback that can considerably restrict the potential uses of microemulsion polymerization since high solid contents and low surfactant amounts are usually desirable for most applications [4].

In microemulsions, generally, the initial surface area of the micelles is larger by several orders (ca. 3) of magnitude than the total surface area of final polymer particles. The small fraction of micelles is nucleated or used for the stabilization of polymer particles. The polymer particles, thus, can only slightly compete with the monomer swollen micelles in capturing radicals. Each entry of a radical to a microemulsion monomer droplet leads to a nucleation event. However, the nucleation of monomer swollen micelles leads to the formation of colloidal unstable primary particles which agglomerate either between themselves or with other monomer swollen micelles and form colloidal stable polymer particles. The locus of initiation in the microemulsion polymerization of hydrophobic monomer (styrene, butyl acrylate, etc.) initiated by a water or oil soluble initiator is the microemulsion droplet. The initiation is a two-step process. In the first step, the initiating radicals are formed by the decomposition of initiator in the aqueous phase. In the second step, the formed oligomers radicals enter the micelles and start the growth events (the nucleation

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of monomer-swollen micelles, re-initiation, etc.) or terminate the particle growth. In the oil-soluble case, two main approaches are suggested for the production of radicals: (1) in the monomer swollen polymer particles, formed radicals desorb to the aqueous phase; and (2) in the aqueous phase, formed radicals are generated from the fraction of the oil-soluble initiator dissolved in water and initiate the growth of the polymer chains in both the aqueous phase (the formation of oligomers radicals) and the monomer-swollen micelles or polymer particles (by radical entry) [5]. The principle behind the formation of microemulsion (with a droplet diameter 10–50 nm) is penetration of co-emulsifier into the water/oil interface, thereby decreasing surface tension and increasing interface area. Coemulsifier also decreases the rigidity of interface film due to increasing the molecular disorder. Coemulsifier promotes the formation of a more curved interfacial area and this is reflected in smaller size of oil droplets [6].

When conventional surfactants are used in emulsion or dispersion polymerization, difficulties are encountered which are inherent in their use. Conventional surfactants are held on the particle surface by physical forces, thus, adsorption/desorption equilibria always exist, which may not be desirable. They can be easily desorbed when subjected to high shear or to freeze-thaw cycle. Flocculation occurs and peptization of the flocs is not always possible. Furthermore, surfactants can interfere with adhesion to a substrate and may be leached out upon contact with water. Surfactant migration affects film formation and their lateral motion during particle–particle interactions can cause destabilization of the colloidal dispersions. When films are formed from the latexes, the major part of them remains in hydrophilic domains buried inside the films. These hydrophilic domains are then responsible for accumulation of water when the films are exposed to high humidity conditions. Furthermore, conventional non-ionic surfactants are small and mobile and these surface-active molecules can migrate to the surface layer of a polymeric film. This kind of action can have a negative effect on the application properties (e.g. adhesion and water resistance of pressure-sensitive adhesives). One approach to alleviate the surfactant migration problem is to use a polymerizable surfactant, which has a carbon–carbon double bond and can be chemically incorporated into the latex particles during polymerization. An interesting alternative arises with the use of unsaturated macromonomers as reactive amphiphilic surfactants. Amphiphilic poly(ethylene oxide) (PEO) macromonomers and the PEO graft copolymers present all the typical properties of conventional non-ionic surfactants, such as micelle formation, critical micellar concentration (CMC), emulsifying activity, craft-point, interfacial tension reduction, etc. In addition ‘reactive surfactants’ contain polymerizable group, thus, they can overcome some of the difficulties encountered with conventional surfactants and can function not only surfactants, but can also incorporated into the surface layer of the latex particles by polymerization or copolymerization with low-molecular weight comonomers. In such a way, the desorption of the anchored surfactants is no longer possible. The incorporation of PEO group into the particle surface (into the polymer matrix) can be performed by several ways. If the PEO amphiphiles include an initiator group or a transfer agent group, the surfactants can be incorporated to the polymer matrix via the initiation and chain-transfer processes. In the former case, the initiating radicals formed by decomposition of initiator contained PEO unit. In the latter case, the chain-transferred radicals that contained the PEO unit can either re-initiate the polymerization or terminate growing radicals. Furthermore, the most efficient way of incorporation of PEO units into the polymer matrix is via propagation of unsaturated PEO macromonomer or copolymerization with comonomer. In these manners, the reactive surfactants are prevented from subsequent migration [7].

Polymerizable surfactants have recently gained a renewal of interest in microemulsion polymerization in the last few years [8–12]. Ito et al. have used polymerizable PEO surfactants and reported that amphiphilic PEO macromonomers can undergo a fast micellar polymerization in water [13]. Macromonomeric azoinitiators (macroinimers; MIM) which have the properties of, macrocrosslinkers, macroinitiators and macromonomers can also be used as a reactive surfactants or cosurfactants. By this connection, MIM which is based on poly(ethylene oxide) with the molecular weight of 400 g/mole have been synthesized and used as a cosurfactant in the microemulsion polymerization of styrene using ammonium peroxodisulfate/sodium thiosulfate redox pair at 25 °C. Furthermore, the effect of emulsifier type on the microemulsion polymerization of styrene at low temperature is investigated.

2. Experimental

2.1. Materials

Commercially available styrene (St) was purified by usual methods. Ammonium peroxodisulfate (APS; Fluka), sodium thiosulfate (STS; Fluka) and polyethylene glycol (PEG; Fluka) were used as supplied. The emulsifiers used were the reagent-grade sodium dodecyl sulfate (SDS) provided by Fluka and Tween 20 (non-ionic emulsifier, polyoxyethylene sorbitan monolaurate, provided by Serva in the form of a 97% aqueous solution). In all experiments doubly distilled water was used as a continuous polymerization medium.

2.2. Synthesis of macroinimer

A typical macroinimer (MIM) can be synthesized by the reaction of 4,4′-dicyano-4,4′-azovaleryl chloride, polyethylene glycol (PEG) and 4-vinylbenzyl chloride as described in Ref. [14].

2.3. Polymerization procedure

Batch microemulsion polymerization of St was carried out at 25 °C with the recipe comprising 7.5 g St, 15 g SDS (or Tween 20), 75 g water, 0.2372 g STS and 0.3424 g APS. The amount of MIM was taken as 2 and 10% of monomer (St), that is, 0.15 and 0.75 g.

2.4. Characterization

A 200 MHz Bruker-AC 200L NMR and a Nicolet 510 P FT-IR spectrometer were used for recording the spectra of MIM. GPC chromotogram was taken on a Shimadzu GPC instrument including a CR-4A chromotopac computer and printer, a column furnace, an RID-6A dedector and an LC-9A liquid pump. Distilled THF was used as eluent at a flow rate of 0.75 ml/min, and slope was 300 μV/min. Polystyrene standards with M_w of 200,000, 90,000, 50,000 and 2000 of low dispersity (Polyscience) were used as reference samples.

The molecular weight, M_n, of the MIM determined by GPC as 1.5×10^3 g/mole which is in good agreement with the theoretical molecular weight, 1.3×10^3 g/mole.

IR spectra of MIM: 1100 (CH_2–etheric bonds of PEG), 1620 (vinyl and benzyl groups), 1750 (carbonyl of ester group), 2250 cm^{-1} (bond of C≡N).

^{1}H NMR spectra of MIM: $\delta = 3.6$ (CH_2CH_2O groups in PEG), 4.6 (s, CH_2 group in vinylbenzyl group), 5.2 and 5.8 (m, CH_2=CH– group in vinylbenzyl group), 6.8 (CH_2=CH– group in vinylbenzyl group), 7.2 (s) phenyl group in vinylbenzyl group.

Vinyl content of the MIM was determined by the bromination procedure [15]. Vinyl content of MIM per unit was 1.95.

The monomer conversion was determined gravimetrically with ethanol as precipitant for polystyrene (PSt). The particle sizes of the PSt particles were determined by light scattering.

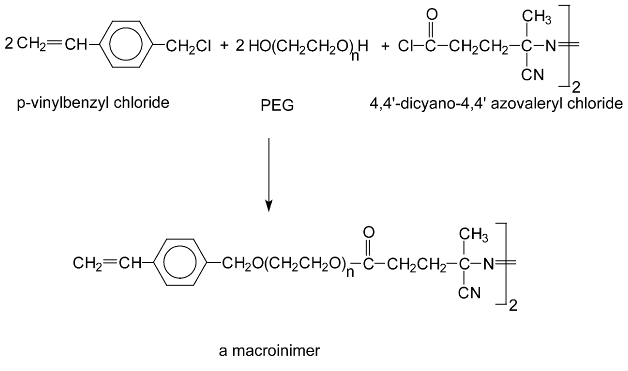
3. Results and discussion

3.1. Macroinimer synthesis

Macromonomeric azoinitiator (macroinimer; MIM) (Scheme 1) was synthesized and characterized then used in the free radical polymerization of St as a cosurfactant.

3.2. Rate of polymerization

The electrostatically (SDS)-stabilized microemulsion polymerization of styrene initiated by ammonium peroxodisulfate (APS)/sodium thiosulfate (STS) redox pair was carried out at room temperature. The variation of monomer conversion in the SDS-stabilized microemulsion polymerization of styrene with time and concentration of MIM is summarized in Fig. 1. The amount of MIM was 2 and 10 wt% of monomer, respectively. The shape of conversion type somewhat deviates from the S-shape typical for the emulsion polymerization but favors more the microemulsion polymerization. The final conversion (at 5 h) was observed to slightly decreased with the MIM concentration: 89%/without MIM, 86%/10 wt% MIM, 82%/2 wt% MIM. The limiting conversion (very slow polymerization at high conversion) can be attributed to the partial consumption of both initiator and monomer and the formation of crosslinked polymer network. The mixed MIM/SDS micelles and crosslinked polymer particles accumulate can act as a radical scavenger [16] especially at high conversion.



Scheme 1.

The shape of conversion curves of the sterically (Tw 20)-stabilized microemulsion polymerization of styrene (Fig. 2), however, strongly differs from that of the SDS-stabilized microemulsion (Fig. 1). The very fast polymerization in the former system led to final conversion during a few minutes. This was attributed to the higher micellar Tw 20 concentration and increased solubilization of MIM (comonomer concentration in the polymer particles). The final

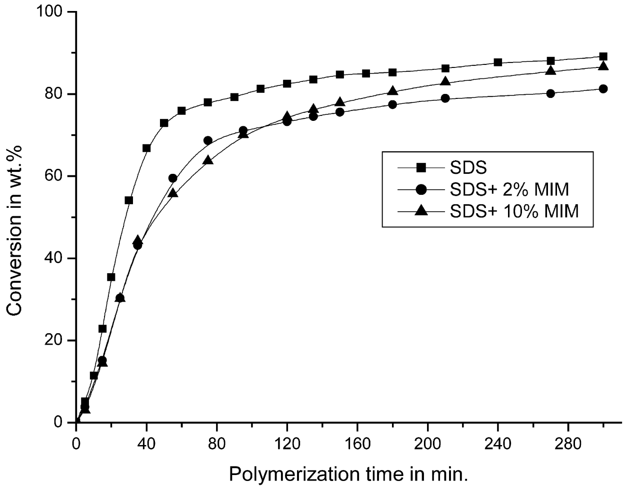


Fig. 1. Variation of monomer conversion in the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in SDS media) with the reaction time. Recipe: 7.5 g St, 15 g SDS, 75 g water, 0.2372 g STS and 0.3424 g APS. The amount of MIM was taken as 2 and 10% of monomer (St), that is, 0.15 and 0.75 g.

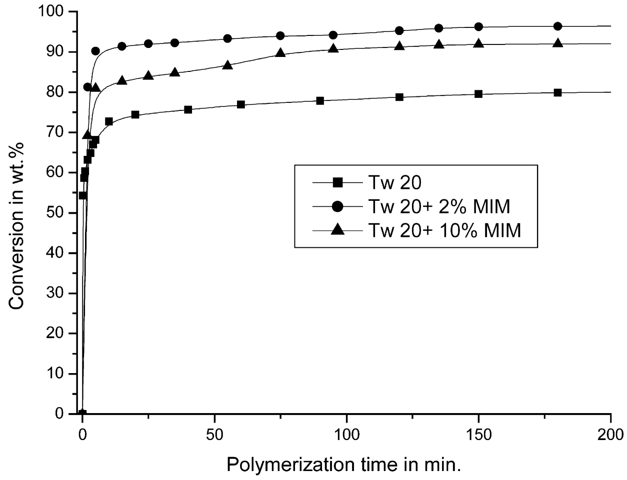


Fig. 2. Variation of monomer conversion in the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in Tween 20 media) with the reaction time. The recipe comprising 7.5 g St, 15 g Tween 20, 75 g water, 0.2372 g STS and 0.3424 g APS. The amount of MIM was taken as 2 and 10% of monomer (St), that is, 0.15 and 0.75 g.

conversion of the Tw 20-stabilized microemulsion (at 5 h) was observed to increase with the MIM concentration: 80%/without MIM, 92%/2 wt% MIM, and 96%/10 wt% MIM. In these runs, the addition of MIM favors the growth events.

Variations of the rate of polymerization (R_p) with emulsifier type, conversion, time and MIM concentration are shown in Figs. 3–6. The three rate intervals (with a distinct Interval 2) typical for the emulsion polymerization do not appear. On the contrary, the profiles of non-stationary rate intervals, typical for the microemulsion polymerization, appear [17]. First the rate of polymerization (R_p) abruptly increases to the maximum ($R_{p,max}$) and then strongly decreases with conversion or time. In the SDS-stabilized systems, the $R_{p,max}$ is located at ca. 30–35% conversion range. The addition of MIM decreases the rate of polymerization and the decrease in R_p is nearly independent of MIM concentration. The two distinct two-rate intervals and the appearance of maximal polymerization rate favor the microemulsion polymerization mode. The two non-stationary rate intervals are generally discussed in terms of two opposite effects; (1) the continuous increase of particle number and (2) decrease of monomer concentration at the reaction loci with conversion [16,18]. The presence of a large number of unnucleated microdroples or monomer-swollen micelles initiates the continual particle nucleation up to the high conversion.

Figs. 4 and 6 (the dependence of R_p vs. conversion or time) show that the Tw 20-stabilized microemulsion is by one order, at least, in magnitude faster than the SDS-

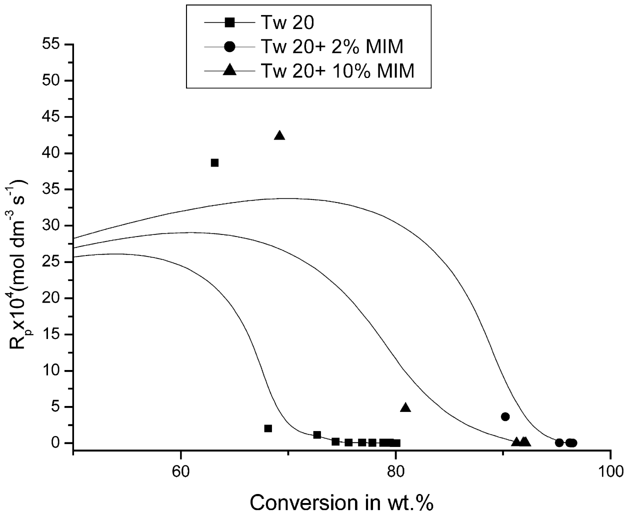


Fig. 4. Variation of the polymerization rate the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in Tween 20 media) with monomer conversion. Other conditions see in the legend to Fig. 2.

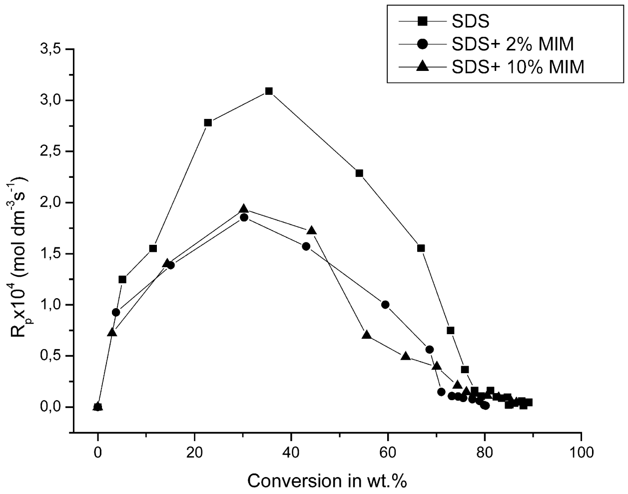


Fig. 3. Variation of the polymerization rate the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in SDS media) with the monomer conversion. Other conditions see in the legend to Fig. 1.

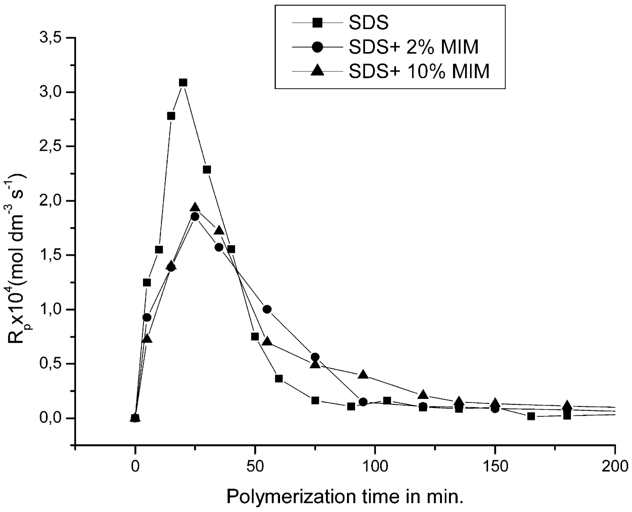


Fig. 5. Variation of the polymerization rate the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in SDS media) with the polymerization time. Other conditions see in the legend to Fig. 1.

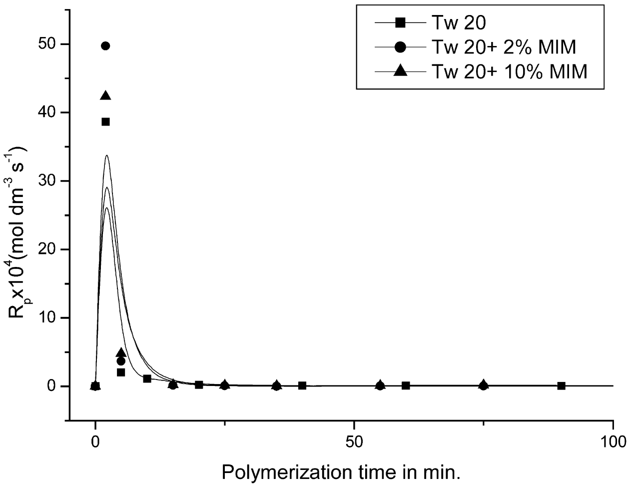


Fig. 6. Variation of the polymerization rate the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in Tween 20 media) with the polymerization time. Other conditions see in the legend to Fig. 2.

stabilized microemulsion (Figs. 3 and 5). This can be attributed to the higher micellar Tw 20 concentration (see Section 3.3) and the increased solubilization of MIM in the Tw 20-stabilized systems, comonomer concentration in particles, and concentration of radicals derived from MIM in the polymer particles (formed through the interaction of entering radicals with MIM in the interfacial layer). The peroxide units (stored or formed during polymerization) in Tw 20 system can also increase the rate of polymerization in the Tw 20-stabilized systems [19]. Furthermore, the maximal rate of Tw 20-stabilized polymerization and conversion ca. 50% are reached within ca. 2 min. On the contrary, the maximal rate of SDS-stabilized polymerization is reached within 20–25 min.

3.3. Colloidal parameters

Figs. 7 and 8 show that the large monomer/polymer particles stabilized by SDS alone and by the mixture of SDS and MIM appear after the start of polymerization. The abrupt growth of polymer particles can be attributed to the flocculation of unstable particles between themselves or with microdroplets. In the former case (the agglomeration of unstable polymer particles) the monomer polymer particles with large fraction of polymer appear and the particle size increase with conversion. In the latter case the highly monomer-swollen polymer particles (particles with a low fraction of polymer) can be formed. The continuous decrease of particle size up to ca. 50% conversion should favor more the latter case. The shrinking of large (highly monomer-swollen) polymer particles with increasing conversion can decreases the particle size. The light-scattering measurements did not detect the large polymer particles at medium or high conversion. This supports the idea that the initial large particles were formed by the agglomeration of unstable polymer particles with monomer droplets. The

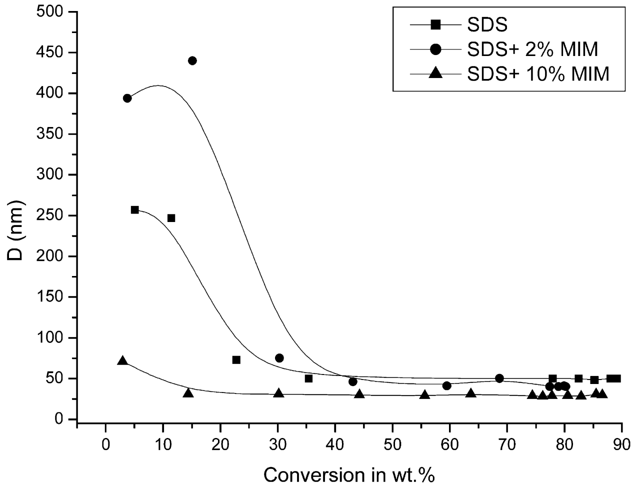


Fig. 7. Variation of the particle size (D/nm) in the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in SDS media) with conversion. Other conditions see in the legend to Fig. 1.

formed highly-monomer swollen polymer particles serve as a monomer reservoir. This can be one of reasons why the large particles disappear already at medium conversion. Furthermore, the additional particle nucleation decreases the average particle size. The particle size did not change ca. up to 15% conversion in the microemulsion polymerization of styrene stabilized by SDS/1-pentanol carried out at 70 °C [16]. The slight formation of large particles or negligible agglomeration of primary particles with microdroplets can be attributed to the presence of coemulsifier (pentanol) which increases the stability of the reaction system. Furthermore, the St/SDS microemulsion behaviors differently at 25 and 70 °C. For example, the degree of micelle ionization increases while the agglomeration number of SDS decrease with increasing temperature [20]. The

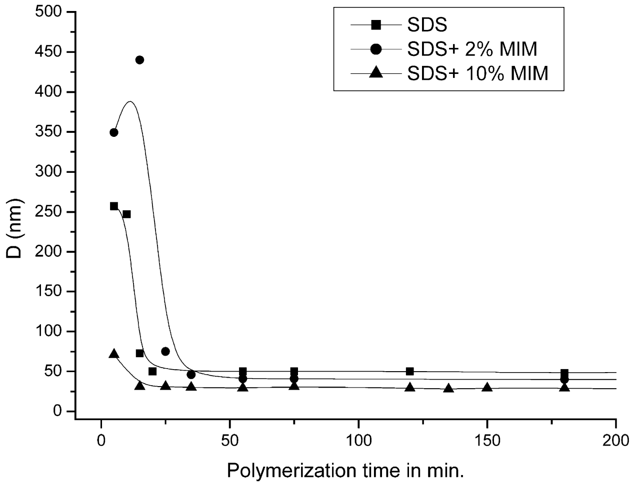


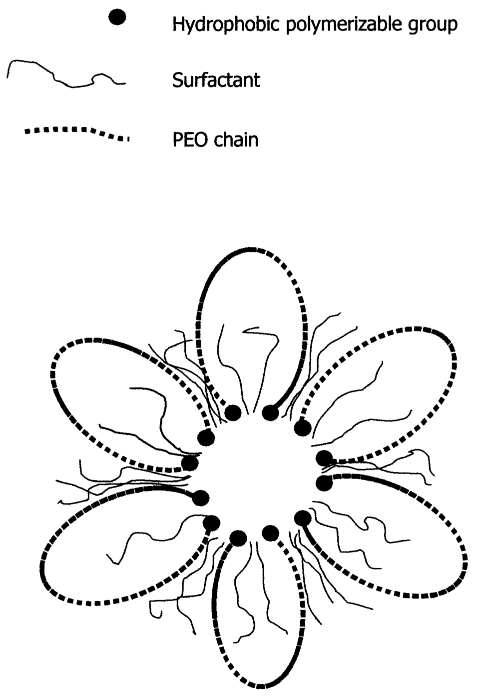
Fig. 8. Variation of the particle size (D/nm) in the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in SDS media) with the reaction time. Other conditions see in the legend to Fig. 1.

stabilizing activity of SDS, thus, increases with temperature. The higher temperature the larger number of micelles.

The large initial particles are also observed in the SDS/2 wt% MIM system (Figs. 7 and 8). The larger amount of MIM (10 wt%), however, strongly depresses the size of both initial and final polymer particles. The decrease in the initial and final average particle size is proportional to the MIM concentration. This can be attributed to the coemulsifier activity of PEO-derived MIM (Schemes 1 and 2) similar to the activity of pentanol in the SDS/pentanol system. Furthermore, the increased accumulation of MIM within the interfacial layer can increase the induced formation of radicals through the interaction of entering radicals with MIM.

In the Tw 20-stabilized microemulsion there are no particle size data at low and medium conversion (below 50% conversion or the shorter reaction time than 2 min) due to a very fast polymerization which did not allow to take out samples in shorter intervals than 2 min (Figs. 9 and 10). The particle diameter vs. time or conversion dependence, however, seems to be similar to that obtained for SDS systems (the particle size decreases with increasing conversion).

According to the micellar nucleation model, the number of polymer particles (N_p) remains relatively constant except of the beginning of polymerization [21]. Figs. 11 and 12 show that the concentration of SDS-stabilized polymer particles increases with conversion and time nearly up to the end of polymerization. The observed continuous increase in N_p with conversion is a typical feature of the microemulsion polymerization. The addition of MIM increases the particle concentration and the increase in N_p is proportional to the MIM concentration. The larger the concentration of MIM, the larger the number of micelles and polymer particles as well. The particle concentration slightly decreases at very high conversion in the run with 10 wt% MIM probably due to the particle agglomeration caused by interparticle crosslinking. Generally, the larger the particle concentration the faster the polymerization. This is not the case in SDS/MIM systems (see Section 3.2) and this deviation can be attributed to the two opposing effects: (1) The hydrophilic MIM increases the homogeneous polymerization or the bimolecular termination in the aqueous phase (the polymerization rate decreases). (2) The accumulation of MIM or its graft copolymer increases the number of micelles or reaction loci (the polymerization rate increases). Furthermore, the induced formation of radicals derived from MIM



Scheme 2. Micelle structure of MIM.

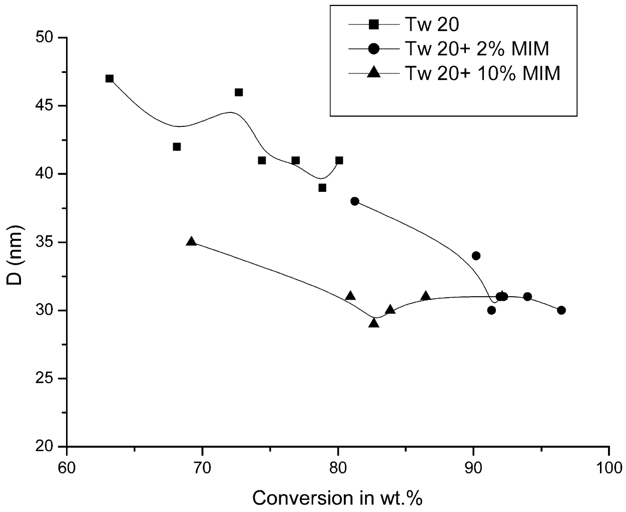


Fig. 9. Variation of the particle size (D/nm) in the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in Tween 20 media) with conversion. Other conditions see in the legend to Fig. 2.

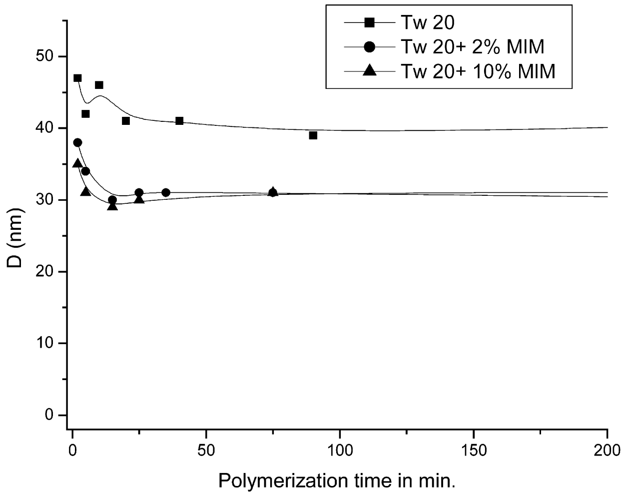


Fig. 10. Variation of the particle size (D/nm) in the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in Tween 20 media) with the reaction time. Other conditions see in the legend to Fig. 2.

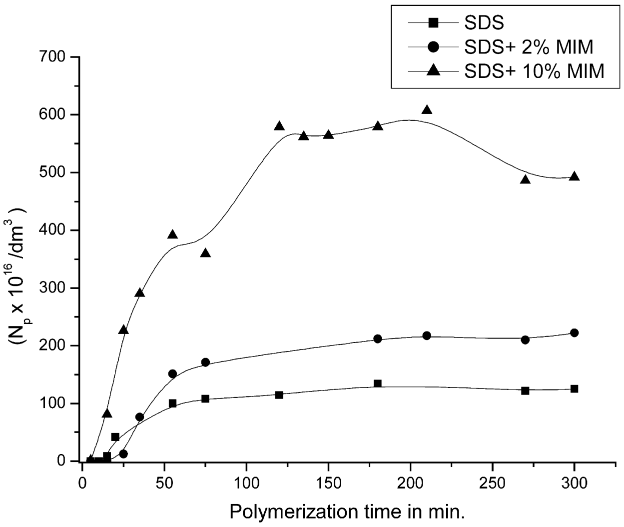


Fig. 11. Variation of the particle number (N_p) in the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in SDS media) with the reaction time. Other conditions see in the legend to Fig. 1.

in the interfacial layer is supposed to increase the both the radical and particle concentrations.

The particle concentration variations with conversion and time in the Tw 20-stabilized microemulsions without and with MIM are summarized in Figs. 13 and 14. These figures show that the number of particles increases slowly with conversion and MIM concentration and the robust nucleation occurs at conversion above 70%. This behavior strongly deviates from that discussed for the SDS-stabilized microemulsions. The robust particle nucleation at high conversion probably results from the release of non-ionic emulsifier and MIM from the oil phase leading to the increase in the micelle number [22]. In the Tw 20/MIM system, the rate of polymerization is proportional to the particle concentration. MIM or its graft copolymer favors both the particle nucleation and stabilization.

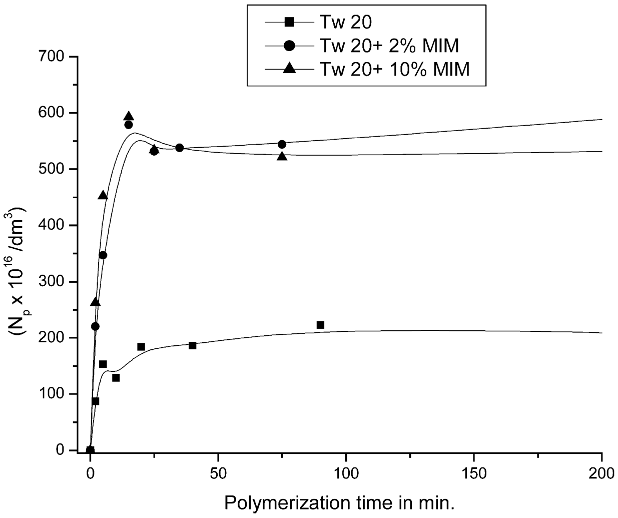


Fig. 12. Variation of the particle number (N_p) in the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in Tween 20 media) with the reaction time. Other conditions see in the legend to Fig. 2.

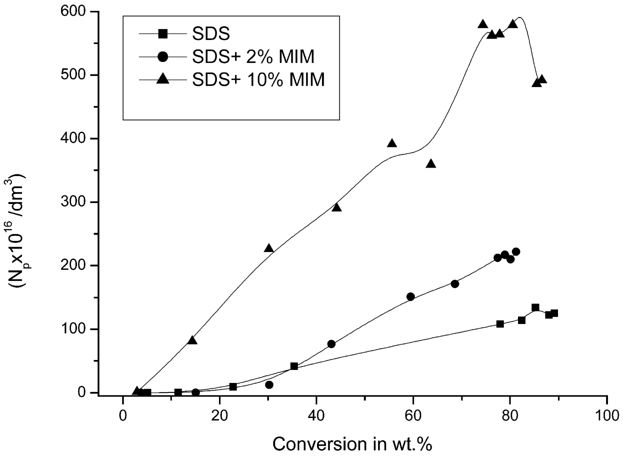


Fig. 13. Variation of the particle number (N_p) in the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in SDS media) with conversion. Other conditions see in the legend to Fig. 1.

The number of polymer particles is larger in the SDS-stabilized microemulsion than in the Tw 20-stabilized microemulsion. However, the polymerization is faster in the Tw 20-stabilized systems. This deviation can be attributed to the following parameters (see also above discussion). In the SDS runs, the SDS concentration was well above its CMC ([SDS] = ca. 86 × CMC). In the Tw 20 runs, the Tw 20 concentration ([Tw 20] = ca. 2040 × CMC) was larger than in the SDS system. The ratio $CMC_{Tw\ 20}/CMC_{SDS}$ is ca. 24. This indicates that the Tw 20 system contains a large number of micelles or emulsified micro-droplets than the SDS system. Under such a condition, initiating radicals will be absorbed more efficiently by Tw 20-stabilized microdroplets than by SDS-stabilized microdroplets. The solubilization of hydrophilic MIM is

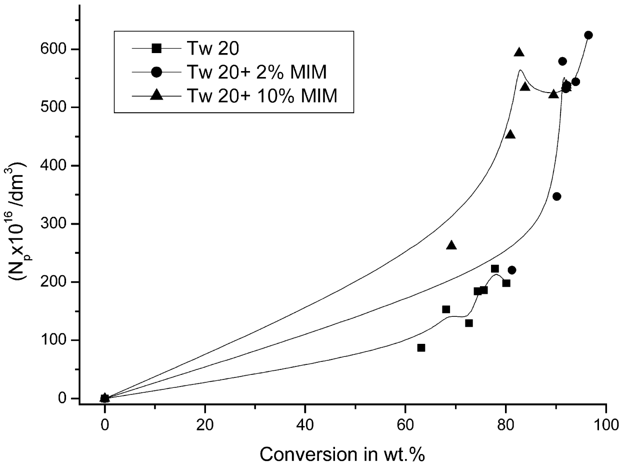


Fig. 14. Variation of the particle number (N_p) in the microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in Tween 20 media) with conversion. Other conditions see in the legend to Fig. 2.

proportional to the micellar emulsifier concentration or micelle number. Thus, Tw 20-stabilized microdroplets will solubilize larger fraction of MIM than the SDS-stabilized microdroplets. The increased amount of MIM increases the concentration of monomer at the Tw 20-reaction loci. Furthermore, the radical induced decomposition of MIM increases the concentration of radicals in the Tw 20-polymer particles. The bridging particle flocculation via the PEO (Tw 20 and MIM) chains at the surface of sterically-stabilized particles can lead to the formation of larger final particles [22].

The prepared polymer latexes (isolated polymer) were found to be insoluble in all good solvents for polystyrene (PSt) as well as in polar solvents, such as toluene, THF, etc. This indicates that MIM act as a croslinker. The prepared PSt/MIM copolymer particles were used to initiate the seed emulsion polymerization of styrene or butyl acrylate (without addition of any other initiator). In both seed emulsion polymerizations, the polymerization did not start. This was attributed to the consumption of azo groups due to radical induced decomposition [23]. In the latter case the radicals formed via decomposition of azo groups in the MIM could not escape from the cage (particle). The high viscosity and low monomer concentration at the reaction loci does not allow the escape of radical from the cage.

4. Conclusions

The microemulsion polymerization of styrene stabilized by ionic emulsifier SDS and non-ionic emulsifier Tween 20 is investigated. The polymerization was carried out at very low temperature to depress both the degree of dissociation of SDS and the oil solubility of Tween 20. Under the comparable reaction conditions the microemulsion polymerization was much faster with Tween 20 than with SDS. This was attributed to the higher Tween 20 concentration and the increased solubilization of macroinimer (MIM) in the Tw 20-stabilized systems, comonomer concentration in particles, and concentration of radicals derived mainly from MIM in the polymer particles (formed through the interaction of radicals with MIM). The rate of polymerization vs. conversion curve shows the two non-stationary rate intervals. This behavior is a result of the continuous particle nucleation and the decrease of monomer concentration at the reaction loci during the polymerization. The addition of MIM slightly decreases the polymerization rate in the SDS-stabilized systems but increases the rate in the Tw 20-stabilized systems. Furthermore, the addition of MIM favors the additional particle nucleation and the increase in the particle concentration. The SDS-stabilized microemulsion polymerization of styrene is accompanied with the formation of large initial polymer particles whose size continuously decreases with increasing conversion and reaches a plateau at ca. 30% conversion. The formation of large polymer particles was attributed to the agglomeration of polymer particles with monomer droplets. The continuous decrease in the average particle size is attributed to the shrinking of highly monomer-swollen polymer particles and the additional particle nucleation. The continuous particle nucleation proceeds in the electrostatically-stabilized microemulsion. In the sterically-stabilized microemulsion the low particle nucleation appears at low and medium conversion but the robust one proceeds at high conversion.

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