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On the fine emulsion polymerization of styrene with non-ionic emulsifier

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Summary

The fine emulsion polymerizations of styrene initiated by a redox system ammonium peroxodisulfate/sodium thiosulfite stabilized by a non-ionic emulsifier were kinetically investigated. The dependence of the rate of polymerization on conversion or the emulsifier concentration was described by a curve with maximum at medium conversion. The maximum rate of polymerization is proportional to the - 0.45th and 1.5th power of initiator and emulsifier concentration, the number of particles to the 0.32nd and 1.3rd power of initiator and emulsifier concentration and the molecular weight to the - 0.62th and -0.97th power of initiator and emulsifier concentration, respectively. The results show a strong decrease in turbidity at around 20% conversion when emulsion turns into translucent latex. Deviation from the micellar nucleation model was attributed to the solubility of emulsifier in monomer, high level of nonmicellar aggregates, thick interfacial layer and transfer emulsion to microemulsion. The strong decrease of molecular weight with increasing emulsifier concentration is attributed to chain transfer events promoted by the high level of emulsifier at the reaction loci.

Introduction

In the conventional emulsion polymerization, monomer is emulsified in monomer droplets and micelles, and dissolved in the aqueous phase as well. Monomer droplets of diameter 1 - 10 µm are formed. Furthermore, emulsifier is located in the monomer swollen micelles, adsorbed at the droplet surface and dissolved in the aqueous phase. Under such conditions, the presence of large number of monomer-swollen micelles favors the micellar nucleation mechanism. When an oil-in-water emulsion is created by a larger amount of emulsifier and coemulsifier, a very fine emulsion might be prepared. Here, the tiny monomer droplets can take part in the particle nucleation mechanism.

Although the emulsion polymerization has been studied extensively, many mechanistic aspects of emulsion polymerization, especially in the presence of nonionic emulsifier still remains unclear. Furthermore, there are little information on the kinetics of the sterically-

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stabilized fine emulsion (1-3). It was concluded that the steric stabilization effect provided by pure emulsifier is not enough to prohibit the interactive particles from flocculating with one another (4). These systems were reported to deviate from the micellar model (5). For example, the parameter x or y (from the dependence of N_p vs. $[\text{emulsifier}]^x$ or N_p vs. $[\text{initiator}]^y$) was found to be 1.8 or - 0.5 (6).

The relatively large latex particles with a very thick shell of nonionic emulsifier molecules make the emulsion polymerization very complicated, in particularly, the capture of radicals by such particles. Besides, the relatively high hydrophobicity of nonionic emulsifier may induce burying of emulsifier species in the interior of monomer droplets and particles due to which decreases the micellar fraction of emulsifier. The use of nonionic emulsifier opens some interesting questions with respect to formation and stabilization of latex particles. This results from continuous release of emulsifier from nonmicellar aggregates. Furthermore, a high monomer solubility of nonionic emulsifier, an appearance of nonmicellar aggregates at a high level of emulsifier and a thick shell of nonionic emulsifier making a barrier for entering radicals strongly influence the polymerization kinetics (7). The presence of hydrophobic compound (nonionic emulsifier) in the monomer droplets is supposed to depress "diffusional degradation" of monomer droplets (8). These are the main subjects for the present study.

Experimental part

Materials

Commercially available styrene (St) was purified by the usual methods (9, 10). Extra pure ammonium peroxodisulfate (APS, Fluka) and sodium thiosulfite (STS, Fluka) were used as supplied. The emulsifier used was the reagent-grade Tween 20 (non-ionic emulsifier, polyoxyethylene (20 oxyethylene units) sorbitan monolaurate, provided by Serva in the form of a 97% aqueous solution, Tw). Doubly distilled water was used as a polymerization medium.

Polymerization procedure

The batch polymerizations were carried out at 20 °C. Oxygen was removed from the reaction mixture by first applying vacuum then charging the emulsion into dilatometer and finally purging with nitrogen. In all runs the recipe comprises 15 g water and 1.5 g St. Amounts of Tw, APS and STS varied as given later. In all runs the mole ratio [APS]/[STS] = 1 was used.

Polymer and latex characterization

The polymerization technique and the measurements of particle size (D_n) and number (N_p) (light scattering, LS) were the same as described earlier (10-12). Conversion of monomer was determined by dilatometric measurements (checked by gravimetry). Limiting viscosity numbers [η] were determined with Ubbelohde viscometer in toluene at 25 °C and used to estimate the viscosity - average molecular weights (13,14).

Results and Discussion

Polymerization rate

The dependence of the rate of polymerization (R_p) versus conversion (X) in the fine emulsion polymerization of styrene stabilized by Tw and initiated by a APS/STS initiator system is described by a curve with maximum at ca. 10 - 20% conversion (Fig. 1). R_p first increases rapidly with conversion as the particle nuclei (reaction loci) continue to form, presumably via the micellar nucleation mechanism (5). In all runs, [Tw] is much above its CMC ([Tw] = ca. 133-266 x CMC, CMC_{Tw} = 3 x 10^{-4} $mol.dm^{-3}$, [Tw] was ranged from 0.04 $mol.dm^3$ to 0.08 $mol.dm^3$). Under such conditions, the micellar nucleation and formation of stable latex particles should be operative. In the classical emulsion polymerization (micellar model (5)), R_p remains constant during the Smith-Ewart Interval II (20% < X < 60%). This is followed by significant reduction in R_p toward the end of polymerization as a result of the continuous decrease of monomer concentration in the latex particles. In the current polymerization, however, Interval II does not appear. Furthermore, R_p strongly decreases after 10 or 20% conversion. These data indicates that the emulsion polymerization of styrene in the presence of a large amount of nonionic emulsifier (Tw) strongly deviates from the classical emulsion polymerization. The same dependence was obtained in the microemulsion polymerizations of styrene ($R_{p,max}$ at ca. 10 - 20%) in the presence of cationic emulsifier (DTAB - dodecyl trimetylammonium bromide)(15) or anionic emulsifier SDS ($R_{p,max}$ located at ca. 20 - 25% conversion) (16). Owing to the high concentration of monomer swollen micelles (or microdroplets) and polymer particles, it is expected that the monomer core of microdroplets disappear at low conversion (16). The formed polymer particles grow via the supply of monomer from the microdroplet cores which is already suppressed at medium conversion.

The polymerization behavior is interpreted in terms of the long nucleation period and the decrease of the monomer concentration in the latex particles with increasing conversion. The very high concentration of monomer-swollen micelles (the weight ratio Tw/St varied from 0.5 to 1.0) prolongs the nucleation period. The initial increase in the particle concentration would account for the increasing of R_p, and the decrease of monomer concentration at the reaction loci for the subsequent decrease in R_p. The larger the number of the polymer particles, the lower is the average monomer concentration in monomer/polymer particles. Besides, the relatively high hydrophobicity of nonionic emulsifier induces burying of emulsifier species in the interior of droplets and particles due to which decreases the micellar fraction of the emulsifier. Indeed, SEC chromatograms for polymer indicated the presence of small molecules (emulsifier). Furthermore, styrene is very good solvent for Tw. The partitioning of emulsifier among monomer-swollen micelles, nonmicellar aggregates, and monomer droplets significantly varies the amount of free emulsifier for particle nucleation (stabilization).

A maximum rate ($R_{p,max}$) of the microemulsion polymerization of styrene with SDS and DTAB appeared at ca. 20 - 25% (16) and 10 -20% (15), respectively. In the present runs, $R_{p,max}$ appears at ca 10 - 20% conversion (Table 1). These data indicate that the continuous nucleation (microemulsion polymerization mechanism) is operative in the current runs. However, the present St/Tw/water systems were either semitransparent or milky. It is interesting to note that turbidity of the St/Tw/water systems decreases with increasing conversion. The milky systems were transformed by polymerization to semitransparent ones reaching ca. 10% conversion. The emulsions turn into transparent/translucent and stable latexes, mimicking the properties of microemulsion latexes, on polymerization. The reverse is true for St/SDS/water or St/DTAC/water microemulsions where the transparent monomeric microemulsion became semitransparent or milky during polymerization.

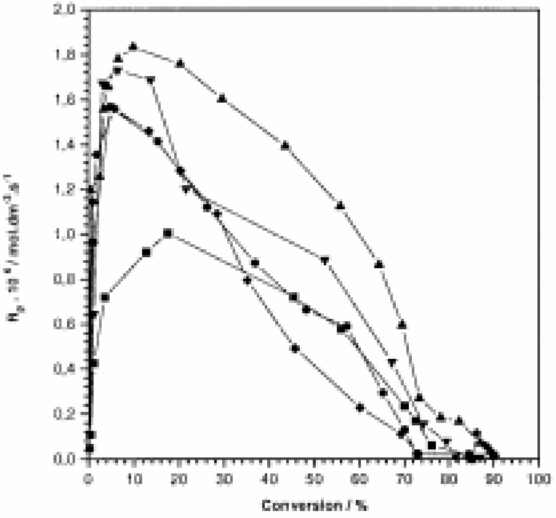

Fig. 1. Variation of the rate of polymerization in the emulsion polymerization of styrene with Tw concentration and conversion. The receipe comprises 15 g of water, 1.5 g of styrene, initiator at concentration of 5.10^{-3} mol.dm^{-3}, and Tw in amount of: (ν) 0.75 g; (λ) 0.94 g; (σ) 1.125 g; (τ) 1.32 g; (υ) 1.5 g.

Nonionic emulsifiers are known to form large aggregates even at concentrations slightly above their CMC (17). The formation of nonmicellar aggregates and liquid crystalline phases are found at higher nonionic emulsifier concentration (18). Furthermore, the phase separation occurs at high level of emulsifier in the system, i.e., one water-rich and one emulsifier - rich phase. Nonmicellar aggregates which do not take part in stabilization of microdroplets (or solubilization) are supposed to increase turbidity. As temperature is raised, the oil solubility increases and a critical point (cloud point) may be reached at which large aggregates of nonionic amphiphiles separate out of the aqueous solution into a distinct (nonmicellar) phase. For example, the cloud point for ethoxylated nonylphenols with an average of 30 - 50 oxyethylene units per molecule was reported to be 65-75 °C [19]. The oxyethylene group of emulsifier is assumed to form hydrogen bonds with water. As temperature is raised, these relatively weak bonds begin to dissociate and water molecules are gradually driven out of the (shell) region occupied by PEO chains. Furthermore, the length and excluded volume of PEO per amphiphile in organized aggregates decrease with increasing temperature. As temperature increases, the fraction of amphiphile being in contact with water decreases, PEO chains are close-packed at the droplet surface, and the amphiphile molecule prefers to remain in the inner part of the oil-water interface. In order to suppress the above mentioned events the polymerizations were carried out at a very low temperature.

The steric stabilization provided by Tw alone is not efficient to prevent small latex particles from flocculation during polymerization as a result of coagulative nucleation. As a consequence, the resultant latex particles stabilized only by nonionic emulsifier are quite large (500 nm - 1000 nm). On the other hand, the electrosterically stabilized latex particles are stable and small due to the synergistic stabilization effect provided by anionic and nonionic emulsifiers (20,21). The final latex particle size is presumably related to the fraction of the particle surface covered by Tw or the ratio of the thickness of the Tw adsorption layer to that of the electric double layer of the latex particles. The electric double layer around the particles originates from the sulphate group ($-SO4^-$) on the particle surface derived from the peroxodisulfate initiator.

The absence of Interval II or the nonstationary state polymerization in the present emulsion polymerization results from following contributions: 1) continuous nucleation of particles, 2) decrease of monomer concentration at reaction loci with increasing conversion, 3) accumulation of surface active charged oligomers (with end SO_4^- group) with conversion, 4) conversion of nonmicellar aggregates into free emulsifier or micelles and 5) migration of dissolved emulsifier in monomer to the aqueous phase or the particle surface.

Furthermore, the presence of a hydrophobic compound (nonionic emulsifier) in the monomer droplets is supposed to depress diffusional degradation of monomer droplets and enhance the droplet stability [7]. Indeed, addition of PEO type of nonionic emulsifier to styrene/alkyl methacrylate/SDS reaction system strongly decreased the rate of Ostwald ripening (22). Accumulation of nonionic emulsifier in the monomer droplets increases with increasing conversion. This increases stability of monomer droplets (depressed monomer droplet degradation) and their participation in the particle nucleation mechanism. The depressed diffusion of monomer decreases the monomer concentration at the reaction loci and so the rate of polymerization.

The rate of polymerization is found to decrease with increasing APS concentration (Table 1):

$$R_{p,max} \propto [APS]^{-0.45}$$

This behavior strongly deviates from the micellar model (5) and microemulsion polymerization of styrene (15,16) where the rate of polymerization increases with increasing initiator concentration (the exponent x on [initiator] varies from 0.3 to 0.5). The behavior cannot be attributed to the primary radical termination or the water-phase termination due to the low initiator concentrations and the large number of monomer-swollen micelles or microdroplets. The microdroplets effectively absorb the oligomer radicals before they might terminate in the aqueous phase. The barrier to the entering radicals formed by the thick interfacial shell or close-packing surface structure (via bridging of polyoxyethylene chains (23)) on the particle might be a reason for such a behavior. Table 1 shows that with increasing [APS] increases the particle number and so the fraction of the thick interfacial layer. The latter is connected with the radical entry efficiency.

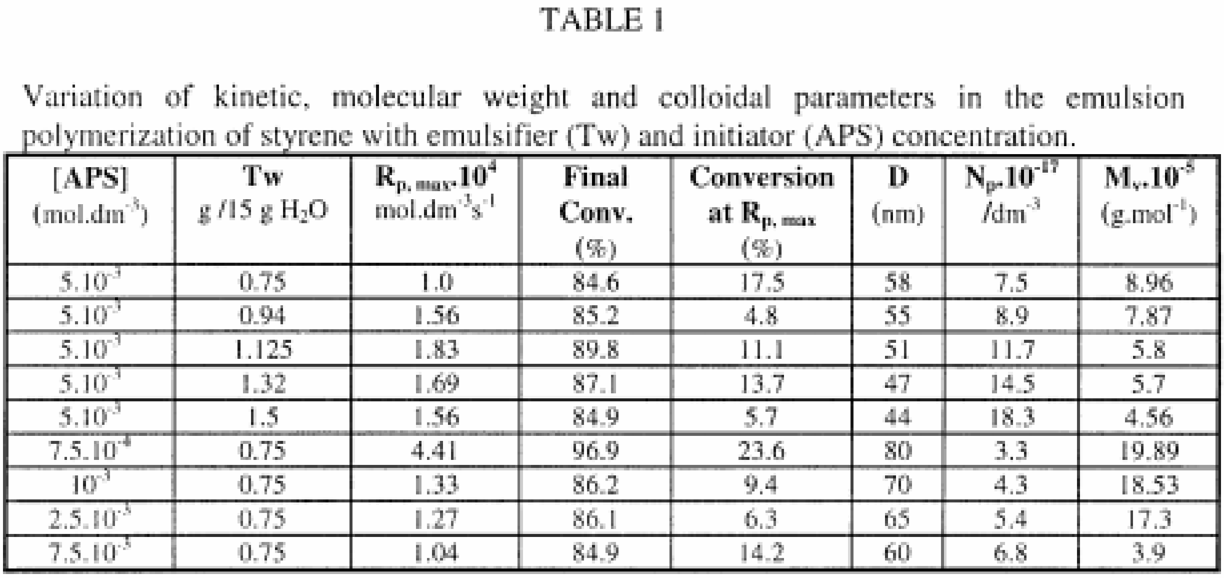

TABLE 1

Variation of kinetic, molecular weight and colloidal parameters in the emulsion polymerization of styrene with emulsifier (Tw) and initiator (APS) concentration.

[APS] (mol.dm^{-3})	Tw g /15 g H_2O	$R_{p,max}.10^4$ mol.dm^{-3}s^{-1}	Final Conv. (%)	Conversion at $R_{p,max}$ (%)	D (nm)	$N_p.10^{-17}$ /dm^{-3}	$M_v.10^{-5}$ (g.mol^{-1})
5.10^{-3}	0.75	1.0	84.6	17.5	58	7.5	8.96
5.10^{-3}	0.94	1.56	85.2	4.8	55	8.9	7.87
5.10^{-3}	1.125	1.83	89.8	11.1	51	11.7	5.8
5.10^{-3}	1.32	1.69	87.1	13.7	47	14.5	5.7
5.10^{-3}	1.5	1.56	84.9	5.7	44	18.3	4.56
$7.5.10^{-4}$	0.75	4.41	96.9	23.6	80	3.3	19.89
10^{-3}	0.75	1.33	86.2	9.4	70	4.3	18.53
$2.5.10^{-3}$	0.75	1.27	86.1	6.3	65	5.4	17.3
$7.5.10^{-3}$	0.75	1.04	84.9	14.2	60	6.8	3.9

The radical entry or exit in the sterically stabilized latex particles is very complex. For example, the exit rate coefficient in a polystyrene latex stabilized by poly(oxyethylene)-nonylphenol type emulsifier gave an exit rate coefficient an order of magnitude smaller than that for electrostatic - stabilized particles of the same size (24,25). This suggest that accumulation of entered surface active oligomeric radicals in the thick interfacial layer promotes termination events and the decrease of R_p. Thus, the longer residence time of radicals within the "hairy" layer favors deactivation events.

The dependence of the rate of polymerization on [Tw] was described by a curve with a maximum at [Tw] = 1.125 mol.dm^{-3}:

$R_{p,max} \propto [Tw]^{1.5}$ (up to [Tw] = 1.125 mol.dm^{-3})

This behavior can be discussed in terms of the transfer of electrosteric to steric stabilization mechanism by increasing emulsifier concentration due to which decreases the radical entry rate to the polymer particles and so the rate of polymerization. Furthermore, the transfer of emulsion to microemulsion is a function of Tw concentration and so the lower polymerization rates at higher emulsifier concentration can be attributed to the microemulsion polymerization. Besides, the accumulation of emulsifier in the monomer droplets decreases the monomer concentration at reaction loci (dilution approach) and increases the chain transfer events to emulsifier. Indeed, the strong decrease of molecular weigh was observed at a higher Tw concentration (Table 1).

Colloidal and molecular weight parameters

As expected the number of polymer particles increases with increasing emulsifier concentration:

$$N_p \propto [Tw]^{1.3}$$

The increase in particle concentration, however, is much more pronounced than that proposed by the micellar model (5). Deviation can be attributed to a monomer solubility of n Tw (26) due to which the amount of emulsifier available for the nucleation and stabilization of polymer particles is decreased and the decrease is more pronounced for the runs with a low emulsifier level.

The number of polymer particles increases with increasing initiator concentration:

$$N_p \propto [APS]^{-0.32}$$

The reaction order is smaller than 0.6 proposed by the micellar model. This deviation results from decreased radical entry efficiency by increasing the fraction of thick interfacial layer (with increasing [APS] decreases the particle size and increases the particle number).

The viscosity-average molecular weight decreases with increasing concentration of initiator and emulsifier:

$$M_v \propto [APS]^{-0.62} \text{ and } M_v \propto [Tw]^{-0.97}$$

These data indicates that the molecular weight decreases with increasing the particle number (or decreasing the particle size). In both cases, the decrease of monomer concentration at the reaction loci decreases the polymer growth. The decreases is more pronounced in the Tw runs which is typical for the microemulsion polymerization (27) The strong decrease of M_v with increasing [Tw] may also result from chain transfer events. Indeed, the PEO type of emulsifier is known to be active in the radical chain - transfer (28). The high solubility of emulsifier in the monomer phase promotes the radical chain - transfer.

Conclusion

From the foregoing discussion, it results that the dependence of the rate of polymerization on conversion was described by a curve with a maximum at a certain conversion. The maximum rate of polymerization was observed to increase much stronger with increasing emulsifier concentration than that proposed by a micellar model. Furthermore, the polymerization rate decreases with increasing initiator concentration. Deviation from the micellar nucleation model was attributed to the high monomer solubility of emulsifier, the high level of nonmicellar aggregates, the thick interfacial layer, accumulation of charged surface active oligomers at the interface and formation of the electric double layer around the particles originating from the sulphate group ($-SO_4^-$) derived from the peroxodisulfate initiator. The strong decrease of molecular weight with increasing emulsifier concentration is attributed to radical chain transfer events promoted by the high level of emulsifier at the reaction loci.

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