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Winsor I-like (micro)emulsion polymerization of styrene initiated by oil-soluble initiator

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Abstract

Batch emulsion polymerization of styrene initiated by an oil-soluble initiator and stabilized by non-ionic emulsifier (Tween 20) has been investigated. The rate of polymerization vs. conversion curve shows the two non-stationary rate intervals typical for the non-stationary-state polymerization. This behavior is a result of the continuous particle nucleation and the decrease of monomer concentration at the reaction loci with increasing conversion. The initial increase of the polymerization rate is attributed to the increase of particle number and the polymerization proceeding under the monomer-saturated condition—the Winsor I-like (micro)emulsion polymerization. The decrease of the polymerization rate is the result of the depressed transfer of monomer from the monomer reservoir to the reaction loci. Above 50 °C the monomer emulsion separates into two phases: the upper transparent monomer phase and the lower blue colored (microemulsion) phase. The polymerization mixture consists of the microdroplets (act as the reaction loci) and large degradable monomer droplets (act as the reservoir monomer and emulsifier). The continuous release of emulsifier from the monomer phase and the microdroplets induce the continuous particle nucleation up to high conversion. The initial formation of large particles results from the agglomeration of unstable growing particles and monomer droplets. The size of large (highly monomer-swollen) particles decreases with conversion and they merge with the growing particles at ca. 40–50% conversion. The coarse initial emulsion transformed during polymerization to the fine (semi-transparent) polymer emulsion as a result of the continuous particle nucleation, the shrinking of highly monomer-swollen polymer particles and the depletion of monomer droplets. The low overall activation energy of polymerization is mainly ascribed to the decreased barrier for entering radicals into the latex particles with increasing temperature. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polymerization; Emulsion; Styrene

1. Introduction

The emulsion polymerization stabilized by non-ionic emulsifier becomes interesting from both theoretical and practical point of view. Non-ionic emulsifiers of the alkyl- or aryl-poly(oxyethylene) (PEO) type are very popular as emulsion stabilizers, and for oil-in-water emulsions emulsifiers that are mostly water-soluble are used. They enhance the chemical and freeze–thaw stability of the latex products. The coarse polymer emulsions are formed by emulsion polymerization stabilized by non-ionic emulsifier [1,2]. The growth of particles is accelerated by the limited flocculation. The coagulative nucleation contributes to the particle growth and formation [3]. The colloidal stability of polymer latex stabilized by the PEO non-ionic emulsifier is temperature dependent. The extension of PEO chains into the aqueous phase decreases with increasing temperature. The particle flocculation is often observed below the cloud point (CP) of the emulsifier [4]. The hydrophobicity of the interfacial emulsifier film increases with temperature due to dehydration of the PEO chain of emulsifier [5]. The high temperature-sensitivity of emulsion stabilized by non-ionic emulsifier arises from the increased oil-solubility of non-ionic emulsifier and the decrease of the CMC with increasing temperature [6,7]. The conformation of PEO chains of non-ionic emulsifier at high coverage is extended, making a packing monolayer, increasing the colloidal stability of polymer particles.

The charged latex particles are stabilized via the electrostatic repulsion force between two approaching particles (the electrostatic stabilization) [8,9]. The electrostatic repulsion between particles is formed by electrical double layers that surround them when covering the particles with charged species, such as ionic emulsifiers. In the sterically stabilized particles the repulsion between particles is provided by steric repulsion between approaching particles [10,11]. The thick interfacial layer formed by non-ionic emulsifier

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can make a barrier for entering radicals and/or prolong the time interval between entries of two radicals as well as the lifetime of growing radicals. For example, the reaction order form the dependence R_p vs. [initiator] is very close to 1 for the sterically stabilized latex particles prepared by the radical polymerization of styrene and methacryloyl-terminated PEO (PEO–MA) macromonomer [12,13].

The models developed for the electrostatically stabilized latex particles [3] are only partially applicable when dealing with latexes stabilized by electrosteric or steric mechanism. Furthermore, the electrosterically stabilized latexes show smaller values of both entry (k_a) and exit (k_{des}) rate coefficients as compared to the electrostatically stabilized latex particles of the same size at pH 7 [14–16]. The decreased k_a or k_{des} in the sterically stabilized latexes is ascribed to a ‘hairy’ layer around the particles, which retards diffusion of oligomeric radicals. The entering radicals may be terminated prior to the actual entry into the latex particles occurs.

In the previous work [17], we have studied the emulsion polymerization of styrene initiated by water-soluble peroxodisulfate initiator and stabilized by non-ionic emulsifier. The rates of particle formation and polymerization strongly increased with increasing temperature. The particle nucleation proceeded up to the high conversion and the increase in the particle size was more pronounced up to ca. 40% conversion. The partial agglomeration of polymer particles and larger particles were formed at and above 70 °C. The electric double layer originated from the sulfate group ($-SO_4^-$) on the particle surface derived from peroxodisulfate took part in the particle stabilization (electrostatic). The entered negatively charged (surface active) oligomeric radicals formed the electrical double layer around the polymer particle. The experimental data (the number of polymer particles vs. the rate of initiation) agreed very well with the micellar model [18]. The major thrust of this work is to study the emulsion polymerization of styrene initiated by the oil-soluble initiator AIBN and stabilized by non-ionic emulsifier Tween 20. This excludes the formation of charged oligomeric radicals and the electrical double layer around the particles as well. The transport of radicals derived from oil-soluble initiator within the multiple phase system is expected to be less hindered than those derived from peroxodisulfate. The second item of this work is to study the connection between the phase behavior and the polymerization kinetics.

2. Experimental

2.1. Materials

Commercially available styrene (St, Fluka) was purified by distillation under reduced pressure. Extra pure 2,2′-azobisizobutyronitrile (AIBN, Fluka) was used as supplied. The emulsifiers used were the reagent-grade Tween 20 (Tw 20, non-ionic emulsifier, polyoxyethylene sorbitan monolaurate, provided by Serva in the form of a 97% aqueous solution) and sodium dodecyl sulfate (SDS, provided by Fluka). Doubly distilled water was used as a polymerization medium.

2.2. Recipe and procedures

Batch emulsion polymerization of St was carried out at different temperatures (50, 60, 70 and 80 °C) with the recipe comprising 150 g water, 15 g St, 7.5 g Tw 20, and 5 mM AIBN. The monomer conversion was determined by the dilatometric and gravimetric methods. The polymerization technique, the preparation of polymer latex for particle size (transmission electron microscopy (TEM) and light scattering) measurements and the particle number estimation were the same as described earlier [19–24]. The measurements of average hydrodynamic diameter of monomer-swollen polymer particles were performed by a dynamic light scattering method as described earlier [25]. The (relative) particle size distribution was estimated as described by Schork et al. [22,23]. The coefficient of variation and the polydispersity index were related according to the Hunter’s approach [26].

2.3. Cloud-point measurements

The aqueous solutions of Tw 20 (100 g water and 9.9 g Tw 20) and the mixture of Tw 20 (9.9 g), St (1.3 g) and water (100 g) were prepared in flasks, stirred for 1 h at 25 °C. The temperature of the circulator was increased 0.2 °C each time until equilibrium was achieved. Each time, the turbidity of the emulsifier solution was checked. Once the turbidity of solution was slightly increased, the temperature was determined to be the CP of the emulsifier solution.

2.4. Ostwald ripening measurements

The miniemulsion (fine emulsion) was prepared by dissolving the mixture of emulsifier (Tw 20 or SDS) ($0.01\ \mathrm{mol\ dm^{-3}}$) and styrene (40 g) in water (100 g) and mixed with a mechanical agitator at 400 rpm for 10 min. The resultant coarse emulsion was homogenized by the homogenizer Ultra Turrax (IKA Works, USA) for 5 min. The average monomer droplet size of diluted miniemulsion as a function of aging time was determined by the dynamic light scattering method. The colloidal stability of the (non-diluted) miniemulsion product was monitored by placing about 100 ml sample in a glass vial at 25 °C. The position of the creaming line from the bottom of the sample and the time necessary for a visible monomer phase on the top of sample to appear were then recorded.

2.5. Partition coefficient measurements

The aqueous solution of water (100 g), Tw 20 (7.5 g) and St (15 g) was prepared in a flask, slightly stirred for 1–2 min and then stored at 25 °C for 48 h (without mixing).

Approximate 20 g sample was pipetted from the bottom aqueous phase and then dried in air and later in an oven. The dried amount of emulsifier was used to calculate the partition coefficient.

3. Results and discussion

3.1. Rate of polymerization

The conversion-time data for the emulsion polymerization of styrene initiated by AIBN in the presence of Tween 20 (Tw 20) are shown in Fig. 1. Temperature was varied from 50 to 80 °C. The shape of conversion curves is typical for the emulsion polymerization carried out under the non-stationary state conditions (microemulsion, miniemulsion, or precipitated polymerization) [22,23,27,28]. The conversion time curves are concave downward without any linear portion. The limiting conversion increased from 80 to ca. 95% with increasing temperature from 50 to 80 °C. Generally, the limiting conversion is discussed in terms of the consumption of initiator and/or immobilization of monomer within the (non)micellar aggregates. The slight consumption of initiator at 50 °C, however, excludes the initiator consumption. The more reasonable explanation for the limiting conversion is the immobilization of monomer as well initiator in the (non)micellar aggregates.

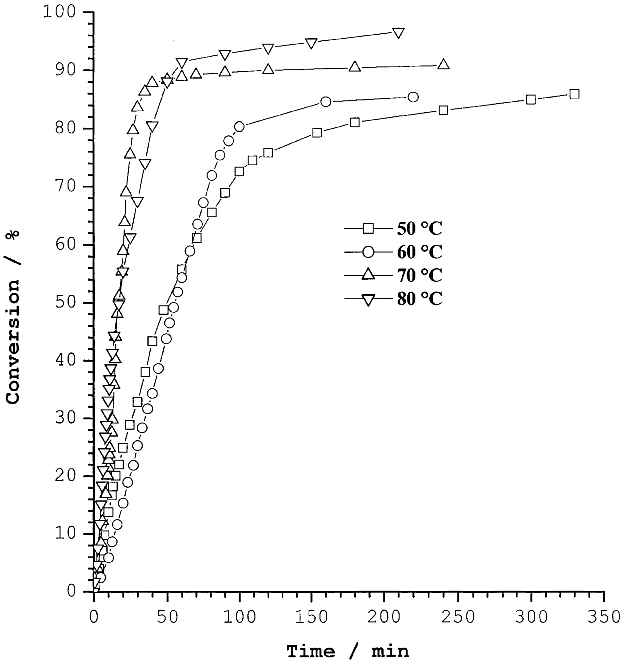


Fig. 1. Variation of monomer conversion in the emulsion polymerization of styrene initiated by AIBN with the reaction time and temperature. Recipe: 150 g water, 15 g styrene, 7.5 g Tween 20, 0.023 g AIBN, 0.025 g $NaHCO_3$.

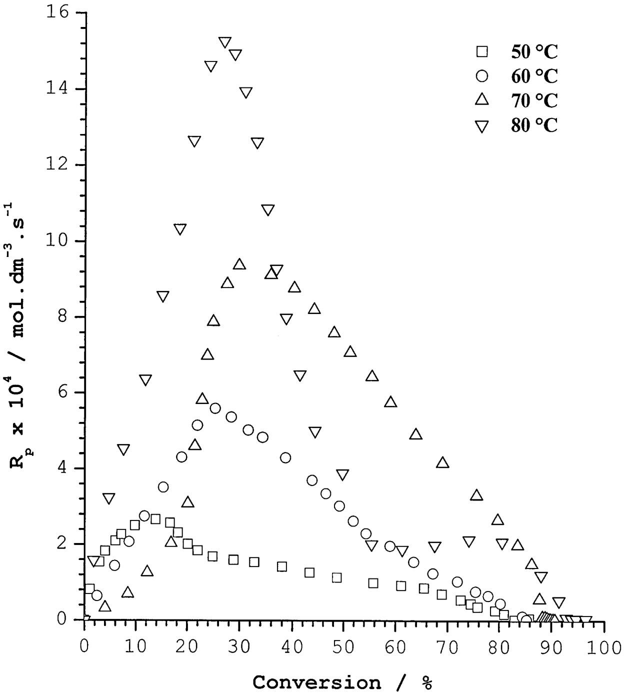


Fig. 2. Variation of the rate of polymerization in the emulsion polymerization of styrene initiated by AIBN with conversion and temperature. For other conditions see Section 2 and Fig. 1.

Variations of the rate of polymerization with conversion are illustrated in Fig. 2. 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 appear. First the rate of polymerization (R_p) abruptly increased to the maximum ($R_{p,max}$) and then, on the contrary, abruptly decreased with conversion. The most pronounced decrease in the polymerization rate beyond $R_{p,max}$ was observed at 80 °C. In the classical emulsion polymerization of hydrophobic St monomer, the rate of polymerization (R_p) increases during Interval 1, reaches the constant (maximum) value during Interval 2 and then decreases (Interval 3) [29]. In the microemulsion polymerization, two non-stationary rate intervals appear and in the miniemulsion even four non-stationary rate intervals appear. The two non-stationary rate intervals are generally discussed in terms of two opposite effects: (1) the continuous increase of particle number (N_p) and (2) decrease of monomer concentration at the reaction loci with conversion [27,30,31]. The very fast initial polymerization can be ascribed to the increased N_p (see later) and the polymerization under monomer-saturated condition. The abrupt decrease in R_p beyond ca. 20% conversion indicates the strong 'deactivation' of reaction loci. This can be connected with the decrease of the monomer concentration at the reaction loci and the transfer of reactive radicals to less reactive ones as well.

The phase behavior and its role in the polymerization process results from the following discussion. The St/Tw 20/water solution separated into two phases after stirring ceased (at 25 °C): the upper milky monomer phase and the lower milky aqueous phase. After stirring ceased at

60 °C, the milky emulsion also separated into two phases: the upper transparent monomer phase and the lower semitransparent (blue colored—typical for microemulsion) one. The increased temperature from 25 to 60 °C was thus accompanied with the transformation of lower milky phase to the semitransparent (microemulsion) one. Stirring the lower phase (microemulsion) with excess of monomer (upper monomer phase) generates the kinetically stable coarse emulsion. The monomer emulsion at polymerization temperatures above 60 °C contains the microdroplets and large highly degradable monomer droplets. The very high surface area of microdroplets strongly competes for radicals with the large monomer droplets and polymer particles. The monomer droplets are expected to serve as a monomer reservoir of growing polymer particles. The increased formation of polymer was reported in the two-phase reaction system consisting of the microemulsion (lower phase) and the styrene (upper) phase (a Winsor I-like system) [32]. The locus of polymerization was in the microemulsion phase while the styrene (upper) phase served as a single monomer reservoir. The formation of polystyrene (PSt) polymer particles in the microemulsion phase can be viewed as seeds for the absorbing of monomer from the aqueous phase released from the degradable large monomer droplets. The polymer-containing microdroplets compete for monomer with the large monomer droplets and unpolymerized microdroplets and swell more effectively than microdroplets and large monomer droplets. The increased swelling of polymer particles is supported by a thermodynamic model which predicts the depletion of monomer cores of microdroplets already at 4% conversion [30]. The consumption of larger fraction of monomer droplets initiates the transformation of the kinetically stable reaction system to the microemulsion with larger number of polymer particles. The increased size and particle number was observed in the Winsor I-like polymerization system [32].

The shelf-life for the SDS/St/water miniemulsion sample was 3 h while that for the Tw 20/St/water sample was prolonged up to 2 weeks. The time necessary for appearance of a visible styrene phase on the top of the SDS/St/water miniemulsion sample was 3–4 h while that for the emulsion sample stabilized by Tw 20 did not appear even after one month. The origin of this phenomenon can be attributed to a several possible hypotheses. It is possible that association of Tw 20 forms colloids other than the spherical micelles at relatively high emulsifier concentration and these transport oil differently [33,34]. The non-ionic emulsifiers can form multilayers around the monomer droplets, which retard the movement of oil molecules from the droplets to the surrounding aqueous phase. The non-ionic emulsifier can act as hydrophobe at high temperature [35–37]. The presence of inverse micelles in the o/w monomer emulsion (double emulsion) stabilized by non-ionic emulsifier can be somehow related to the stability of monomer droplets [38,39]. The increased solubility of non-ionic emulsifier in the oil phase changes the orientation of the emulsifier molecule at the interface. The Winsor I system can increase the solubilization of monomer and so the stability of monomer emulsion.

The partition coefficient (k_{rcoef}, between water and styrene) for Tw 20 at 25 °C is found to be 6.9 at 25 °C when styrene is added to the aqueous solution of Tw 20 [17]. The increased temperature was accompanied by the formation of the thick interfacial layer (or zone) between water and oil and increased turbidity of both phases. Under such conditions, k_{rcoef} could not be determined. It was reported that the amount of non-ionic emulsifier increased ca. 5–10 times in the oil phase by increased temperature from 25 to 60 °C [40]. This indicates that at temperatures above 60 °C the large amount of emulsifier will be located in the monomer phase (monomer droplets).

Non-ionic emulsifier is not a good stabilizer at high temperature (ca. 70–80 °C) but rather it can act as a hydrophobe [37–41]. This is due to the fact that the CP of PEO containing emulsifier is ca. 65–80 °C [42]. The temperature (CP) at which clouding of the Tw 20 aqueous solution (0.1 mol dm^{-3}) occurs was observed to be 93 °C. The addition of styrene (0.06 or 0.12 mol dm^{-3}) strongly decreased clouding temperature. For example, the aqueous solution of Tw 20 (0.1 mol dm^{-3}) saturated with 0.06 or 0.12 mol dm^{-3}) the clouding temperature was estimated to be 58 or 42 °C. The presence of monomer is accompanied by the transfer of Tw 20 into the monomer phase due to which decreases the micellar fraction of emulsifier. Indeed, the thermodynamically stable monomer swollen micelles present below 40 °C were transformed to the larger (the phase separation) droplets at temperatures above 40 °C. The similar phenomenon (the decreased colloidal stability of the polymer latex) was observed in the sterically stabilized polymer particles (the system containing Tw 20 or NP40) with increasing temperature [37,41].

The increased participation of monomer droplets in the polymerization process results from the accumulation of PSt in the monomer phase. This increases the colloidal stability of monomer droplets [43] but decreases the transfer of monomer from the monomer reservoir to the reaction loci. Under such conditions, the polymerization rate decreases even though the reaction system contains free monomer droplets. For example, the predissolved PSt (ca. 0.5 wt%) in the monomer phase increased the stability of monomer droplets (reduced monomer droplet aggregation or Ostwald ripening) [41,43]. The increased accumulation of PSt in the monomer droplets can result from the thermal polymerization (the single radicals formed by decomposition of styrene Diels–Alder product initiate polymerization) [43–47]. For example, the monomer conversion achieved by the thermally induced emulsion polymerization of St stabilized by Tw (ca. 0.04 mol dm^{-3}) at 80 °C is ca. 0.3% conversion per hour [17]. The similar value (0.1% conversion per hour) was observed in the thermally initiated emulsion polymerization of styerene (70 °C) stabilized by SDS [48]. The slow thermal polymerization excludes the presence of Tw 40 peroxides

Table 1
Variation of kinetic and colloidal parameters of the (micro)emulsion polymerization of styrene with the reaction conditions (*I*-Initiator, Co(e)Emulsifier)

$[I] \times 10^3$ (mol dm^{-3})	Temp. (°C)	[(Co)E] (mol dm^{-3})	[St]	$R_i \times 10^8$ (mol dm^{-3} s^{-1})	$R_p \times 10^5$ (dm^3)	$N_{mic} \times 10^{20}$ (dm^3)	$N_p \times 10^{18}$ (dm^3)	Lit.
0.66[a]	70	0.38[b] (0.58)[c]	0.57	3.2	0.89	50		[29]
2.15[a]	70	0.38[b] (0.58)[c]	0.57	10.5	1.5	50	5	[29]
5.0[d]	50	0.04[e]	0.97	1.5	26	0.1		This work
5.0[d]	60	0.04[e]	0.97	6.3	560	0.1	5	This work

[a] ABMN.
[b] SDS.
[c] Pentanol.
[d] APS.
[e] Tw 20.

and their participation in the initiation as well as the explanation that the fast initial polymerization was caused by the Tw 20 peroxides. The contribution of thermal polymerization (R_p ca. 10^{-6} mol dm^{-3} s^{-1}) to the overall rate of polymerization ($R_{p,max,80\,°C} = 1.6 \times 10^{-3}$ mol dm^{-3} s^{-1}) is negligible. In the emulsion polymerization, however, the increased accumulation of PSt in the monomer phase [49] can decrease the diffusion of monomer from the stable monomer droplets (highly monomer-swollen polymer particles) to the reaction loci and so the rate of polymerization (abrupt decrease of R_p beyond ca. 20% conversion).

The two-rate intervals (a broad shaped R_p vs. conversion curve) were also observed in the microemulsion polymerization of St stabilized by SDS/1-pentanol and initiated by oil-soluble initiator (2,2′-azobis-(2-methyl butyronitrile) AMBN [30]. Table 1 shows that the emulsion polymerization of styrene stabilized by Tw 20 is much faster than the rate of microemulsion polymerization stabilized by SDS. The rates of initiation (R_i) and monomer concentrations are comparable in both systems. The emulsifier concentration, the number of micelles (5×10^{21} dm^{-3}), the propagation rate constants and the number of polymer particles (5×10^{18} dm^{-3}) were larger in the SDS system then those in the Tw 20 system. This would lead to a faster polymerization with SDS. Furthermore, the emulsion polymerization stabilized by ionic emulsifier was faster than that stabilized by non-ionic emulsifier [6,50]. The present study shows that the reverse is true. The seeded (micro)-emulsion polymerization or the Winsor I-like polymerization is suggested to be responsible for the observed behavior.

According to the micellar model, the reaction order x from the relationship $R_{p,max} \propto R_i^x$ is 0.4 [18]. The reaction order $x = 0.43$(50–80 °C) obtained from the relationship $R_{p,max} \propto R_i^x$ ($R_i = 2fk_d$[AIBN], where $f(= 0.5)$ [51] is the initiator efficiency and k_d is the decomposition rate constant ($k_d = 1.29 \exp(-127.6/8.314 \times 10^{-3}\mathrm{T})\mathrm{s}^{-1}$) [51] (Fig. 3) is in a good agreement with the micellar nucleation model [18]. This finding is very similar to that in the microemulsion polymerization of styrene initiated by AMBN (0.39 power, $R_{p,max} \propto [\mathrm{AMBN}]^{0.39}$ [30]. At temperatures ≤50 °C the reaction system mainly contains initiating radicals derived primarily from AIBN. At higher temperatures (above 60 °C), additional single radicals can result from the thermal decomposition of styrene Diels–Alder product [44–47,52]. Correction on the thermal initiation would decrease the reaction order x to a value below 0.43. The reaction order $x1 = -0.93$(50–80 °C) was obtained from the relationship $R_{pp,max} \propto R_i^{x1}$ (Fig. 3). $R_{pp,max}$ is the maximal polymerization particle. The similar finding was observed in the classical microemulsion polymerization systems [27]. The strong decrease in $R_{pp,max}$ with temperature can be attributed to the decreased radical flux per particle, the increased termination and chain transfer rate (due to the increased concentration of non-ionic emulsifier in the monomer phase) and the decreased monomer concentration at the reaction loci. For example, the size of polymer

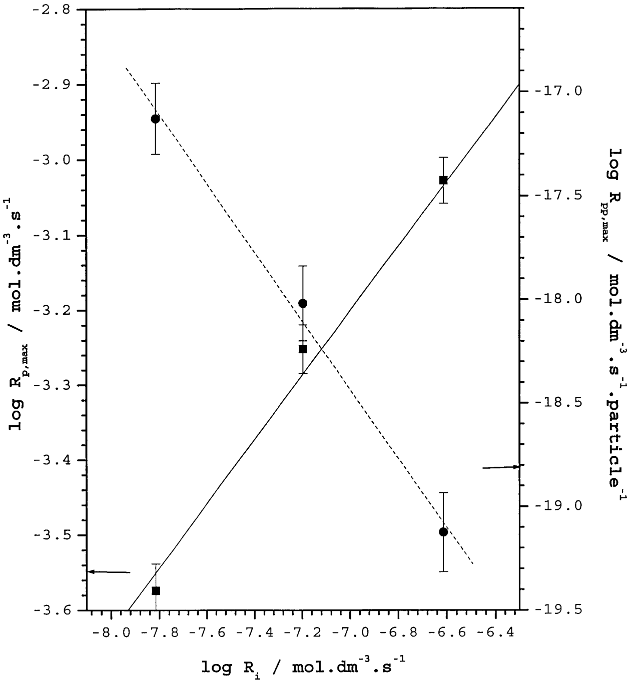


Fig. 3. Variation of the maximum polymerization rate ($R_{p,max}$) and the maximum polymerization rate per particle ($R_{pp,max}$) in the emulsion polymerization of styrene initiated by AIBN with the rate of initiation (R_i). For other conditions see Section 2 and Fig. 1.

particles (D(nm)) at $R_{p,max}$ decreases with temperature in the following order:

D(nm)/temp.(°C): 800/50,400/60,200/80,180/70.

3.2. Activation energy

The overall activation energy (E_o) for solution (or bulk) ($E_{o,sol}$) or emulsion ($E_{o,emul}$) polymerization can be expressed as follows: [18,53]

$$E_{o,emul} = 0.6E_p + 0.4E_d \tag{1}$$

$$E_{o,sol} = E_p - 0.5E_t + 0.5E_d \tag{2}$$

where E_p is the activation energy for propagation, E_t is the activation energy for termination, and E_d is the activation energy for decomposition of initiator. For most monomers, E_p, E_t, and E_d are 30, 20, and 125 kJ mol^{-1}, respectively [51]. Using Eqs. (1) and (2), the overall activation energy is estimated to be ca. 90 kJ mol^{-1} for solution or bulk polymerization and ca. 70 kJ mol^{-1} for emulsion polymerization, respectively. The $R_{p,max}$ data from Fig. 2 were used to get the Arrhenius plot (In $R_{p,max}$ vs. $1/T$) and the overall activation energy ($E_{o,emul}$) as well (Fig. 4). The estimated $E_{o,emul}$ 56.6 kJ mol^{-1} is much smaller than that calculated from Eq. (2) and the literature values for emulsion polymerization of styrene [48,51]. For example, the overall activation energy ($E_{o,emul}$) for the microemulsion and miniemulsion polymerization of styrene stabilized by SDS in the temperature range 50–70 °C is 94.6 kJ mol^{-1} and 61.5, respectively [30,48,54]. The $E_{o,emul}$ estimated from the initial rates of microemulsion polymerization of styrene at higher temperature range (about 80 °C), however, was much lower (34.3 kJ mol^{-1}) [55]. The increased barrier for radicals entering the polymer particles increased the value of $E_{o,emul}$ (increased E_d contribution) [56,57]. $E_{o,emul}$(= 56.6 kJ mol^{-1}) can be discussed in terms of a decreased barrier for entering radicals due to the decreased thickness of the interfacial surface layer with temperature. For example, the effective thickness of the adsorbed layer of non-ionic emulsifier octaoxyethylene glycol *n*-dodecyl monoether on PSt polymer particle decreased with increasing temperature from a value 6.2 nm at 15 °C to 2.2 nm at 43 °C [58]. Furthermore, the transformation of classical emulsion (≤50 °C) to (seeded) microemulsion (≥60 °C) is expected to influence the overall activation energy as well.

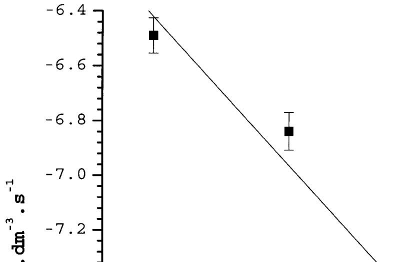


Fig. 4. The Arrhenius plot (ln $R_{p,max}$ vs. $1/T$) for the emulsion polymerization of styrene initiated by AIBN. For other conditions see Section 2 and Fig. 1.

3.3. Fate of radicals

The formation of small latex particles is connected with increased desorption of monomer (emulsifier) transferred radicals and decreased rate per particle [59,60]. For the electrostatically stabilized latexes, exit of radicals out of the particles is postulated to occur by the chain transfer reaction to monomer, resulting in a monomeric radical which then desorbs from the particles into the aqueous phase. The fate of desorbed monomeric radicals into the aqueous phase in the (micro)emulsion polymerization of styrene initiated by peroxodisulfate and electrostatically stabilized by SDS (est) [30] or sterically stabilized by Tw 20 (ster) at ca. 70 °C can be understood by considering following kinetic parameters [30].

$$t_{aq,est} = N_A/(k_a N_p + k_a N_{mic})\phi_w = 0.03\ \text{s} \tag{3}$$

$$t_{aq,ster} - N_A/(k_a N_p + k_a N_{mic})\phi_w = 3.7(37)\ \text{s} \tag{4}$$

$$t_{prop} = 1/(k_p[\text{St}]_{aq,sat}) = 1.3\ \text{s} \tag{5}$$

$$t_{ter} = 1/(k_{t,w}[\text{R}]) = 0.15\ \text{s} \tag{6}$$

where t_{aq} is the average residence time in the aqueous phase before re-entry into a particle of micelle, t_{prop} is the average time to add one monomer unit in the aqueous phase, and t_{ter} is the average time for a termination reaction with another radical in the aqueous phase, k_a the entry rate coefficient into the polymer particle (4×10^6 dm^3 mol^{-1} s^{-1}), k_a the entry rate coefficient into the micelle (7×10^2 dm^3 mol^{-1} s^{-1}), N_{mic} the number of micelles (4.6×10^{21} dm^{-3}), N_p the number of polymer particles (3×10^{18} dm^{-3}), ϕ_w the volume fraction of aqueous phase (0.865) [30], k_p the rate constant for styrene propagation (100 dm^3 mol^{-1} s^{-1} at 60–70 °C) [61], $[\text{St}]_{aq,sat}$ the styrene-saturated water phase (7.24 mM at ca. 60–70 °C) [62], $_{tw}$ the rate constant for termination in the aqueous phase (1.07×10^8 dm^3 mol^{-1} s^{-1} at 60–70 °C) [51] and the radical concentration ($[R] = 7 \times 10^{-8}$ mol dm^{-3}, estimated from the equation for the steady-state condition: R_i (the rate initiation) = R_t (the rate of termination)). By comparing the values of $t_{aq,est}$,

t_{prop}, and t_{ter}, it was concluded that the most probable fate of desorbed monomer radicals is re-entry into the electrostatically stabilized polymer particles or microdroplets (charged particle surface) [30].

The k_a (or k_a) value was reported to be by one or two orders in magnitude larger for electrostatically stabilized polymer particles than that for sterically stabilized polymer particles [14,15]. Under such condition, the estimated $t_{\mathrm{aq,ster}}$ for the electrostatically stabilized polymer particles, that is, $t_{\mathrm{aq,ster}}$ is 3.7 or 37 when the ratio $k_{\mathrm{a,est}}/k_{\mathrm{a,ster}}$ is 10 or 100, respectively, where $k_{\mathrm{a,est}}$ is the coefficient for entry into the electrostatically stabilized polymer particles and $k_{\mathrm{a,ster}}$ is the coefficient for entry into the sterically stabilized polymer particles, respectively. The experimental data $N_{\mathrm{p}} = 1 \times 10^{16}\ \mathrm{dm}^{-3}$, $\phi_{\mathrm{w}} = 0.87$, and $N_{\mathrm{mic}} = 1 \times 10^{19}\ \mathrm{dm}^{-3}$ (estimated from the aggregation number of Tw 20 = 125 (at 25 °C) [63] and the micellar fraction of Tw 20 = ca. 0.1) were used for the $t_{\mathrm{aq,ster}}$ estimation. By comparing the values of $t_{\mathrm{aq,ster}}$, t_{prop}, and t_{ter}, it can be concluded that the re-entry of desorbed radicals is not any more the rate dominating process. This is due to the fact that the thick interfacial layer forms a barrier for radicals entering the monomer-swollen micelles or a cage for the entered radicals. Therefore, the termination (t_{ter}) becomes more important.

3.4. Colloidal parameters

The mixture of Tw 20, water and styrene forms an unstable milky-like monomer emulsion at room temperature which after the ceased stirring separates into two milky phases. The ionic emulsifier usually forms the translucent or transparent initial monomer emulsions under the similar condition (at high emulsifier concentration) [27,64]. At higher temperatures (above 50 °C) the lower milky phase is transformed to the transparent (blue-colored microemulsion) phase. The colloidal stability of Tw 20/St/water coarse emulsion increased after the start of polymerization. The emulsion containing ca. 5 wt% polymer does not cream after one day ageing at room temperature. The average particle size decreased with increasing conversion and reached the plateau (*D* ca. 100 nm) at ca. 35 % conversion (Fig. 5). The reversed behavior was observed in the classical emulsion polymerization of stabilized by non-ionic emulsifier where the particle size increased with increasing conversion and the increase was more pronounced at low conversion [1,2,65]. The appearance of large polymer particles had been interpreted in terms of the limited particle flocculation and the coagulative nucleation. Fig. 5 shows the formation of large particles (ca. 1000 nm) after the start of polymerization. The average size of polymer particles, however, continuously decreased with conversion and reached plateau (ca. 100 nm in diameter) at ca. 50% conversion. Both small and large particles appear after the start of polymerization and the large particles disappear at ca. 50% conversion (Scheme 1). Simultaneously, the size of small particles increased with increasing conversion (70 °C):

D(nm)/Conv.(%): 40/4, 55/9, 66/23, 73/44, 79/59, 74/90.

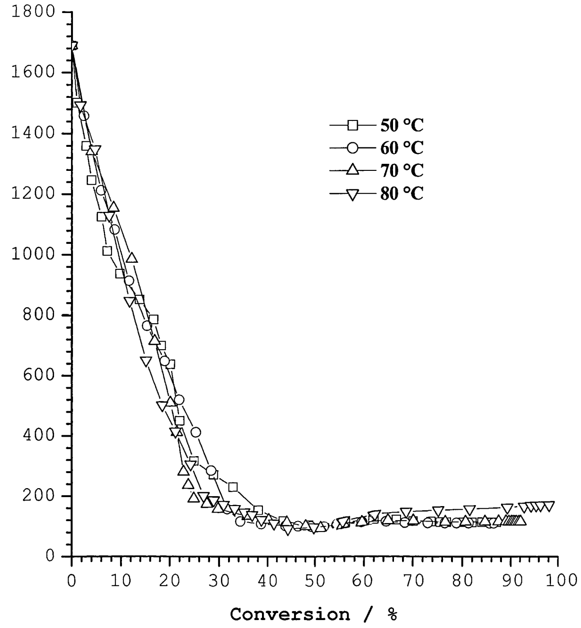
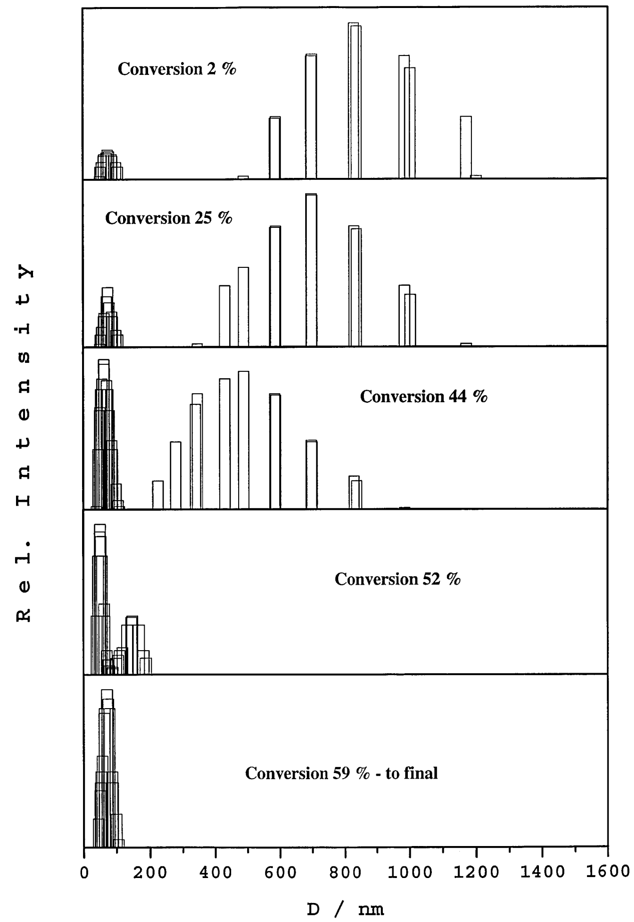


Fig. 5. Variation of the average particle diameter (*D*) in the emulsion polymerization of styrene with conversion and temperature. For other conditions see Section 2 and Fig. 1.

The large monomer/polymer (highly monomer-swollen) particles were reported to be formed by the heterocoagulation of unstable polymer particles and monomer droplets [66,67]. The initial fusion of an unstable polymer particle with an emulsifier-saturated monomer droplet leads to the formation of highly monomer-swollen polymer particle. This process is accompanied by the displaced of emulsifier from the core of the formed highly monomer-swollen polymer particle (emulsifier is incompatible with PSt) to its shell and the aqueous phase as well. The formation of unstable highly monomer-swollen polymer particles might be also formed by the initiation of polymerization in the monomer phase by the oil-soluble initiator AIBN. The formation of the highly monomer-swollen polymer particles was confirmed by the dialysis that decreased the initial polymer particle size with diameter ca. 500 nm to ca. 100–200 nm. Furthermore, TEM confirmed the presence of small particles ca. $D_{\mathrm{n}} = 100$ nm at low conversion. The preparation of polymer latex for TEM measurements includes the process of monomer evaporation due to which the initial large highly monomer-swollen polymer particles strongly shrunk to much smaller ones. The size of final polymer particles was nearly independent of temperature except of 80 °C. The slight increase of particle size at 80 °C results from a partial destabilization of colloidal system. Oxyethylene polar groups of emulsifier extended into the water form hydrogen bonds with water. The increased dehydration of PEO chains with temperature is responsible for the decreased stabilization efficiency of



Scheme 1.

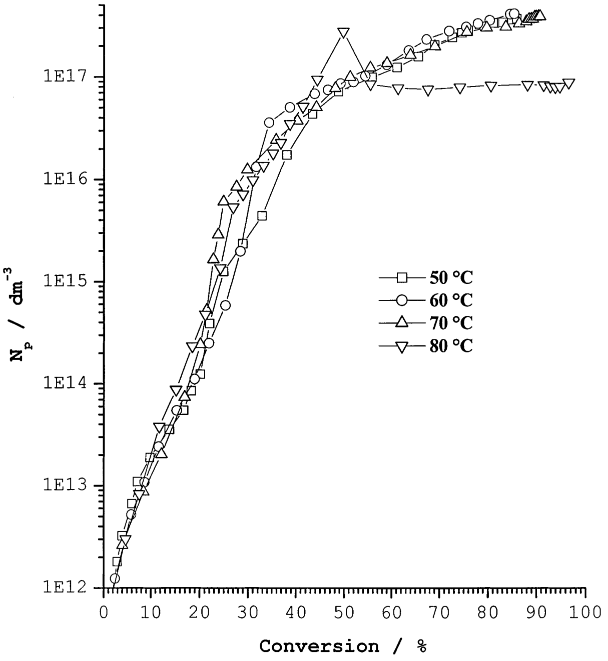


Fig. 6. Variation of the particle number (N_p) in the emulsion polymerization of styrene with conversion and temperature. For other conditions see Section 2 and Fig. 1.

Tw 20. As temperature is raised, these relatively weak bonds begin to dissociate and water molecules are gradually driven out of the (shell) region occupied by POE chains. Furthermore, the increased accumulation of emulsifier within the monomer phase with temperature decreases the amount of emulsifier available for stabilization. The shortage of emulsifier leads to the particle agglomeration and the formation of larger polymer particles.

The apparent particle size distribution (D_w/D_n) (the light scattering method) of final polymer latexes was observed to be ca. 2 at the low conversion and decreased with conversion and reached value ca. 1.2 at final conversion. $D_w/D_n < 1.1$ was obtained by TEM. The depletion of large monomer/polymer particles at high conversion supports the idea that these monomer/polymer particles serve as a monomer reservoir. Furthermore, the formation of relatively monodisperse final polymer particles favors the kinetics of seeded microemulsion polymerization [32].

Fig. 6 shows the variation of the particle number with temperature and conversion. The number of polymer particles (N_p) continuously increased up to the final conversion and the increase was much more pronounced up to 40% conversion. In the microemulsion polymerization the number of particles increased with a constant rate up to the final conversion [27,64]. In the miniemulsion polymerization N_p increased up to ca. 40–50% conversion [16,68]. The continuous nucleation results from the nucleation of microdroplets and the accumulation of released emulsifier (micelles) from the degrading monomer droplets in the aqueous phase. The transformation of coarse emulsion to fine one results from the continuous nucleation of microdroplets, the shrinking of the highly monomer-swollen polymer particles, the depletion of large monomer degradable droplets, the depressed growth of polymer particles containing the low fraction of monomer etc. At 80 °C, the dependence of N_p vs. conversion is more complex. First N_p continuously increased to a maximum at ca. 50% conversion and then decreased and reached a plateau. The decreased number of polymer particles beyond ca. 50% conversion is typical for the polymerization with a lower emulsifier concentration (coagulative nucleation) [1,2]. The high oil solubility of emulsifier, the decreased stabilizing efficiency of emulsifier at high temperature and very fast polymerization strongly decreased the amount of emulsifier available for particle nucleation and stabilization.

According to the micellar nucleation model, N_p remains relatively constant or slightly decreases with increasing conversion except of the beginning of polymerization. Fig. 6 shows that the evolution of N_p strongly deviates from the micellar model. Furthermore, the relationship between $N_{p,\mathrm{Rpmax}}$ and the initiator concentration (or the rate of initiation) $N_{p,\mathrm{Rpmax}} \propto R_i^{\alpha} (\alpha = 1.36)$ strongly deviates from the micellar model, Case 2 ($\alpha = 0.4$). $N_{p,\mathrm{Rpmax}}$ is the number of polymer particles at the maximal polymerization rate. The

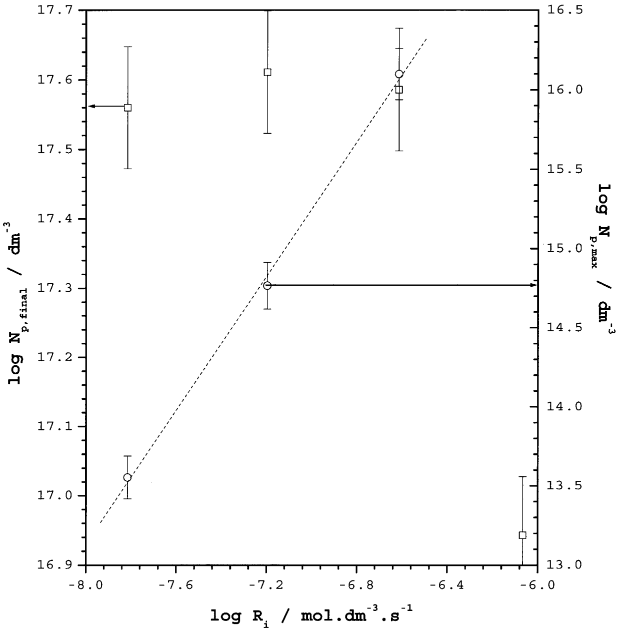


Fig. 7. Variation of the particle number ($N_{p,max}$ at $R_{p,max}$ and $N_{p,final}$) at final conversion in the emulsion polymerization of styrene with the rate of initiation (R_i). For other conditions see Section 2 and Fig. 1.

reaction order $\alpha = 1.36$ obtained from the dependence $N_{p,Rpmax} \propto R_i^{\alpha}$ (Fig. 7) strongly deviates from the micellar model [18] and the emulsion polymerization of styrene initiated by peroxodisulfate ($\alpha = 0.67$) [17]. The particle nucleation rate formation (the reaction order α) is a result of two opposing effect: (1) the increased radical rate formation and (2) the decreased amount of emulsifier available for particle nucleation and stabilization with increasing temperature. N_p data show that the radical rate formation dominates the particle formation at low and medium conversion. This can be attributed to the increased number of microdroplets (the transformation of coarse emulsion to microemulsion with increased temperature) and thermal initiation. Furthermore, the decreased thickness of the interfacial layer (barrier for entering radicals) with increased temperature increases the radical rate entry (particle rate formation). At final conversion, however, $N_{p,final}$ is nearly independent of R_i (Fig. 7). The radical formation is overcome by the decreased stabilizing efficiency of emulsifier and the increased amount of emulsifier buried in the polymer matrix.

4. Conclusion

Tween 20 (Tw 20)/styrene (St)/water emulsion is unstable and separates into two milky phases at room temperature. The increased temperature is accompanied with the transformation of the lower milky phase into the semi-transparent (blue-colored microemulsion) one. The initial reaction system (during stirring) consists of the micro-droplets and large monomer droplets. The polymerization proceeds under the seed (micro)emulsion condition (the Winsor I-like polymerization system). The large (kinetically stable) monomer droplets saturated with emulsifier can provide the reaction loci with the continuous flux of monomer and emulsifier. After the start of polymerization, the large and small particles appear. The large (the highly monomer-swollen) particles are formed by agglomeration of polymer particles and monomer droplets. The large highly monomer-swollen polymer particles merged with the smaller ones at ca. 40–50% conversion. The formation of highly monomer-swollen polymer particles was confirmed by dialysis and TEM measurements as well. In the former case the particle size strongly decreased with dialysis. In the latter one the small particles were confirmed. The apparent particle size distribution was broad at low conversion and decreased with increasing conversion. TEM confirmed the formation of monodisperse polymer latexes. The dependence of the polymerization vs. conversion curve shows two distinct non-stationary rate intervals. The abrupt initial increase in the polymerization rate results from the continuous particle formation and polymerization under monomer-saturated condition (the Winsor I-like polymerization-seeded (micro)emulsion polymerization). The decrease in the polymerization rate is attributed to the depletion of large monomer droplets and the polymerization under monomer-starved condition. The continuous particle nucleation results from the nucleation of microdroplets and the additional emulsifier releasing from the degrading large monomer droplets into the aqueous phase. The low overall activation energy of polymerization is ascribed to the low barrier for entering radicals into the latex particles. The reaction order $\alpha = 1.36(N_{p,Rpmax} \propto R_i^{\alpha})$ results from the increased thermal initiation, the polymerization under monomer-saturated condition (the Winsor I-like microemulsion polymerization and the increased radical entry rate (due to the decreased thickness of the interfacial layer with temperature).

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References

[1] Piirma I, Chang M. J Polym Sci Polym Chem Ed 1982;20:489.
[2] Capek I, Barton J, Tuan LQ, Svoboda S, Novotny V. Makromol Chem 1987;188:1723.
[3] Gilbert RG. Emulsion polymerization. A mechanistic approach. London: Academic Press, 1995.
[4] Haq Z, Thomson L. Colloid Polym Sci 1982;260:212.
[5] Rosen MJ. Surfactants and interfacial phenomena. New York: Wiley, 1998. p. 119.
[6] Dittman-McBain CB, Piirma I. J Appl Polym Sci 1989;37:1415.
[7] Mahdi SM, Skold RO. Colloid Surf 1992;66:203.

[8] Deryagnin BV, Landau LD. Acta Physicochim USSR 1941;14: 633.

[9] Verwey EJW, Overbeek JThG. Theory of the stability of lyophobic colloids. New York: Elsevier, 1943.

[10] Napper DH. Polymeric stabilization of colloidal dispersions. London: Academic Press, 1983.

[11] Ottewill RH. J Colloid Interf Sci 1977;58:357.

[12] Capek I. Adv Polym Sci 1999;145:1.

[13] Bovey FA, Winslow FH. Macromolecules—introduction to polymer science. In: Bovey FA, Winslow FH, editors. London: Academic Press, 1972. p. 92.

[14] Coen E, Lyons RA, Gilbert RG. Macromolecules 1996;29:5128.

[15] Kusters JMH, Napper DH, Gilbert RG, German AL. Macromolecules 1992;25:7043.

[16] Miller CM, Sudol ED, Silebi CA, El-Aasser MS. J Polym Sci Polym Chem Ed 1995;33:1391.

[17] Chudej J, Capek I. J Polym Sci 2001, in press.

[18] Smith WV, Ewart RH. J Am Chem Soc 1948;70:3695.

[19] Capek I. Makromol Chem 1989;190:789.

[20] Potisk P, Capek I. Angew Makromol Chem 1994;222:125.

[21] Capek I, Chudej J. Polym Bull 1999;43:417.

[22] Reimers J, Schork FJ. J Appl Polym Sci 1996;59:1833.

[23] Reimers J, Schork FJ. J Appl Polym Sci 1996;60:251.

[24] Lin SY, Capek I, Hsu TJ, Chern CS. Polym J 2000;32:932.

[25] Capek I, Funke W. Makromol Chem 1990;191:2549.

[26] Hunter R. Foundation in colloid science. New York: Oxford University Press, 1989.

[27] Capek I. Adv Colloid Interf Sci 1999;80:85.

[28] Capek I, Chern CS. Adv Polym Sci 2001;155:101.

[29] Blackley DC. Emulsion polymerization. London: Applied Science, 1975.

[30] Guo JS, Sudol ED, Vanderhoff JW, Elaasser MS. J Polym Sci Polym Chem 1992;30:691–703.

[31] Capek I, Potisk P. Eur Polym J 1995;31:1269.

[32] Gan LM, Lian N, Chew CH, Li GZ. Langmuir 1994;10:2197.

[33] Jorgensen HB, Olsson U, Iliopoulos I. Langmuir 1995;11:1934.

[34] Dimitrova GT, Tadros ThF, Luckham DF, Kipps MR. Langmuir 1996;12:315.

[35] Weiss J. Langmuir 2000;16:6833.

[36] Weiss J, McClements DJ. Langmuir 2000;16:5879.

[37] Lin SY, Capek I, Hsu TJ, Chern CSJ. Polym Sci Polym Chem 1999;37:4422.

[38] Miller CM, Sudol ED, Silebi CA, El-Aasser MS. Macromolecules 1995;28:2754.

[39] Hansen FK, Fagerheim H. Colloids Surf A Physicochem Engng Aspects 1998;137:217.

[40] Hergeth WD, Bloss O, Biedenweg F, Abendroth P, Schmutzler K, Wartenwig S. Macromol Chem Phys 1990;191:2949.

[41] Ostwald W. Phys Chem 1901;37:385.

[42] Schott H, Han SK. J Pharm Sci 1975;64:658.

[43] Miller CM, Sudol ED, Silebi CA. Macromolecules 1995;28:2772.

[44] Kauffmann HK, Olaj OF, Breitenbach JW. Makromol Chem 1976;177:939.

[45] Mehnert P. Angew Chem 1974;86:869.

[46] Pryor WA, Lasswell LD. Adv Free-Radical Chem 1974;5:27.

[47] Kast H, Funke W. Makromol Chem 1981;182:1553.

[48] Chern CS, Lin SY, Hsu TJ. Polym J 1999;31:516.

[49] Capek I, Chern CC. Adv Polym Sci 2001;155:101.

[50] Piirma I, Kamath VR, Morton M. J Polym Sci Polym Chem Ed 1975;13:2087.

[51] Brandrup J, Immergut EH. Polymer handbook. 3rd ed. New York: Wiley, 1989.

[52] Edelhauser H, Braitenbach JW. J Polym Sci 1959;35:423.

[53] Odian G. Principles of polymerization. 2nd ed. New York: Wiley, 1981.

[54] Choi YT. PhD Dissertation, Lehigh University, Bethlehem, PA, 1986.

[55] Feng L, Ng KYS. Macromolecules 1990;23:1048.

[56] Capek I. Adv Colloid Interf Sci 2001;92:195.

[57] Gan LM, Chew CH, Lim JH, Lee KC, Gan LH. Colloid Polym Sci 1994;272:1089.

[58] Thomson L, Pryde DNJ. Chem Soc Faraday Trans 1 1981;77:2405.

[59] Harada M, Nomura M, Eguchi W, Nagata SJ. Chem Engng Jpn 1991;4:54.

[60] Nomura M, Ikoma J, Fijita K. J Polym Sci Polym Chem 1993; 31:2103.

[61] Olaj OF, Bitai IS. Eur Polym J 1989;25:635.

[62] Barton J, Capek I. In: Horwood E, editor. Radical polymerization in disperse systems. Bratislava: Chichester and Veda, 1994.

[63] Haque MdE, Das AR, Moulik SP. J Colloid Interf Sci 1999;217:1.

[64] Capek I. Adv Colloid Interf Sci 1999;82:253.

[65] Lin SY, Capek I, Hsu TJ, Chern CS. Polym J 2000;32:932.

[66] Capek I, Potisk P. J Polym Sci Polym Chem 1995;33:1675.

[67] Kimn DR, Napper DH. Macromol Rapid Commun 1994;164:163.

[68] Choi YY, El-Aasser MS, Sudol ED, Vanderhoff JW. J Polym Sci Polym Chem Ed 1985;23:2973.