Available online at www.sciencedirect.com

SCIENCE DIRECT

Polymer 46 (2005) 1385–1394

polymer

www.elsevier.com/locate/polymer

Stability of monomer emulsion droplets and implications for polymerizations therein

Klaus Tauer*

Max Planck Institute of Colloids and Interfaces Am Mühlenberg, D-14476 Golm, Germany

Accepted 30 September 2004
Available online 13 December 2004

Abstract

The Lifshitz–Slezov–Wagner (LSW) theory of Ostwald ripening [I.M. Lifshitz, V.V. Slezov, Zh Exp Teor Fiz 35 (2(8)) (1958) 479–492; C.Z. Wagner, Elektrochemistry 65 (7/8) (1961) 581–591. [1,2]] and Kabalnov's extension [A.S. Kabalnov, A.V. Pertzov, E.D. Shchukin, Colloid Surf 24 (1987) 19–32 [3]] is applied to theoretically analyze the stability of single and two component monomer emulsion drops (C1—monomer, C2—additional compound with low solubility in the continuous phase), respectively. The analysis is carried out for monomers frequently used in heterophase polymerizations such as methyl methacrylate (MMA), butyl acrylate (BA), styrene (STY), tert-butyl styrene (TBS), and lauryl methacrylate (LMA) and C2 with varied solubility in the continuous phase. Conclusions are drawn from the results regarding heterophase polymerizations carried out with such monomer emulsions. The calculations show that the solubility of both C1 and C2 in the continuous phase in combination with the concentration of C2 and the average emulsion drop size as well as the width of its distribution determines essentially the stability of emulsions.

Keywords: Monomer emulsions; Droplet stability; Ostwald ripening

1. Introduction

The ability to control the composition and the properties of particles in polymer dispersions by preparation of corresponding monomer emulsions might be desirable and advantageous goal as all imponderableness of the polymerization process could be avoided. Furthermore, semibatch polymerization procedures with seed particles, which are the state of the art in many industrial procedures to prepare polymer dispersions [4] could be replaced by technically much simpler batch operations. The most important step towards this goal is controlling the composition and the stability of the monomer emulsion droplets. Generally, emulsions can be prepared either by comminution or by condensation techniques [5]. Condensation techniques such as the swelling of seed latexes are purely thermodynamically driven and result in stable emulsions whereas it needs a lot of efforts to get stable emulsions by comminution procedures. With respect to the drop-size-stability coalescence and Ostwald ripening (OR) are the crucial degradation mechanisms. Nowadays it is no problem by proper selection of surfactants to protect emulsions against degradation by coalescence, which requires basically preventing of close contact between two droplets. Contrary, Ostwald ripening does not require close contact between drops as it occurs via diffusion through the continuous phase, which is governed by the solubility of the monomer. This contribution deals with aqueous monomer emulsions made by comminution techniques such as high shear homogenizers or ultrasound nozzles with average droplet diameters below 1000 nm, which are assumed to be stable against degradation by coalescence, and focuses especially on thermodynamical contemplations regarding emulsion stability.

2. Results and discussions

The excess chemical potential of monomer emulsion droplets ($\mu_{1,\mathrm{r}}$) composed of two components (monomer:

---

* Tel.: +49 331 567 9611; fax: 49 331 567 9512.
E-mail address: klaus.tauer@mpikg-golm.mpg.de.

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.11.062

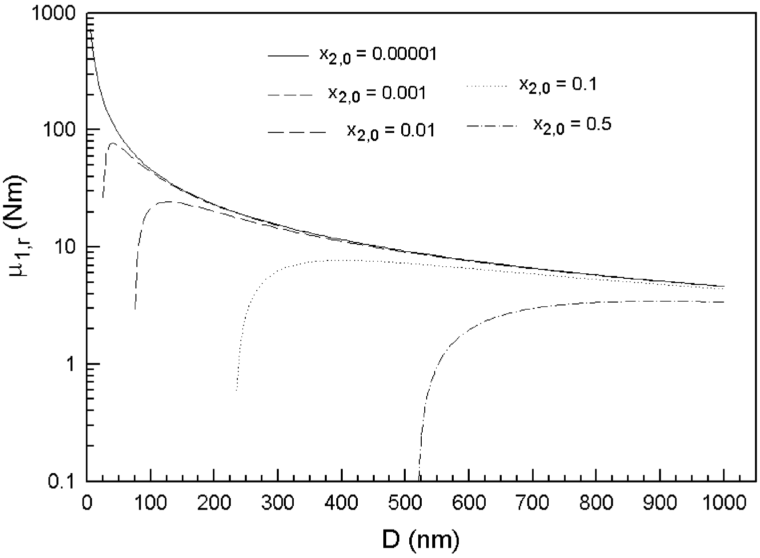


Fig. 1. Change of the excess chemical potential in dependence on the drop size for various molar fractions of the second component.

compound C1 and another compound C2, which has zero solubility in water) as given by Eq. (1) illustrates the contributions arising from the size (first term on the right hand side leading to an increase in $\mu_{1,r}$) and the droplet composition (second term on the right hand side leading to a decrease in $\mu_{1,r}$).

$$\mu_{1,r} = \mu_1 - \mu_1^* = \frac{4\sigma v_{m,1}}{D} + RT \ln x_1 \tag{1}$$

μ_1 is the chemical potential of the monomer in the droplet of diameter D, μ_1^* is the chemical potential of the pure bulky monomer phase, σ is the interfacial tension between the drop and the continuous phase, $v_{m,1}$ is the molar volume of the monomer, R is the molar gas constant, T is the absolute temperature, and x_1 is the mol fraction of monomer in the drop. Basically, both D and x_1 are from practical point of view independent parameters, which can be freely chosen by the experimenter. However, Eq. (1) allows to derive a relation showing that for stable droplets of a desired size the composition of the drops cannot be freely chosen. Assuming spherical drops and allowing that after emulsification the drop sizes are distributed around the initial (or target) value D_0 Eq. (1) can be transformed into Eq. (2) where $x_{2,0}$ is the initial (or nominal) mol fraction of the water-insoluble component (C2) (cf. also [3]).

$$\mu_{1,r} = \mu_1 - \mu_1^* = \frac{4\sigma v_{m,1}}{D} + RT \ln\left(1 - x_{2,0}\frac{D_0^3}{D^3}\right) \tag{2}$$

The course of $\mu_{1,r}$ as plotted for $D_0 = 100$ nm, $\sigma = 10\ \mathrm{mN\,m^{-1}}$, and different $x_{2,0}$—values as presented in Fig. 1 contains information regarding the stability of the emulsion after finishing the comminution.

The equilibrium as described by Eqs. (1) and (2) is stable if for all droplet sizes in the emulsion $\partial\mu_{1,r}/\partial D > 0$, which means that in this case a thermodynamical stable situation can be reached during a maturation period after emulsification.

For the particular model calculations put together in Fig. 1 the solid line ($x_{2,0} = 10^{-5}$) describes a situation where an equilibrium state is unattainable as $\partial\mu_{1,r}/\partial D < 0$ for the entire range of droplet sizes whereas for all other cases an equilibrium state is eventually attainably (cf. below).

It is to emphasize that $\partial\mu_{1,r}/\partial D > 0$ does not mean that after stopping the homogenization the emulsion is stable per se unless the droplet size distribution is extremely (almost perfectly) monodisperse and D_0 and $x_{2,0}$ obey the relation given by Eq. (3).[1]

$$x_{2,0} = 1 - \exp\left(-\frac{4\sigma v_{m,1}}{RTD_0}\right) \tag{3}$$

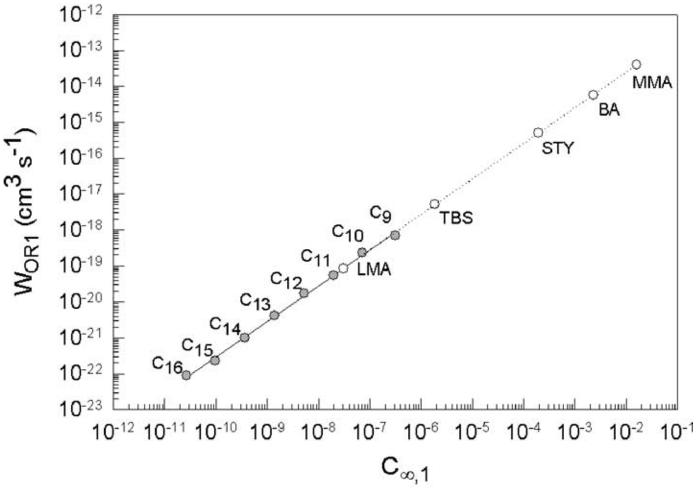
As it is rather unlikely to control emulsification processes in such a way that Eq. (3) is fulfilled any emulsion will mature after the external shear forces have been stopped. The change of the droplet size distribution during the maturation period depends on the sign of $\partial\mu_{1,r}/\partial D$. If the sign of $\partial\mu_{1,r}/\partial D$ is negative in the vicinity of D_0 the emulsion is not able to reach a stable equilibrium state and OR takes place until macroscopic phase separation is completed.

2.1. Single component emulsion drops

The rate of OR for a single component drop (W_{OR1}) can

---

[1] The condition given by Eq. (3) follows from the consideration of two coexisting drops with sizes D^a and D^b in equilibrium, which means that $\mu_{1,r}^a = \mu_{1,r}^b = ((4\sigma v_{m,1})/D^a) + RT \ln x_1 = \mu_{1,r}^b = ((4\sigma v_{m,1})/D^b) + RT \ln x_1$ and the assumption that for one drop $D \rightarrow \infty$ and $x \rightarrow 1$. As will be shown below this result seems to be an upper limit for x_{02}.



Data of alkanes from A. S. Kabalnov, K. N. Makarov, A. V. Pertzov, E. D. Shchukin J. Coll. Interf. Sci. 138 (1990) 98-104

Fig. 2. Relation between the water solubility ($C_{\infty,1}$) and the rate of OR (W_{OR1}) for *n*-alkanes (C_9 to C_{16} denote the carbon number) and for some common monomers (abbreviations cf. Table 1).

Table 1

Molecular data of the monomers used for the calculations at 25 °C MMA—methyl methacrylate, BA—butyl acrylate, STY—styrene, TBS—tert-butyl styrene, LMA—lauryl methacrylate; the data for the monomer densities for MMA, BA, and STY are taken from [7] and the data for TBS and LMA are estimates; the data of the water solubilities for MMA and STY were taken from [8], for BA from [9], and the values for TBS and LMA were estimated from regressions given in [10]; for all monomers at 25 °C $\sigma = 10$ mN m^{-1}

Monomer	ρ (g cm^{-3})	$v_{m,1}$ (cm^3 mol^{-1})	C_w (mM)	$C_{\infty,1}$	W_{OR1} (cm^3 s^{-1})
MMA	0.938	106.8	150	1.60×10^{-2}	3.97×10^{-14}
BA	0.894	143.4	16	2.29×10^{-3}	5.77×10^{-15}
STY	0.900	115.7	1.68	1.94×10^{-4}	4.99×10^{-16}
TBS	~0.86	~186.3	~0.01	$\sim186\times10^{-6}$	$\sim4.97\times10^{-18}$
LMA	~0.83	~306.5	~0.0001	$\sim3.06\times10^{-8}$	$\sim8.44\times10^{-20}$

be expressed according to the Lifshitz–Slezov–Wagner (LSW) theory [1,2] in a steady-state regime by Eqs. (4a) and (4b) where $D(t)$ is the droplet diameter after time t, $\tilde{D}_1$ is the diffusion coefficient of the monomer in water, and $C_{\infty,1}$ is the dimensionless solubility of the monomer in water expressed as ml of monomer per ml of water.

$$D(t) = \sqrt[3]{W_{OR1}t + D_0^3} \tag{4a}$$

$$W_{OR1} = \frac{8\tilde{D}_1 C_{\infty,1} \sigma v_{m,1}}{9RT} \tag{4b}$$

For a homologous series of organic compounds W_{OR} mainly depends on the water solubility as it was experimentally proven for *n*-alkanes in the group of Kabalnov [6]. The experimental data for OR of *n*-alkanes in aqueous emulsions stabilized with sodium dodecyl sulfate (SDS) in dependence on the water solubility as depicted in Fig. 2 clearly prove the linear relation between W_{OR}^1 and $C_{\infty,1}$ as predicted by Eq. (4b). In this graph are also plotted data for common monomers with different water solubility whereby the experimental data for $C_{\infty,1}$ were used in order to derive values for W_{OR1}. This procedure might be justified as for the monomers no experimental W_{OR1} data available. Furthermore, the differences are in the range of orders of magnitude so that even an error of a factor of 5 does not really change the conclusions drawn in further discussions.

Table 1 summarizes the data of the monomers used for the following estimations and calculations. With the data in Table 1 it is possible to get an idea about the rate of OR for neat monomer droplets (drops composed only of compound C1).

Fig. 3 illustrates again the overwhelming influence of the water solubility on W_{OR1} expressed as increase in the average droplet diameter after finishing the comminution. These data clearly show that MMA, BA, and STY emulsions degrade within minutes whereas TBS emulsions show a much slower increase in droplet size and LMA emulsions are practically stable over a period of time of several hours. OR is assumed to be controlled by diffusion of the droplet phase through the aqueous phase where there is no barrier at the interface. This might be a reasonable assumption for emulsions stabilized with common, low molecular weight surfactants [11]. Under these conditions the concentration of C1 near the droplet surface ($C_{1,S}$) is

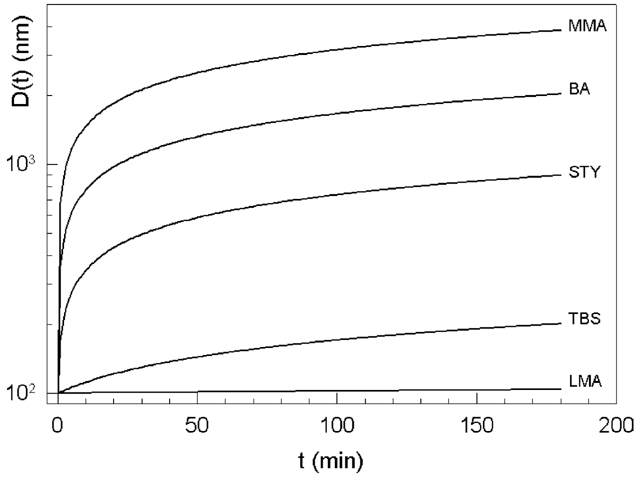


Fig. 3. Growth of average droplet diameter of monomer emulsions after stopping emulsification according to Eqs. (4a) and (4b) and data in Table 1 starting at a drop size of 100 nm.

given by the corresponding Kelvin Eq. (5),[2] which accounts for the different chemical potential of the monomer in the droplets of different size.

$$C_{1,S} = C_{\infty,1} \exp\left(\frac{4\sigma v_{m,1}}{RTD}\right) \tag{5}$$

The relative increase that is $C_{1,s}/C_{\infty,1}$ strongly depends on the droplet size as it is shown in Fig. 4 for the monomers under consideration (25 °C, $\sigma = 10$ mN m^{-1}). It is interestingly to note that first, the relative increase in the monomer concentration near the droplet surface is higher the lower the water solubility of the monomers except BA and STY.

Secondly, the increase becomes remarkable only for droplets with a size below 20 nm. This means that only for heterophase polymerizations where swollen micelles are present the monomer concentration in the aqueous phase should be higher than the water solubility of the monomer. Higher water solubility might have consequences for the polymerization kinetics in the continuous phase. It is interestingly to note, that this is obviously not the case for miniemulsion and suspension polymerizations but it should be of importance for microemulsion polymerizations during the entire reaction and during the initial stage of normal emulsion polymerizations with surfactant concentrations above the critical micelle concentration.[3]

2.2. Two component emulsion drops

Since the pioneering work of Higuchi and Mishra [12] it is known that emulsions can be stabilized against OR by co-emulsifying a second, highly water-insoluble compound (C2) with the main component (C1). C2 acts as OR retarder due to its low solubility in the continuous phase that is, it retains also C1 inside the drops for thermodynamic reasons provided there is compatibility or miscibility between C1 and C2. Such a situation can be described with Raoult's law were a solute reduces the vapor pressure and the chemical potential of the main component (expressed by the $RT \ln x$ term in Eq. (1)). The thermodynamical equilibrium between solutions with different solute concentrations ($x_{2,0}$) is reached when the chemical potentials are equalized due to distillation or diffusion of solvent (C1) from the higher to the lower concentrated solution (a process, which is called isothermal distillation or recondensation). Another possibility is the consideration of an osmotic pressure caused by C2 as it is sometimes introduced to explain the stability (cf. [13,14] and references therein). This means that the continuous phase between two drops acts as semipermeable membrane of however variable thickness and hence this approach does not contribute to better understanding especially if both C1 and C2 are soluble in the continuous phase (cf. discussion below). Moreover, the assumption of an osmotic pressure requires the presence of a pure phase C1 which however, is not the case under the experimental conditions considered. Thus, using the osmotic pressure assumption means that there is not a single osmotic pressure in the emulsion but the osmotic pressure differs in dependence on drop size and/or composition. Higuchi and Mishra [12] carried out their investigations in aqueous emulsions made of carbon tetrachloride as C1 and Nujol[4] or hexadecane as C2 with Aerosol OT as stabilizer. Ugelstad and coworkers [15] applied this principle to stabilize aqueous monomer emulsions such as styrene (C1) with octadecyl pyridinium bromide as surfactant and hexadecane or hexadecanol as C2. Experimental values of OR rates (W_{OR}) for aqueous styrene (C1) emulsions with anionic (SDS) and nonionic surfactants (ethoxylated nonylphenyl products) and a variety of C2 compounds such as hexadecane and C_{12}- and C_{18}-methacrylates were measured with dynamic light scattering by Chern and Chen [16]. These results clearly prove that degradation of styrene emulsions can be retarded due to the presence of C2. Exemplary, for emulsions stabilized with NP-40 (nonylphenol with 40 ethylene oxide units) and hexadecane as C2 with an initial drop diameter of 133 nm the authors measured OR of 28.3 nm s^{-1} at 35 °C. This value is about four times lower than that given in Table 1 (98.4 nm s^{-1}) for neat styrene drops, which was estimated based on experimental values of W^1_{OR} for n-alkanes. For styrene miniemulsions prepared with nonionic surfactants OR was found to be strongly dependent on the kind of C2 as W_{OR} for hexadecane was found to be by a factor six lower than for hexadecanol and the stearyl methacrylate retarded OR

---

[2] Eq. (5) follows from $C_{1,S} = C_{\infty,1} \exp(\Delta\mu_{1,r})$ with the assumption of only one component drops that is $x_1 = 1$.

[3] If the polymerization reaction should be confined inside emulsified monmer droplets the absence of micelles is a necessary prerequisite.

[4] Nujol is a paraffine, that is a mixture of higher alkanes.

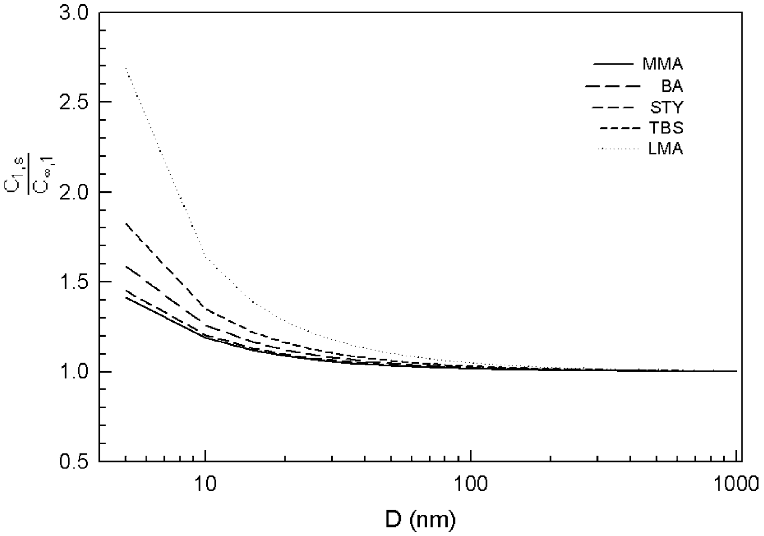


Fig. 4. Relative increase in monomer concentration near the droplet surface in dependence on drop diameter according to Eq. (5) (25 °C, $\sigma = 10$ mN m^{-1}, other parameters see Table 1).

stronger than LMA. For emulsions made with SDS as surfactant the authors observed decreasing W_{OR} with increasing $x_{2,0}$ (LMA as C2) whereas the initial drop diameter after homogenization was independent of $x_{2,0}$ at about 133 ± 10 nm. The experimental study of Chern and Chen [16] leads to important conclusions. First, OR can easily be retarded by co-emulsification with C2 but it is not that easy to prevent it at all. Second, W_{OR} depends besides on the chemical nature of C2 also on the drop composition ($x_{2,0}$). From a theoretical point of view these experimental findings are not surprising. A deeper understanding of emulsion stability and OR is possible by means of Eqs. (1) and (2) as it will be discussed in the following parts.

The derivative of Eq. (2) allows quantification of the condition $\partial\mu_{1,r}/\partial D > 0$ as expressed by inequality (6).

$$\frac{\partial\mu_{1,r}}{\partial D}(D_0) > 0 \Rightarrow x_{2,0} > \frac{4\sigma v_{m,1}}{(3RTD_0 + 4\sigma v_{m,1})} \tag{6}$$

As $4\sigma v_{m,1}$ is by orders of magnitude smaller than $3RTD_0$[5] the inequality (6) can be simplified to (7) assuming that the drop size distribution at the end of the comminution is sufficiently narrow. This relation describes a lower limit for $x_{2,0}$ whereas Eq. (3) gives the upper limit. Both expressions differ only by a factor of 3, which becomes obvious if Eq. (3) is developed in a series to replace the exponential.

$$x_{2,0} > \frac{4\sigma v_{m,1}}{3RT\bar{D}_0} \tag{7}$$

Inequality (7) describes the necessary relation between the (minimum) average initial drop size $\bar{D}_0$ and the mol fraction of C2 per (average) drop that should be realized by the experimenter during emulsion preparation in order to get an emulsion, which is able to reach an equilibrium size distribution. A real emulsion is at the end of the comminution process not perfectly monodisperse but the drop sizes distribute over a certain range. As $x_{2,0}$ is the same in each drop the chemical potential of the drops is different and hence, the drops start to change their composition by OR of only C1 as C2 has zero solubility in water. Regarding OR the following cases have to be distinguished.

$$C_{\infty,2} = 0 \quad \text{and} \quad \frac{\partial\mu_{1,r}}{\partial D} > 0 \tag{1.A}$$

The zero solubility of C2 in the continuous phase ($C_{\infty,2} = 0$) means that the number of drops remains constant. Assuming further that the stability condition given by Eqs. (6) and (7) is fulfilled, only C1 diffuses from the smaller to the larger drops leading to a change in the droplet composition that is x_1 and x_2 increases in the larger and smaller drops, respectively. Consequently, the chemical potential of C1 in the smaller drops is lower than in the larger drops. However, this effect might be compensated by the contribution of the curvature to the chemical potential (first term on the right hand side of Eq. (1)), which is larger for smaller drops. Thus, eventually a situation is reached where the chemical potentials of C1 equal in each drops of different size. At this point OR of the emulsion by C1 stops and in the case of zero solubility of C2 in the continuous phase OR stops at all. The drop size distribution has changed in this case in a way that its width has broadened compared to the initial situation at the end of the comminution process. Within this scenario subsequent polymerization, assuming the initiation is fast enough and the thermodynamical conditions in the drops do not change, may lead to

---

[5] Assuming styrene emulsion at 25 °C, $\sigma = 10$ mN m^{-1} $4\sigma v_{m,1} = 4.63 \times 10^{-6}$ N m^2 mol^{-1} and $3RTD = 2.23 \times 10^{-3}$ N m^2 mol^{-1}.

predominantly polymerization in the preformed emulsion droplets.

$$\underline{C_{\infty,2} = 0 \quad \text{and} \quad \frac{\partial \mu_{1,\mathrm{r}}}{\partial D} < 0} \tag{1.B}$$

Assuming now the experimenter has not met the necessary condition for reaching an equilibrium that is $\partial\mu_{1,\mathrm{r}}/\partial D < 0$ or $x_{2,0} < 4\sigma v_{\mathrm{m},1}/3RT\bar{D}_0$ OR of C1 will not lead to an equilibration of the chemical potentials but will rather increase the differences between drops of different sizes. In the course of this process the smaller drops become richer in x_2 and might reach a situation where the equilibrium condition $\partial\mu_{1,\mathrm{r}}/\partial D > 0$ for their drop size is fulfilled. Consequently, these drops will form a fine-drop fraction, which means that the initially monomodal drop size distribution becomes bimodal. The large-size drop fraction continues with OR thus, the fraction of larger drops in the drop size distribution decreases while the fraction of small-sized drops increases. Polymerization may be initiated in this case in the fine-drop fraction, which then might be regarded as seed particles where monomer is supplied from the larger drops until they become itself locus of initiation, as they do not completely disappear due to the presence of C2.

$$\underline{C_{\infty,2} > 0} \tag{2.}$$

This situation is highly important for practical polymerization processes in preformed emulsions with droplet diameters in the sub-micrometer range as low molecular weight C2 components always possess a nonzero water solubility.[6] Under theses conditions it is necessary to consider volume fluxes of C1 and C2 ($\dot{J}_1$, $\dot{J}_2$) from the drops according to the LSW-theory (Eqs. (12a) and (12b)) where the concentrations of C1 and C2 near the drop surface are given be Eqs. (11a) and (11b), the α's are the characteristic lengths of C1 and C2 $\alpha_1 = (4\sigma v_{\mathrm{m},1})/RT$, $\alpha_2 = (4\sigma v_{\mathrm{m},2})/RT$, $\tilde{D}_1$, $\tilde{D}_2$ are the diffusion coefficients of C1 and C2 in the continuous phase, respectively, and c_1, c_2 are their concentrations in the continuous phase.

$$C_{\mathrm{s},1} = C_{\infty,1}(1 - x_2)\exp\left(\frac{\alpha_1}{D}\right) \tag{11a}$$

$$C_{\mathrm{s},2} = C_{\infty,1}x_2\exp\left(\frac{\alpha_2}{D}\right) \tag{11b}$$

$$\dot{J}_1 = 2\pi\tilde{D}_1 D\left[c_1 - C_{\infty,1}(1 - x_2)\exp\left(\frac{\alpha_1}{D}\right)\right] \tag{12a}$$

$$\dot{J}_2 = 2\pi\tilde{D}_2 D\left[c_2 - C_{\infty,2}x_2 \exp\left(\frac{\alpha_2}{D}\right)\right] \tag{12b}$$

If $C_{\infty,1} > C_{\infty,2}$ the situation is comparable with that described above for zero solubility in water where the fast distribution of C1 between the droplets causes the sharp retardation of its mass transfer in a kind of self-terminating process. However, due to the nonzero solubility of C2 in the continuous phase OR continues with correspondingly reduced rate after the distribution of C1 is finished. In this case a pseudo- steady state might be reached where further changes in the drop size composition and drop size distribution take place at much longer time scales than needed to finish polymerization.

In the practical case of a polydisperse drop size distribution there are with respect to the volume flux three kinds of drops: drops with a size smaller than a critical size (D_{C})[7] for which $\dot{J}_2 < 0$, drops with $D > D_{\mathrm{C}}$ for which $\dot{J}_2 > 0$, and the critical drops for which $\dot{J}_2 = 0$. Expressing the concentration of C2 in the medium (c_2) from $\dot{J}_2(D_{\mathrm{C}}) = 0$ results Eq. (13) from (12b) where x_2 is expressed as dependent on the drop size.

$$\dot{J}_2 = 2\pi\tilde{D}_2 C_{\infty,2}\left[x_2(D_{\mathrm{C}})\exp\left(\frac{\alpha_2}{D_{\mathrm{C}}}\right) - x_2(D)\exp\left(\frac{\alpha_2}{D}\right)\right] \tag{13}$$

Assuming the average drop size and x_2 of the maturating emulsion are close to an equilibrium situation regarding C1 corresponding to Eq. (2)[8] follows finally Eq. (14) when the equilibrium molar fraction of C2 in dependence on D and D_{C} are expressed according to Eq. (3) and if the exponential terms are expanded in a Taylor series truncated after the second term.

$$\begin{aligned} \dot{J}_2 &\approx 2\pi\tilde{D}_2 C_{\infty,2}[x_2(D_{\mathrm{C}}) - x_2(D)] \\ &\approx 2\pi\tilde{D}_2 C_{\infty,2}\left(\frac{\alpha_1}{D_{\mathrm{C}}} - \frac{\alpha_1}{D}\right) \end{aligned} \tag{14}$$

Supposing for the following considerations that $x_2 \gg \alpha_1/\bar{D}_0$ after finishing comminution and that this relation becomes more reliable during the maturation as the average drop size increases. The changes in x_2 may now be illustrated by consideration of two arbitrary drops (indicated by superscripts 'a' and 'b') where the changes in C2 are governed by Eqs. (15a) and (15b)[9] assuming the two drops are in equilibrium as indicated by the subscript 'e' (cf. also Footnote 1).

$$x_{\mathrm{e},2}^{\mathrm{b}} - x_{\mathrm{e},2}^{\mathrm{a}} = \alpha_1\left(\frac{1}{D_{\mathrm{e}}^{\mathrm{b}}} - \frac{1}{D_{\mathrm{e}}^{\mathrm{a}}}\right) \tag{15a}$$

---

[6] It is to note, that the situation might be different in so-called inverse emulsions where an organic solvent forms the continuous phase.

[7] The critical drop size with respect to C2 is given by: $D_{\mathrm{C}} = \alpha_2/(\ln[c_2/(C_{\infty,2}x_2(D_{\mathrm{C}}))])$.

[8] From the situation found close to an equilibrium an equation follows such that $(1 - x_2(D_{\mathrm{C}}))\exp(\alpha_1/D_{\mathrm{C}}) \approx (1 - x_2(D))\exp(\alpha_1/D)$, which allows us to assume that $D_{\mathrm{C}} \approx D$ for developing the exponentials in Eq. (13). Note, that $\dot{J}_1 = 0$ follows strictly from the equilibrium.

[9] (15a) and (15b) describing the same situation whereby (15a) is obtained if the $\ln(1 - x_{\mathrm{e},2})$ terms are approximated by a Taylor series truncated after the first term.

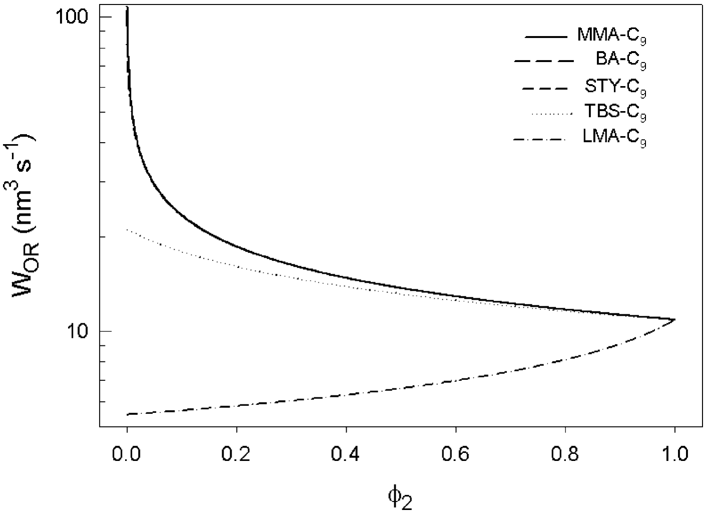


Fig. 5. Dependence of W_{OR} on ϕ_2 (nonane) for various monomers (values for W^1_{OR} and W^2_{OR} taken from Table 1).

$$\frac{1-x^{\mathrm{a}}_{\mathrm{e},2}}{1-x^{\mathrm{b}}_{\mathrm{e},2}} = \exp\left[\alpha_1\left(\frac{1}{D^{\mathrm{b}}_{\mathrm{e}}} - \frac{1}{D^{\mathrm{a}}_{\mathrm{e}}}\right)\right] \qquad (15\mathrm{b})$$

Eqs. (15a) and (15b) show that the change in the mol fraction of C2 are in the order of $\Delta x_2 \sim \alpha_1/\bar{D}$ where $\bar{D}$ is the average drop size and that the relative change in the drop composition due to recondensation is small ($\Delta x_2/x_2 \ll 1$).

It is a reasonable assumption that the volume fluxes of the components ($\dot{J}_1$, $\dot{J}_2$) are proportional to their volume fractions in the droplets (ϕ_1, ϕ_2) and that the sum of the volume fluxes of C1 and C2 equals the droplet volume change rate as expressed in Eq. (16).[10] For the subsequent discussion of this equation it is necessary to remind that for the condition under consideration OR is governed by diffusion of the barely soluble component C2.

$$\dot{J}_1 + \dot{J}_2 = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\pi}{6}D^3\right) = 2\pi\tilde{D}_2\frac{C_{\infty,2}\alpha_1}{\varphi_2}\left(\frac{D}{Dc} - 1\right) \qquad (16)$$

Eq. (16) is similar to the volume growth law of the LSW theory for one-component particles. It is noteworthy to mention that for the two component particles the characteristic length of C1 and the diffusion coefficient of the second component enter the expression and that the solubility is expressed by $C_{\infty,2}/\varphi_2$. Thus the analogous expression to W_{OR1} (Eq. (4b)) for two-component particles (W_{OR2}) is given by Eq. (17) and the reduction factor of OR caused by the presence of C2 (F_{red}) is defined by Eq. (18).[11]

$$W_{\mathrm{OR2}} = \frac{8C_{\infty,2}\sigma v_{\mathrm{m},1}}{9\varphi_2 RT} \qquad (17)$$

$$F_{\mathrm{RED}} = \frac{W_{\mathrm{OR}}}{W_{\mathrm{OR2}}} = \frac{\tilde{D}_1 C_{\infty,1}\varphi_2}{\tilde{D}_2 C_{\infty,2}} \qquad (18)$$

For the subsequent discussion Eq. (18) is rearranged illustrating that it is composed of three ratios R_{DC}, R_{S}, and ϕ_2 the ratio of the diffusion coefficients of C1 and C2, the ratio of the solubilities of C1 and C2, and the volume of C2 per drop volume, respectively.

$$F_{\mathrm{RED}} = R_{\mathrm{DC}} R_{\mathrm{S}} \phi_2 \qquad (19)$$

Kabalnov showed [3] in numerical simulations that for low molecular weight components C1 and C2 the product $R_{\mathrm{S}}\,\phi_2$ determines the recondensation process. If $R_{\mathrm{S}}\phi_2 \geq 1$ the second, barely soluble component determines the rate of OR whereas if $R_{\mathrm{S}}\,\phi_2 \leq 1$ OR takes place with the same rate as in the absence of C2. Kablanov [3] fitted these two kinetic regimes with Eq. (20) neglected any differences regarding the molar volumes and interfacial tensions between C1 and C2 where W^1_{OR} and $W^2_{\mathrm{OR}}$are the rates of OR of the pure components C1 and C2, respectively.

$$W_{\mathrm{OR}} = \left(\frac{\phi_1}{W^1_{\mathrm{OR}}} + \frac{\phi_2}{W^2_{\mathrm{OR}}}\right)^{-1} \qquad (20)$$

The dependence given by Eq. (20) is extremely asymmetric as already small ϕ_2-values cause a substantial retardation of OR. Contrary, even larger amounts of C1 (high ϕ_1-values) practically do not affect OR. Fig. 5 illustrates properties of the Kabalnov—Eq. (20) describing OR by means of some model calculations for monomers of different water solubility as C1 with nonane as C2.

All curves depicted clearly show the influence of the C2 compound. Except for LMA W_{OR} decreases with increasing amount of nonane and reaches in any case the value for pure nonane at $\phi_2 = 1$. LMA shows the opposite behavior as its

---

[10] Note, there is a misprint in the corresponding equation in Kabalnov's original paper [3] (Eq. (17)) where the expression in the parenthesis on the right hand side is written as $((1/a_{\mathrm{c}}) - (1/a))$ where a_{c} and a are the critical radius and the radius, respectively, leading to the wrong dimension of the volume change rate.

[11] It is necessary to mention that the reduction factor as defined by Higuchi and Mishra [12] is incorrect as already stated by Kablanov in his original paper [3].

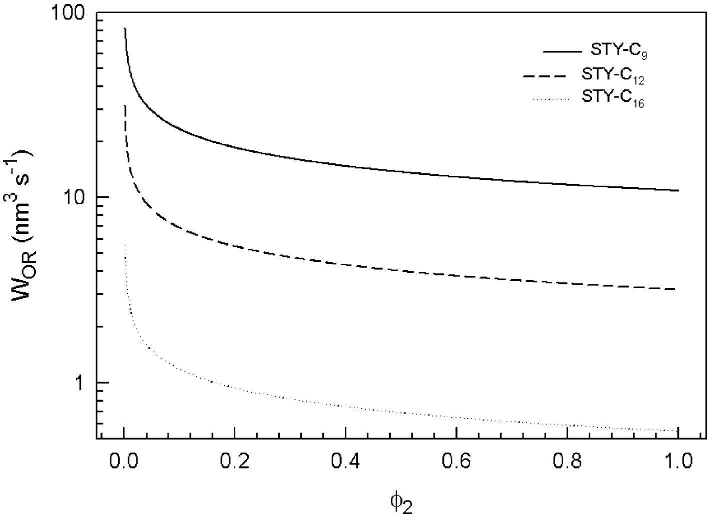


Fig. 6. Dependence of W_{OR} on ϕ_2 of styrene emulsions with nonane, dodecane, and hexadecane as C2 (values for W_{OR}^1 and W_{OR}^2 taken from Table 1).

solubility in water is lower than that of nonane (cf. Table 1). This means that LMA practically acts as C2 for nonane. It is noteworthy that the R_S values of the combinations C1/C2 used for creating Fig. 5 span a range between 5.16×10^4 for MMA and 9.78×10^{-2} for LMA. Furthermore, these data show that regarding the rate of Ostwald ripening MMA, BA, and STY behave almost identical despite their different water solubilities as OR of these emulsions is dominated absolutely by nonane. The strong influence of the $C_{\infty,2}$-value is demonstrated by the data depicted in Fig. 6 for styrene emulsions and nonane, dodecane, and hexadecane as C2.

These curves show that W_{OR} slowed down by more than one order of magnitude when $C_{\infty,2}$ was decreased by four orders of magnitude, that is from 3.1×10^{-7} (nonane) to 2.7×10^{-11} (hexadecane).

2.3. Some considerations for practicing heterophase polymerizations

Some additional remarks are necessary regarding the influence of the nature of C2 on emulsion preparation which might of importance for subsequent polymerization. Eq. (1) and the above discussion regarding Raoult's law implies that only colligative properties in connection with C2, provided its solubility in the continuous phase is low enough, are of importance. But what happens if C2 has a certain surface activity? In this case the surface tension of the droplets becomes dependent on the drop composition. This means that during the period of ripening σ decreases for smaller and increases for larger drops as ϕ_2 increases and decreases, respectively. Besides the concentration influence of C2 the decrease in σ with increasing ϕ_2 would decrease the driving force for recondensation of the main component and hence, additionally protect the droplets against OR (cf. Eqs. (2), (4a) and (4b).

Another interesting aspect deals with the question what happens if C2 is a polymeric material. This is of special interest for subsequent polymerization reaction in emulsions as the polymeric C2 can be of the same or of very similar nature as the monomer or monomer combination forming the emulsion droplets, which means that the final polymer particles are not contaminated with foreign materials. Furthermore, the solubility of polymer molecules like polystyrene in water is above a certain degree of polymerization practically zero thus, favoring a scenario as described in (8) where $C_{\infty,2}=0$ and $\partial\mu_{1,r}/\partial D>0$. This situation should be advantageous for getting an equilibrium droplet size distribution for subsequent polymerizations. Indeed polymers as C2 have been successfully used as C2 in so-called miniemulsion polymerizations either in combination with hexadecane and hexadecanol [17] or as sole C2 [18]. As the retardation of OR and the reaching of an equilibrium droplet size distribution require for a given average droplet size C2 above a certain mol fraction the weight percentage of C2 in the emulsion strongly depends on its molecular weight. Table 2 compares the composition of stable styrene emulsions prepared with either hexadecane or polystyrene with a molecular weight of 5×10^4 g mol^{-1} as C2 for various average drop sizes. The amount of C2 was calculated according to Eq. (3) for a temperature of 5 °C during the homogenization and 1 mol of styrene (104.15 g).

According to the data in Table 2 an emulsion, which is stabilized against OR with a high molecular weight polymer instead of a low molecular weight compound has a

Table 2
Influence of the molecular weight of C2 on the composition of stable styrene emulsions

D (nm)	Hexadecane (226.45 g mol^{-1})	Polystyrene (5×10^4 g mol^{-1})
50	8.63 g	1905 g
150	2.84 g	627 g
300	1.41 g	311 g

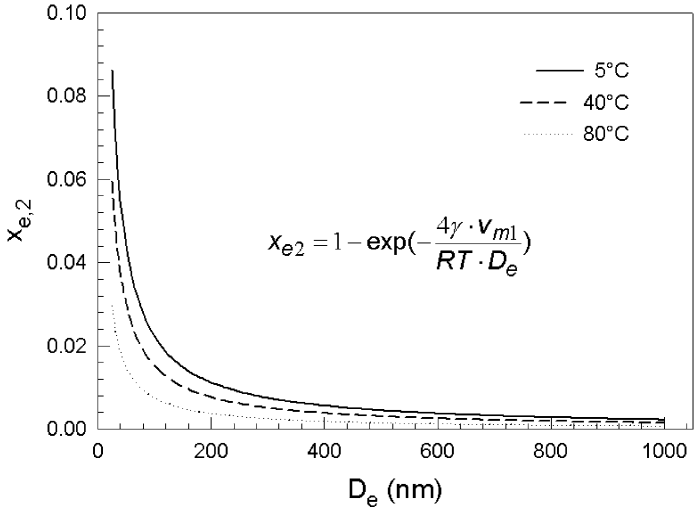


Fig. 7. Dependence of the mol-fraction C2 on the particle size for the equilibrium situation as described by Eq. (3) for different temperatures (the calculation have been carried for styrene with the temperature dependent values given in Table 3).

completely different composition, as the major component by weight is the polymer and not the emulsified oil. Thus, in order to preserve the properties of the main component C2 should have a molecular weight as low as possible. However, the situation is different if a polymeric hybrid system should be obtained after polymerization of the preformed emulsion. In this case, a high polymer as C2 might be a clever solution.

The data depicted in Figs. 5 and 6 allow some conclusions regarding the selection of comonomers for any kind of copolymerization in preformed mixed monomer emulsion droplets. A water-insoluble monomer acts as C2 and might prevent OR of other monomers with much higher solubility in water. However, the situation is much more interesting for stoichiometric polymerizations or polycondensation reactions. In this case it should be possible to get high molecular weight polymers in preformed droplets only if at least one monomer is highly water-insoluble, provided the monomers mixed are compatible. Moreover, the stoichiometric mixture ensures that a rather broad droplet size distribution should be stable.

The LSW theory [1,2] for single component emulsions and the extensions made by Kabalnov et al. [3] for two component emulsions are good theoretical tools to understand OR and its retardation as well as the conditions required to get an equilibrium drop size distribution. The main points that should be considered by experimenters are as follows.

In general, emulsions made by any comminution technique, also two component emulsions containing C2 with a much lower solubility in the continuous phase than the main component C1, are not stable per se against Ostwald ripening unless they are perfectly monodisperse and they contain a mol-fraction of C2 given by relation (6) or Eq. (3). Both equations correlate x_2 with the drop size of the emulsion as it is shown in Fig. 7 assuming the equilibrium as described by Eq. (3) that is denoted by the subscript 'e' (Table 3).

The data in Fig. 7 clearly show that different particle sizes require different amounts of C2. However, according to the inequality given with relation (6) an amount of C2 that is sufficient for a drop size D_1 is able to stabilize also emulsions with size D_2 when $D_2 > D_1$. In this sense results of miniemulsion polymerizations should be mentioned where at given C2 latexes with pretty much different particle sizes have been obtained by variation of the surfactant concentration [19,20]. These data basically confirm the role of the surfactant concentration also for this kind of heterophase polymerization as the amount of hexadecane (C2) was according to Eq. (6) high enough to stabilize droplets with sizes above 35 nm in both set of experiments ($x_2 = 0.01866$ in [19] and $x_2 = 0.01806$ in [20]. Also the experiments described in [19] with variable C2 concentration are not really suited to shed light on the role of hexadecane as by varying x_2 between 0.00152 and 0.02954 the average particle size practically does not change (from 108.5 to 100.6 nm by dynamic light scattering). Except the lowest hexadecane concentration, which according to Eq. (6) is still high enough to stabilize droplets with diameters larger than about 400 nm, all other x_2-values were high enough to stabilize drops with diameters above 80 nm.

Usually the preparation and the polymerization of emulsions are carried out at different temperatures. The data summarized in Fig. 7 show that emulsions prepared at low temperatures and then stored or polymerized at higher

Table 3
Parameters used for the calculations to get the data depicted in Fig. 7

T (°K)	$v_{m,1}$ (m^3 mol^{-1})	σ (N m^{-1})
278.15	1.1345×10^{-4}	0.0115
313.15	1.1743×10^{-4}	0.0085
353.15	1.2257×10^{-4}	0.0045

temperature should face no problem regarding OR as the C2 values are high enough and the temperature increase improves the conditions corresponding to Eqs. (3) and (6).

3. Conclusions

The above theoretical considerations lead to the conclusions that as long as the technique employed to prepare emulsions results in droplets with a size distribution the drop size distribution will change after stopping the comminution. Also, the addition of C2 that is insoluble ($C_{\infty,2}=0$) in the continuous phase cannot prevent this effect. However, if the amount of C2 is so high that for all drops in the emulsion after its preparation $x_{2,0}>(4\sigma v_{\mathrm{m},1})/(3RT\bar{D}_0)$ the emulsion can reach a stable, equilibrium drop size distribution. For practical application it is important that C2 is able to retard OR so strongly that it takes place with characteristic times much longer than the duration of typical polymerization reactions.

References

[1] Lifshitz IM, Slezov VV. Zh Exp Teor Fiz 1958;35(2(8)):479–92.
[2] Wagner CZ. Elektrochem 1961;65(7/8):581–91.
[3] Kabalnov AS, Pertzov AV, Shchukin ED. Colloid Surf 1987;24: 19–32.
[4] Taylor P. Adv Colloid Interf Sci 1998;75:107–63.
[5] Tauer K. Surface chemistry in the polymerization of emulsion. In: Holmberg K, editor. Handbook of applied colloid and surface chemistry. New York: Wiley; 2001. p. 175–200.
[6] Kabalnov AS, Makarov KN, Pertzov AV, Shchukin ED. J Colloid Interf Sci 1990;138(1):98–104.
[7] Daubert TE, Danner RP, Sibul HM, Stebbins CC. Physical and thermodynamic properties of pure chemicals: data compilation. Washington, DC: Taylor and Francis; 1998.
[8] Vanderhoff JW. Chem Eng Sci 1993;48(2):203–17.
[9] Vandezande GA, Smith OW, Bassett DR. Vinyl acetate polymerization. In: Lovell PA, El-Aasser MS, editors. Emulsion polymerization and emulsion polymers. Chichester: Wiley; 1997. p. 563–87.
[10] Yalkowsky SH, Banerjee S. Aqueous solubility—methods of estimation for organic compounds. New York: Marcel Dekker, Inc; 1992.
[11] Taylor MA. Synthesis of polymer dispersions. In: Urban D, Takamura K, editors. Polymer dispersions and their industrial applications. Weinheim: Wiley-VCH; 2002. p. 15–40.
[12] Higuchi WI, Mishra J. J Pharm Sci 1962;51:459–66.
[13] Webster AJ, Cates ME. Langmuir 1998;14:2068–79.
[14] Landfester K. J Disp Sci Technol 2002;23(1–3):167–73.
[15] Ugelstad J, Mork PC, Kaggerud KH, Ellingsen T, Berge A. Adv Colloid Interf Sci 1980;13:101–40.
[16] Chern CS, Chen TJ. Colloid Surf, A: Physicochem Eng Asp 1998;138: 65–74.
[17] Miller CM, Sudol ED, Silebi CA, El-Aasser MS. J Polym Sci: Part A: Polym Chem 1995;33:1391–408.
[18] Wang ST, Schork FJ, Poehlein GW, Gooch JW. J Appl Polym Sci 1995;60(12):2069–76.
[19] Landfester K, Bechthold N, Tiarks F, Antonietti M. Macromolecules 1999;32:5222–8.
[20] Anderson CD, Sudol ED, El-Aasser MS. Macromolecules 2002;35: 574–6.