Modeling Particle Formation in Emulsion Polymerization: An Approach by Means of the Classical Nucleation Theory

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ABSTRACT: A framework for modeling particle nucleation in emulsion polymerization has been developed on the basis of a combination of classical nucleation theory with radical polymerization kinetics and the Flory–Huggins theory of polymer solutions. The basic assumption is that water born oligomers form stable nuclei under critical conditions. The only adjustable model parameter is the activation energy of nucleation. The model allows us to calculate the chain length of the nucleating oligomers, the number of chains forming one nucleus, the diameter of the nucleus, the total number of nuclei formed, and the rate of nucleation.

Introduction

The period of particle formation is a very complex process in emulsion polymerization. During the last decades several models have been developed to describe the particle nucleation stage as, for instance, micellar nucleation,[1,2] homogeneous nucleation,[3–5] or homogeneous coagulative nucleation.[6,7] However, with the experimental data available today it is not possible to refute any of these models. All of them are based on radical polymerization kinetics with an additional assumption regarding the radical capture by micelles or particles as well as assumptions regarding the radical exit. For homogeneous nucleation models it is assumed that nucleation occurs when the chain length of the water soluble oligomer radical, j, has reached a critical value, j_{crit}. A value of $j > j_{\mathrm{crit}}$ leads to the precipitation of the now water insoluble oligomeric chain as particle or precursor particle.

Contrary to this picture, it might be possible to apply the classical nucleation theory (CNT) if one considers that nucleation in emulsion polymerization is the formation of a new phase, as it is also the condensation of vapor, the freezing of a liquid, or the precipitation of a solute from solution. Barrett[8] started to go this way for particle nucleation in dispersion polymerization where the monomers are soluble in the dispersing agent, usually an organic solvent. Therefore, j_{crit} is much higher than that in emulsion polymerization. The approach of Barrett[8] consists of a combination of CNT with the Flory–Huggins theory of polymer solution in order to estimate the nucleation behavior in a qualitative way. Barrett[8] also made some qualitative estimations especially with respect to the influence of the radical polymerization kinetics on nucleation behavior.

The aim of this paper is to develop a framework for modeling particle nucleation in emulsion polymerization based on a combination of CNT, Flory–Huggins theory, and radical polymerization kinetics in a quantitative way. With such a model it might be possible to predict the actual first nucleation step in an emulsion polymerization with respect to j_{crit}, nucleation time (time gap between the start of polymerization and particle appearance), diameter of nuclei, number of oligomeric chains per nucleus, and concentration of nuclei, respectively. Styrene, methyl methacrylate, and vinyl acetate have been chosen as monomers for the calculations. These monomers are some of the best investigated monomers in emulsion polymerization, and the kinetic constants needed are available from literature as well as experimental data regarding j_{crit}. Furthermore, these monomers differ by about 2 orders of magnitude in their water solubility, which is really an essential monomer property for nucleation.

Model Development

It is well established in CNT[9] that, if no foreign phase is present, the formation of a new phase starts with the formation of small clusters. These clusters may redissociate or grow by accretion to become nuclei of the new phase. For emulsion polymerization this process may be described as follows

$$mP_j \rightarrow (P_j)_m$$

where m is the number of oligomeric chains P_j of chain length j forming one cluster. Additionally, the surface energy, σa_{n}, of the clusters impedes the nucleation. Thus, the free energy of formation of a cluster may be written as (1), where S is the supersaturation of the P_j's

$$\Delta G = -mkT \ln S + \sigma a_{\mathrm{n}} \qquad (1)$$

in water (ratio of concentration to solubility), a_{n} is the surface of a nucleus, and σ is the interfacial tension nucleus to water. Substituting a_{n} by m and j one gets (2) describing the energy difference between m molecules in solution and the solid nucleus consisting of m molecules with chain length j.

$$\Delta G = -c_1 m \ln S + c_2 (mj)^{2/3}\sigma \qquad (2)$$

$$c_1 = 4.1868 \times 10^7 RT/N_{\mathrm{A}}\ (erg)$$

$$c_2 = (4\pi)^{1/3}\left(\frac{3\mathrm{MG}_{\mathrm{mon}}}{d_{\mathrm{p}}N_{\mathrm{A}}}\right)^{2/3}\ (cm^2)$$

Here N_{A} is Avogadro's number, R is the gas constant, T is the absolute temperature, d_{p} is the polymer density, and $\mathrm{MG}_{\mathrm{mon}}$ is the molecular weight of the monomer, respectively.

The curve ΔG versus m goes through a maximum; however for small values of m, ΔG is always positive. As the second derivative of ΔG with respect to m is always negative, the equilibrium is not stable; e.g. the

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system shows no tendency to go back to the equilibrium state if once moved a little bit apart from it. This means, that nuclei with m smaller than a critical value, M_c, will dissolve, whereas nuclei with $m > M_c$ will grow indefinitely. M_c is the critical value of m corresponding to the maximum in the ΔG versus m curve. Furthermore, one obtains from (2) eqs 3–5 for $\Delta G_{\max}$ and the

$$\Delta G_{\max} = \frac{4}{27}\frac{c_2^{\,3}}{c_1^{\,2}}\frac{j^2\sigma^3}{(\ln S)^2} \qquad (3)$$

$$M_c = \left(\frac{2}{3}\frac{c_2}{c_1}\frac{j^{2/3}\sigma}{\ln S}\right)^3 \qquad (4)$$

$$D_c = 10^7\frac{2}{3}\left(\frac{6}{\pi}\right)^{1/3}\frac{C_1}{C_2}\left(\frac{\mathrm{MG}_{\mathrm{mon}}}{d_p N_A}\right)^{1/3}\frac{j\sigma}{\ln S} \qquad (5)$$

critical values M_c and D_c (critical nucleus size), respectively. $\Delta G_{\max}$ corresponds to an activation energy of nucleation. Therefore the number of nuclei formed, N_c, and the rate of nucleation, R_n, can be expressed according to Nielsen[10] as follows, leading to (6) and (7). k_n is

$$N_c = \frac{1}{\nu_w}\exp(-\Delta G_{\max}/kT) \qquad (6)$$

$$R_n = k_n N_c \qquad (7)$$

$$k_n = \frac{2d}{\left(\frac{6}{\pi}\frac{\mathrm{MG}_w}{d_w}\frac{1}{N_A}\right)^{2/3}}$$

the nucleation rate constant,[10] v_w is the molar volume of water, and d is the diffusion coefficient of the oligomers in water. To calculate the supersaturation, S, relations are needed for the concentration of oligomers, $C(j,t)$, and for their solubility $C_0(j)$.

Equation 9 should be valid for the solubility of the oligomers dependent on their chain length if an approximation is used to calculate ϕ_2 (ϕ_2 is the volume fraction of oligomers in diluent phase; χ is the Flory–Huggins interaction parameter) proposed by Barrett's[8] equation (8).

$$\ln \phi_2 = j(1 - \chi - 1/j) \qquad (8)$$

$$C_0(j) = \frac{\phi_2 d_p}{j\cdot MG_{\mathrm{mon}}(1 - \phi_2)} \qquad (9)$$

The current total (cumulative) concentration of oligomers, $C(j,t)$, depending on polymerization time and chain length, can be calculated using well-known equations from radical polymerization kinetics,[11] (10)–(12).

$$C(t,j) = \frac{1}{2}\frac{\beta}{(1+\beta)^j}I_0(1 - \exp(-k_d t)) \qquad (10)$$

$$\beta = \frac{(2fk_d I k_t)^{1/2}}{k_p M_w} \qquad (11)$$

$$I = I_0\exp(-k_d t) \qquad (12)$$

In these equations I_0 is the initiator concentration, I is the current initiator concentration at time t, k_d is the initiator decomposition rate constant, $2fk_d$ is the radical flux, f is the radical efficiency factor, k_t is the termination rate constant, k_p is the propagation rate constant, and M_w is the monomer concentration in the water phase.

With (3)–(12) it might be possible to estimate the nucleation behavior in emulsion polymerization by starting with a total homogeneous system consisting of water, monomer, and initiator solved in water, respectively. However, if particles are present, these equations must be modified due to the capture of oligomers by particles, thus reducing the oligomer concentration and subsequently lowering the supersaturation. Furthermore, within this model the supersaturation has different properties than in the case of phase formation without chemical reaction, such as the crystallization of electrolytes. According to eqs 9 and 10, S depends very strongly on the chain length of the oligomers, j, which again depends on the polymerization conditions. The higher the value of j the lower the oligomer solubility and the lower the necessary concentration to reach the supersaturation for phase formation.

The equations are easy to solve numerically, and the solutions may be considered as matrices with the variables t and j. To solve the equations, that means to calculate for which values of j and t nucleation occurs, the following algorithm was applied: (a) nucleation occurs if $\Delta G_{\max} \gg vkT$ (nucleation condition, v is a simple parameter to modify activation energy), (b) nucleation occurs only if $M_c(j,t)$, $D_c(j,t)$, $N_c(j,t)$, and $R_n(j,t)$, are positive (physically meaningful), (c) for negative values $M_c(j,t)$, $D_c(j,t)$, $N_c(j,t)$, and $R_n(j,t)$ were set equal to zero, and (d) a nucleation surface plot was constructed by multiplying the matrices $M_c(j,t)$, $D_c(j,t)$, $N_c(j,t)$, and $R_n(j,t)$ element by element whereby a value greater than zero for the resulting matrix indicates that nucleation can take place for the corresponding j and t values, that means in the j–t plane spikes occur, indicating nucleation.

Model Parameters

Besides the kinetic rate constants which today can be estimated with high certainty, the two key parameters for modeling the nucleation behavior are the Flory–Huggins parameter in water as well as the nucleus to water interfacial tension. As far as is known there are no data published for oligomers, so that both values can only roughly be estimated. For the estimations it is important to point out that only persulfate-initiated polymerization will be considered, leading to oligomers with an ionic group.

Interfacial Tension. The true values of the interfacial tension nucleus to water cannot be determined directly. Swelling experiments of a small sized polymer latex with its own monomer seem to be an access to obtaining good approximations mainly for two reasons: (1) according to the Morton, Kaizerman, and Altier equation[12] the swelling behavior depends strongly on the particle to dispersing agent interfacial tension, and (2) in reality the dispersing agent is not pure water but an aqueous solution of initiator and emulsifier saturated with monomer.

Latex swelling experiments have been summarized by Gardon.[13] He pointed out that σ is in between 1 and 30 mN m^{-1} and should be strongly dependent on the surface concentration of ionic groups, emulsifier concentration, and monomer concentration in the particles and in water. Assuming that just after nucleation the

Table 1. Kinetic Constants and Model Parameters for STY (Styrene), MMA (Methyl Methacrylate), and VAC (Vinyl Acetate)

	STY	MMA	VAC	comment
d, cm^2 s^{-1}	1×10^{-5}	1×10^{-5}	1×10^{-5}	oligomer diffusion in water
f	0.5	0.5	0.5	radical efficiency factor
k_d, s^{-1}	1×10^{-6}	1×10^{-6}	1×10^{-6}	initiator decomposition
k_{pl}, cm^3 mol^{-1} s^{-1}	7×10^5	3.3×10^6	2×10^6	monomer addition to primary radical, initiation
k_{p2}, cm^3 mol^{-1} s^{-1}	4.5×10^5	3.3×10^6	6.5×10^5	first monomer addition after initiation
k_p, cm^3 mol^{-1} s^{-1}	2.6×10^5	3.3×10^6	6.5×10^5	monomer addition if $j \geq 2$
k_t, cm^3 mol^{-1} s^{-1}	3×10^{12}	3×10^{12}	3×10^{12}	radical termination
d_p, g cm^{-3}	1.054	1.17	1.18	density polymer
d_w, g cm^{-3}	1.0	1.0	1.0	density water
I_0, mol cm^{-3}	6×10^{-6}	6×10^{-6}	6×10^{-6}	initial initiator concentration
$\mathrm{MG_m}$	104.15	86.09	100.12	molecular weight of monomer
$\mathrm{MG_w}$	18.0	18.0	18.0	molecular weight of water
$\mathrm{M_w}$, mol cm^{-3}	4.3×10^{-6}	1.5×10^{-4}	2.9×10^{-4}	monomer concentration in water
υ	10	10	10	nucleation criteria: $\Delta G_{\max} > \upsilon kT$
T, K	323.15	323.15	323.15	polymerization temperature
χ	4.8	2.4	2.0	Flory–Huggins interaction parameter
σ, mN m^{-1}	1.5	0.8	0.75	interfacial tension nucleus to water

concentration of ionic groups on the surface should be as high as possible, σ should be as low as possible. Furthermore, σ should be lower the higher the monomer concentration is in the water (monomer solubility in water). As lowest values Gardon[13] found 4.5 mN m^{-1} for the system poly(styrene)/styrene, 3.2 mN m^{-1} for poly(methyl methacrylate)/methacrylate, and 3 mN m^{-1} for poly(vinyl acetate)/vinyl acetate, respectively. He investigated nonpolymerizing latexes with sizes of approximately 100 nm, well above the nucleation size. Therefore, we use for our model calculations values of σ which are still a little bit smaller, e.g. for styrene 1.5 mN m^{-1}, for methyl methacrylate 0.80 mN m^{-1}, and for vinyl acetate 0.75 mN m^{-1}.

Flory–Huggins Interaction Parameter. The Flory–Huggins interaction parameter depends on polymer concentration, molecular weight, and temperature. Especially, for poor solvents it is often found that χ increases strongly with polymer volume fraction.[14] The molecular weight dependence of χ is less pronounced if the molecular weight is higher than some 10^3.[15] In this case χ must be less than 0.5 to ensure miscibility. However, in the low molecular weight range typical for the nucleating oligomers this miscibility condition is shifted to χ values less than 2.[8]

The χ values should be smaller than those reported for polymers due to the following reasons: (1) there is still an influence of the ionic end group on the oligomer properties, especially on the interaction with water, and (2) the interacting solvent is not pure water but, as already mentioned above, an aqueous solution containing the corresponding monomer and emulsifiers. There are only a few values of χ published for hydrophobic polymer/water systems.[16,17] In such systems the swelling of the polymers in water is limited and hence χ values much greater than unity can be expected. So, for instance, for poly(vinyl acetate)[16] at 45 °C a χ value between 3.0 and 2.0 has been found, whereas the increasing water concentration χ becomes smaller. For the poly(styrene)/water system the interaction parameter has been estimated at temperatures between 162 and 230 °C by gas–liquid chromatography.[17] With increasing temperature, χ decreases. The χ–temperature curve gives a straight line so that χ values for lower temperatures are accessible. By this means, for 50 °C a value of approximately 6.5 is obtained for poly(styrene).

Starting from these considerations, it follows for the nucleation model that the χ value should be larger than 2 and increase with decreasing monomer solubility in water. For the calculation the following values have been used proportional to the hydrophobicity of the monomers: 4.8 for oligo(styrene) and for the more hydrophilic oligo(methyl methacrylate) and oligo(vinyl acetate) 2.4 and 2.0, respectively.

Table 1 summarizes the values of the rate parameters and model constants used for the calculations. All kinetic values needed as well as values for j_{crit} for styrene and methyl methacrylate have been found in a paper by Morrison and Gilbert.[18] The propagation rate constant for vinyl acetate was taken from ref 19, and the monomer solubility in water, from ref 20. Values concerning j_{crit} for vinyl acetate have been found in ref 21. In the calculations for styrene and methyl methacrylate we also included the dependence of k_p on the degree of oligomerization as proposed by Gilbert.[18] However, the calculations showed that there is only a very weak influence on the calculated nucleation behavior whether or not one considers a k_p dependence on j.

Results

By means of this model it is possible to calculate the nucleation in an unseeded emulsion polymerization with respect to the first appearance of particles. It should be noted that further events of an emulsion polymerization like coagulation or coalescence of particles, particle growth, and secondary particle nucleation cannot be considered with this model.

Figure 1 shows the results for the three monomers in form of the j–t or "nucleation" plane. Table 2 summarizes the numerical results with respect to the time gap of particle appearance after starting the polymerization (t_c), the degree of oligomerization at which nucleation occurs (j_{crit}), the diameter of the nuclei (D_c), and the number of chains per nucleus (M_c). It should be noted that these results are obtained for $\upsilon = 10$ corresponding to a fairly high activation energy of $10kT$ to satisfy the nucleation condition $\Delta G_{\max} \gg kT$. In principal, υ might be accessible if one will really be able to investigate the particle nucleation in emulsion polymerization experimentally. Until today this is alas not possible, and hence υ is an adjustable parameter.

For different monomers nucleation occurs at quite different times and j values. Thus, the influence of the monomer properties, especially of the different water solubilities is clear. The higher the water solubility the higher j_{crit} and the longer time it takes until particles appear.

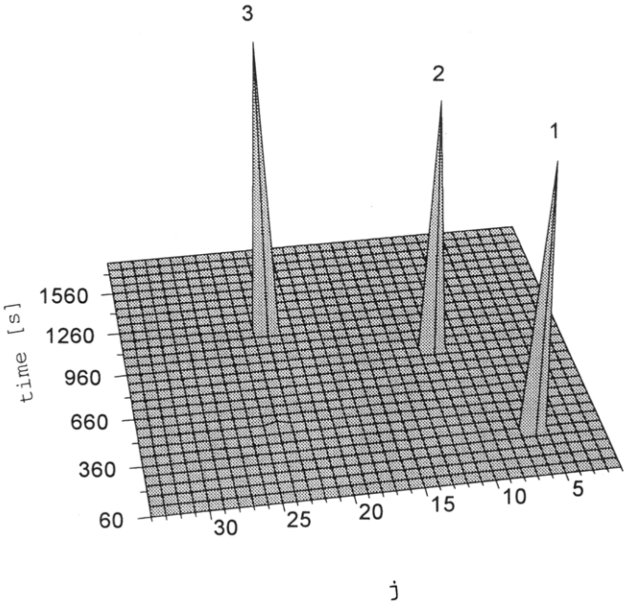

Figure 1. Calculated "nucleation" plane ($j-t$ plane) for styrene (1), methyl methacrylate (2), and vinyl acetate (3) emulsion polymerization (parameters for calculations, see Table 1).

Table 2. Numerical Results Characterizing Particle Nucleation (Explanation of Abbreviations in the Text) and Experimental Data for Critical Chain Length: $j_{\mathrm{crit,exp}}$

monomer	j_{crit}	$j_{\mathrm{crit,exp}}$	t_{c} (min)	D_{c} (nm)	M_{c}
STY	6	5	6	11.8	887
MMA	11	10	16	8.7	223
VAC	22	18–20	20	8.0	110

Especially, the results with respect to j_{crit} correspond well with experimental values for the three monomers. The agreement of calculated and measured values of j_{crit} is amazing in particular, as no special fits have been made to get these results.

By means of this model it is possible to calculate values characterizing the nucleation, D_{c} and M_{c} for instance, which are at present not experimentally accessible. Both values show a strong dependence on the water solubility of the monomers. The higher the water solubility of the monomer the lower both D_{c} and M_{c}.

Conclusions

A new approach has been found to describe essential features of particle nucleation in emulsion polymerization by a combination of the classical nucleation theory, radical polymerization kinetics, and the Flory–Huggins theory of polymer solutions. The main assumption of the model is that m water soluble oligomers of chain length j (dead or alive) nucleate. Subsequently, one considers the difference of the free energy of m oligomers of chain length j in solution and in the solid nucleus. Nucleation occurs if $\Delta G_{\max} = vkT$, wherein v has to be much greater than 1. In this sense, $\Delta G_{\max}$ corresponds to an activation energy of nucleation[22] which has to be determined. For the first calculations with the model a value of $\Delta G_{\max} = 10kT$ has been chosen for all three monomers. This is probably a rough approximation since it is very likely that $\Delta G_{\max}$ should somehow depend on monomer properties. However, experimental values for $\Delta G_{\max}$ are today not yet available. Nevertheless, the first results obtained with this approximation make the predictive power of the model clear. To find experimental access to $\Delta G_{\max}$ is a challenge for further nucleation experiments in emulsion polymerization.

All other parameters needed for the calculations can be found in the literature (kinetic rate constants for radical polymerization in water) or fairly well estimated from latex swelling experiments (nucleus to water interfacial tension) and liquid–gas chromatography (Flory–Huggins interaction parameter with water).

The results reflect the great influence of the water solubility of the monomer on particle nucleation in emulsion polymerization.

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