

Electrostatic and Steric Stabilization of PVC Primary Particles

C. KIPARISSIDES,^{1,*} I. MOUSTAKIS,¹ and A. HAMIELEC²

¹Chemical Engineering Department and Chemical Process Engineering Research Institute, Aristotle University of Thessaloniki, P. O. Box 472, Thessaloniki, 540 06 Greece, and ²Department of Chemical Engineering, Institute for Polymer Production Technology, McMaster University, Hamilton, Ontario, Canada

SYNOPSIS

Problems related to the formation and stability of primary particles in VCM suspension and bulk polymerization were theoretically analyzed, based on the DLVO (Deryaguin-Landau-Verwey-Overbeek) and HVO (Hesselink-Vrij-Overbeek) theories of stability of colloidal systems. In the absence of secondary stabilizers, PVC primary particles were solely stabilized by negative electric charges, as a result of the presence of HCl formed by a chain transfer reaction of chloride radicals to PVC polymer chains. The dependence of the stability of primary particles on the ionic strength of the medium, temperature, and total particle charge was quantitatively investigated in terms of the stability ratio and the particle coalescence rate constant. The steric stabilization of primary particles, arising from the addition of surfactants or polymers to the monomer phase, was examined, using the HVO theory. It was shown that PMMA improved the stability of primary particles and, thus, could alter the particle agglomeration kinetics. The effects of molar mass and the amount of the adsorbed PMMA, as well as the influence of solvent quality on the steric stabilization of primary particles, were also investigated. The experimental results, published on the electrostatic and steric stabilization of PVC primary particles, were in good agreement with the theoretical predictions obtained in this study. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that VCM polymerization is a heterogeneous process, which involves several physical transitions throughout the course of polymerization. As a result, the final product of bulk or suspension polymerization is made up of primary particles and its agglomerates. The nucleation, growth, and aggregation of these particles are responsible for the formation of particle internal morphology and associated properties, such as pore size distribution, and specific surface area.

Rance^{1,2} reviewed the previously published work on the formation of PVC grains and proposed the following mechanism to describe the nucleation, stabilization, growth, and aggregation of PVC primary particles. Primary radicals, formed by initiator

decomposition, rapidly react with the monomer to produce PVC macromolecules that are insoluble in the monomer phase. These closely spaced polymer chains combine together to form unstable polymer microdomains, which have a radius of about 10–20 nm. However, the microdomains (or basic particles) have a limited stability and agglomerate rapidly to generate the primary particle nuclei, also called domains. The initial size of these domains has been found to lie in the range of 80 to 100 nm (i.e., 0.08–0.1 μm). Contrary to the basic particles, the primary particles carry sufficient negative electrostatic charges^{3–5} and, thus, initially form stable colloidal suspensions in the monomer phase. Recent investigations have shown that primary particles can be produced up to about 5–10% monomer conversion. Primary particles grow in size by capturing newly formed basic particles and, to a lesser degree, by polymerization of absorbed monomer. The size and number of primary particles depend on the particle stability, which decreases as the monomer conver-

* To whom correspondence should be addressed.

sion increases. At conversions of 10–30%, aggregation of primary particles results in the formation of a continuous network of primary particles throughout the VCM droplet. The structure of the flocculated network, its porosity, and its strength, will depend on the electrostatic and steric interactions between the primary particles, their size, and their number density. Primary particles grow and aggregate until the free monomer phase disappears. Finally, at higher monomer conversions, primary particles fuse together to form agglomerates 2–10 μm in size.

The development of structure within grains of suspension PVC was experimentally investigated by Smallwood.⁶ One of the most interesting observations of Smallwood was that, although polymers produced at different polymerization conditions (i.e., temperature, stirrer speed, presence of different protective colloids and initiators) had different final porosities, the final size and number of primary particles reached approximately the same limiting values of 1.4 μm and $2.0 \times 10^{11} \text{ cm}^{-3}$, respectively. Smallwood's experimental results show that the product's final porosity is strongly related to the conversion at which the primary particle network is formed. At the critical conversion, the structure and strength of the network will be affected by the size, number, and interaction forces between primary particles, which are in turn influenced by the polymerization conditions (i.e., polymerization temperature, stirrer speed, type and concentration of stabilizers, etc.)

Despite the commercial importance of PVC particle morphology to its end-use applications, there has been little work done on the development of quantitative models relating the size evolution of primary particles in terms of process conditions. Kiparissides⁷ developed a population balance model to describe the time evolution of the primary particle size distribution as a function of the process variables, such as temperature, ionic strength of the medium, and type and amount of steric stabilizer. However, for the solution of the population balance model, we need to know the coalescence rate constant between the primary particles. This, in turn, requires the calculation of electrostatic and steric stabilization forces acting on these particles.

In the present study, we derive expressions for the calculation of the coalescence rate constant of two colloidal particles by taking into account both electrostatic and steric stabilization forces. It is shown that, in the former case, the particle coalescence rate constant can be expressed as a function of temperature, reciprocal Debye length, and the to-

tal particle charge, in accordance with the Müller–Smoluchowski coagulation theory.^{8–10} In the presence of steric stabilization forces, the variables affecting the particle coagulation kinetics are the molar weight and the total mass of the adsorbed polymer and the Flory–Huggins interaction parameter of the monomer-stabilizing polymer system. In the latter case, the Hesselink, Vrij, and Overbeek^{11,12} model is invoked for the calculation of the interaction potential between two particles covered by an adsorbed layer of neutral polymer.

COLLOIDAL STABILITY OF PVC PRIMARY PARTICLES

The population balance equation, describing the evolution of the primary particles in bulk or suspension polymerization, has been derived by Kiparissides⁷ and has the following general form:

$$\begin{aligned} \frac{\partial n(v, t)}{\partial t} + \frac{\partial [I_v n(v, t)]}{\partial v} \\ = \frac{1}{2} \int_{v_0}^{v-v_0} \beta(v-u, u) n(v-u, t) n(u, t) du \\ - \int_{v_0}^{\infty} \beta(v, u) n(v, t) n(u, t) du + r_0(t) \quad (1) \end{aligned}$$

where $n(v, t) dv$ denotes the number of particles of volume, v to $v + dv$, at time t per unit volume of the reaction medium. Equation (1) expresses the change of the density function $n(v, t)$, with respect to time (first term) and volume, due to polymerization in the polymer phase (second term). The first two terms on the right side of eq. (1) represent the rates at which particles enter and leave the size range v to $v + dv$, due to particle–particle coalescence. Finally, the last term represents the rate at which basic particles of volume v_0 are generated in the monomer phase.

The term $\beta(u, v)$ represents the coalescence rate constant of two colloidal particles of volume u and v . Note that the initial particle growth occurs mainly by particle aggregation and, to a smaller extent, by polymerization of the adsorbed monomer in the polymer-rich phase.² Thus, knowledge of analytical expressions for the coalescence rate constant is of profound importance to the solution of the population balance model (1), describing the time evolution of the primary particle size distribution. In what follows, the functional form of $\beta(u, v)$ is de-

rived for both electrostatic and steric stabilization conditions.

ELECTROSTATIC STABILIZATION

The origin of the electrostatic stabilization of PVC primary particles has been the subject of much discussion and speculation. Wilson and Zichy³ and Davidson and Witenhafer⁴ attributed these charges to chlorine ions (Cl^-), resulting from the presence of HCl formed during polymerization. Törnell and Uustalu¹³ investigated the origin of negative chlorine charges, found on the surface of primary particles, and reported that the formation of chlorine ions from an oxygen source could not solely explain the stability of the particles at higher monomer conversions. Furthermore, conductivity measurements during bulk polymerization of VCM showed that the conductivity of the monomer phase decreased while the conductivity of the polymer phase increased.¹⁴ Törnell and Uustalu¹³ suggested that the main source of particle stability should be the polymerization process itself. One possible source of chlorine-ion production can be attributed to the chain transfer of chloride radicals to PVC polymer chains. Hjertberg¹⁵ reported that hydrogen abstraction by chloride radicals can occur at a rate of 1–3 reactions per 10,000 monomer additions. Therefore, one can assume that these electrolytically active species (i.e., HCl), formed during the polymerization, are initially concentrated on the surface of the primary particles, thus providing the necessary negative electrostatic stabilizing forces. However, as the size of the primary particles increases, the contribution of the electrolytically active species located in the core of the primary particles decreases, resulting in a corresponding decrease of the particles' electrostatic stability.

In the case of electrically charged colloidal particles, the coalescence rate constant, $\beta(u, v)$, will be given by the Fuchs^{8,9} modification of the extended Smoluchowski coagulation equation:

$$\beta(v, u) = \beta_{ij} = E_f \frac{2kT(R_i + R_j)^2}{3\mu R_i R_j} \frac{1}{W_{ij}} \quad (2)$$

where k , T , μ , and W_{ij} denote the Boltzmann's constant, the reaction temperature, the viscosity of the monomer phase, and the stability ratio, respectively. R_i is the radius of the i th particle. E_f is a lumping parameter, depending on the degree of agitation and size of primary particles. It is well known that electrostatically stabilized colloidal particles are susceptible to aggregation by shear. Indeed, Davidson

and Witenhafer⁴ have shown that PVC primary particles, dispersed in VCM, aggregate under shear. Thus, strong agitation will favor aggregation of primary particles at low conversions.

In the absence of repulsion forces, every collision of two colloidal particles results in coagulation (i.e., in the case of rapid coagulation). However, in the presence of electrostatic repulsion forces, the rate of coagulation decreases by a factor of $1/W$, since not all particle collisions lead to coagulation. The inverse of the stability ratio, W^{-1} , accounts for the fraction of successful collisions and is used as a quantitative measure of the stability of the particles. Thus, the particle stability increases as the value of W increases (i.e., the repulsion forces increase).

To calculate W , it is necessary to evaluate the total energy of interaction V as a function of the distance separating two electrically charged colloidal particles. According to the DLVO theory, the total interaction energy will be given by the sum of the van der Waals attraction forces, V_A , and the electrostatic repulsion forces, V_R .

$$V = V_A + V_R \quad (3)$$

The attraction energy between two colloidal spherical particles of unequal size can be calculated by¹⁶

$$V_A = -\frac{A}{6} \left[\frac{2R_i R_j}{H_0^2 + 2H_0(R_i + R_j)} + \frac{2R_i R_j}{H_0^2 + 2H_0(R_i + R_j) + 4R_i R_j} + \ln \left(\frac{H_0^2 + 2H_0(R_i + R_j)}{H_0^2 + 2H_0(R_i + R_j) + 4R_i R_j} \right) \right] \quad (4)$$

where A is the Hamaker constant. The value of A for the PVC/VCM has been found to be equal to^{10,17} $A = 5.0 \times 10^{-21} \text{ J}$. R_i is the particle radius and H_0 is the shortest distance between the particle surfaces. Equation (4) can be simplified for small values of H_0 , to eq. (5), by eliminating the H_0^2 terms.

$$V_A = -\frac{A}{6} \left[\frac{R_i R_j}{H_0(R_i + R_j)} + \frac{R_i R_j}{H_0(R_i + R_j) + 2R_i R_j} + \ln \left(\frac{H_0(R_i + R_j)}{H_0(R_i + R_j) + 2R_i R_j} \right) \right] \quad (5)$$

It was found that when the maximum interaction potential occurs at small interparticle distances, the

error obtained in the calculation of V_A by using eq. (5) was less than 10%.

For the calculation of the electrostatic repulsive forces, Prindle and Ray¹⁸ proposed the following expressions:

$$V_R = \frac{4\pi\epsilon R_{ij}^2 \psi_{oi} \psi_{oj}}{H_0 + 2R_{ij}} \exp[-KH_0] \text{ for } KR_{ij} \leq 3 \quad (6)$$

$$V_R = 32\pi\epsilon R_{ij} \left(\frac{kT}{ze}\right)^2 \gamma_i \gamma_j \exp[-KH_0] \quad (7)$$

for $3 < KR_{ij} \leq 10$

$$\gamma_i = \tanh\left(\frac{ze\psi_{oi}}{4kT}\right) \quad (8)$$

where ψ_{oi} is the particle surface potential. R_{ij} is an effective radius, defined either as the arithmetic mean value of R_i and R_j , or as their harmonic mean value.

$$R_{ij} = \frac{1}{2} (R_i + R_j) \quad (9)$$

$$R_{ij} = 2 \left(\frac{1}{R_i} + \frac{1}{R_j} \right)^{-1} \quad (10)$$

For a given colloidal system, the attraction forces are assumed to be constant, while the electrostatic repulsion forces can vary with the concentration of electrolyte. The reciprocal of the thickness of the electrical double layer, K , appearing in the calculation of V_R [eqs. (6) and (7)], expresses the effect of electrolyte concentration on the repulsion forces. The reciprocal Debye length K is defined as¹⁶:

$$K = \left(\frac{e^2 N_A}{\epsilon k T} \sum_i z_i^2 M_i \right)^{1/2} \quad (11)$$

where M_i is the concentration of the ions of type i and z_i is the corresponding valence number. Note that for a completely dissociated 1 : 1 electrolyte, eq. (11) can be expressed in terms of the concentration of the electrolyte (mole/L) and the absolute temperature of the solution. Assuming that the concentration of the ionic species of an unknown 1 : 1 electrolyte in VCM is equal to 1 $\mu\text{mol/L}$, the value of K at 323 K will be approximately equal to $1.3 \times 10^7 \text{ m}^{-1}$.

In the presence of electrostatic forces, Fuchs⁹ derived the following relation between the energy of interaction and the stability ratio:

$$W_{ij} = 2R_{ij} \int_0^\infty \frac{\exp\left[\frac{V(H)}{kT}\right]}{(H_0 + 2R_{ij})^2} dH \quad (12)$$

where $V(H)$ is the total interaction energy and H is the distance separating two particles. It should be pointed out that several approximations have been proposed in the literature to avoid the numerical integration of eq. (12). Often the approximate expression (13)¹⁹ is used to estimate the value of the stability ratio in terms of V_{max} :

$$W_{ij} = \frac{1}{2KR_{ij}} \exp\left(\frac{V_{\text{max}}}{kT}\right) \quad (13)$$

where K is the reciprocal Debye length and V_{max} is the height of the energy barrier preventing particle coalescence. A more accurate approximation of eq. (12) was proposed by Reerink and Overbeek²⁰:

$$W_{ij} = \frac{2R_{ij}^2 \sqrt{\pi}}{(H_{\text{max}} + 2R_{ij})^2 p} \exp\left(\frac{V_{\text{max}}}{kT}\right) \quad (14)$$

where

$$p^2 = - \frac{1}{2kT} \frac{d^2 V}{dH^2} \Bigg|_{\text{max}} \quad (15)$$

The results of the integration of eq. (12) were compared to those obtained by the approximate solutions (13) and (14). It was found that eq. (13) overestimated the value of W_{ij} , while eq. (14) resulted in an error of less than 10%. As a result, eq. (14) was chosen for all subsequent calculations of W_{ij} , due to its simple form and minimum computational effort.

Calculation of Surface Potential

In order to calculate the value of the stability ratio in terms of the total energy of interaction, we need to know the particle surface potential, or, otherwise, the total particle charge as a function of the size of primary particles. In dilute solutions, where the value of K is small, the surface of shear may be regarded as that which coincides with the particle surface and, therefore, the particle potential can be approximated by the zeta potential of the charged particles.¹⁶

$$\psi_{oi} = \frac{Q_i}{4\pi\epsilon R_i (1 + KR_i)} \quad (16)$$

Q_i is the total particle charge and ϵ is the permittivity of the medium (i.e., the permittivity of the vacuum multiplied by the dielectric constant of VCM).

The zeta potential of PVC primary particles has been measured by several investigators^{3,4} and found to be in the range of -80 to -100 mV. Assuming that the size of a primary particle is 300 nm and its surface potential is -100 mV, one can calculate from eq. (16) for $K = 1.3 \times 10^{-7} \text{ m}^{-1}$ and $\epsilon = 4.16 \times 10^{-11} \text{ J}^{-1} \text{ Cb}^2 \text{ m}^{-1}$, that the total particle charge will be equal to 39 electronic charges, or to 6.27×10^{-18} Coulombs.

Törnell et al.¹⁰ proposed the empirical expression (17), which relates the primary particle radius to the total particle charge, in order to investigate the electrostatic stability of PVC primary particles.

$$Q_i = C_p R_i^p \quad (17)$$

where p is an adjustable parameter, taking values in the interval $[0, 2]$. Note that for $p = 0$, eq. (17) will satisfy the case of constant electric charge for all particles. On the other hand, for $p = 2$ and $KR_i \gg 1$, eq. (16) will satisfy the case of constant surface potential. The value of the parameter C_p can be calculated from eq. (17) and the values of Q_i and R_i . Thus, for $Q_i = 6.27 \times 10^{-18}$ Coulombs and $R_i = 0.15 \times 10^{-6}$ m, the numerical value of C_p will be equal to

$$C_p = 6.27 \times 10^{-18} (1.5 \times 10^{-7})^{-p} \quad (18)$$

It appears that the parameter C_p will be a function of the exponent p .

Figures 1 and 2 illustrate the variation of surface potential, with respect to the particle radius for various values of reciprocal Debye length, K , (Fig. 1) and the parameter p (Fig. 2). According to eq. (11), the inverse thickness of the electrostatic double layer, K , increases as the ionic strength of the medium increases. From Figure 1, it can be seen that the particle surface potential, ψ_{oi} , decreases as the value of K increases (i.e., the ionic strength of the medium increases). With decreasing surface potential, the repulsion forces decrease, as does the stability of primary particles. The effect of exponent p in eq. (17) on ψ_{oi} is shown in Figure 2. Note that for $p \leq 1.0$, the surface potential decreases with particle radius, while for $p > 1.0$, the surface potential exhibits a maximum, which is followed by a slow decrease of ψ_{oi} with R_i .

STERIC STABILIZATION

Production of PVC resin, with desired characteristics of porosity, plasticizer adsorption, and residual monomer desorption, is closely related to the control of structure, morphology, and agglomeration of primary particles at the point of network formation. Thus, a PVC resin, with improved uniformity in grain size and porosity, is produced when primary particles are uniform in size, are small, and are substantially spherical in shape.

It has been experimentally determined that the addition of so-called secondary dispersants in the

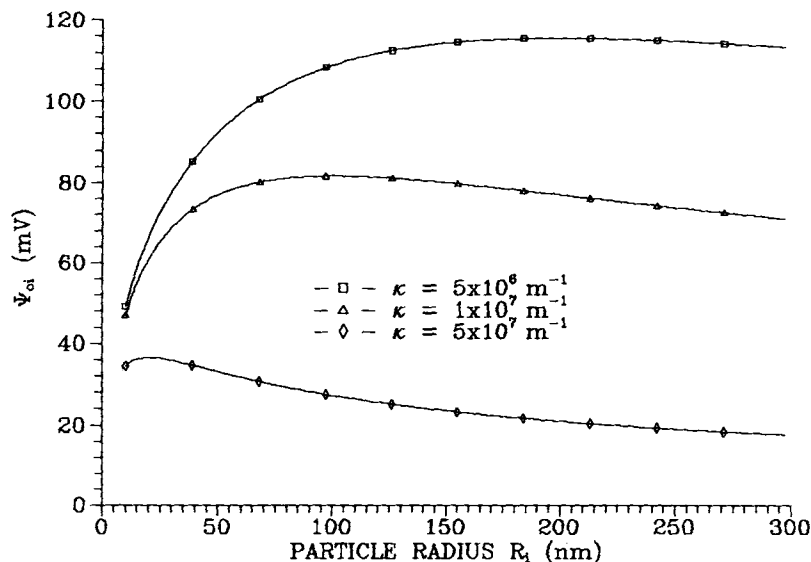


Figure 1 Variation of the surface potential with respect to the radius of particle, R_i : Effect of reciprocal Debye length ($T = 298 \text{ K}$, $p = 1.5$).

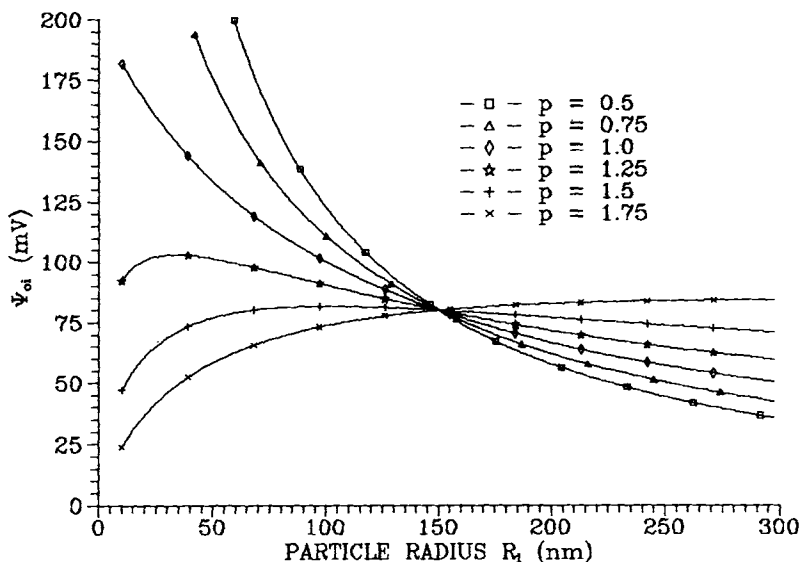


Figure 2 Variation of the surface potential with respect to the radius of particle, R_i : Effect of adjustable parameter p ($K = 1 \times 10^7 \text{ m}^{-1}$, $T = 298 \text{ K}$).

suspension polymerization of VCM can increase the porosity of PVC resin.²¹⁻²³ The commonly used secondary dispersants include sodium lauryl sulfate, sodium dioctyl sulfosuccinate, sorbitan esters, and low molecular weight polyvinyl acetates of a low degree of hydrolysis. In a recent patent,²³ a hydroxy alkylacrylate comonomer is added to the reactants, prior to the onset of polymerization, to improve resin porosity, plasticizer adsorption, and monomer desorption rate.

Despite the importance of surface-active agents in controlling the internal morphology of PVC grains, there is a lack of fundamental models that can quantitatively explain the effects of various additives on the grain morphological properties. Törnell and Uustalu^{13,21} provided sufficient experimental evidence on the influence of additives (i.e., sorbitan monolaurate, PMMA, EVA, and PVAc) on the nucleation and agglomeration of PVC primary particles. They reported that the addition of sorbitan monolaurate to the monomer phase resulted in a decrease of the primary particle size. On the other hand, the addition of polymeric additives improved the stability of primary particles, but had no marked effect on the particle size. In the present study, an attempt is made to quantify the effects of polymeric additives on the agglomeration rate of primary particles.

Polymeric stabilization of dispersions has received considerable attention (Napper,²⁴ Sato and Ruch²⁵), but aggregation and flocculation processes are equally important. When a polymer adsorbs on

a surface, the conformation of adsorbed polymer chains is different from that found in the polymer solution. Actually, in the adsorbed state, only a fraction of the total polymer segments are bound to the interface. These bound segments are referred to as trains. The other segments, which protrude into the solvent, are distributed as loops or tails. Both ends of a loop are attached to corresponding trains. On the other hand, only one end of a tail is terminally bound to a train, while its free part is in contact with the solvent molecules. Steric repulsion forces arise between two approaching particles, covered by polymer chains, due to mixing and entropic effects.

As with the modelling of the properties of polymer solutions, the major approaches in describing polymer adsorption are scaling theories (de Gennes^{26,27}) and mean field theories, as well as Monte Carlo calculations. Several mean field models have been developed to describe the polymer adsorption, both in lattice (Scheutjens and Fleer²⁸⁻³⁰), and in continuum (Ploehn and Russel³¹). The mean field arises from the presence of many interacting chains in the vicinity of the surface. The concentration gradient in the perpendicular direction z gives rise to a field that varies with z . According to the Scheutjens-Fleer model, when two flat plates approach each other, part of the chains are adsorbed on both surfaces simultaneously. In dilute solutions, the attraction, due to bridging, results in adsorption flocculation. At higher concentrations, the segmental overlap and conformational entropy contribute most to the free energy and the system is sterically stabilized.

The HVO Model

In the present study, the Hesselink, Vrij, and Overbeek¹¹ (HVO) model was employed to calculate the change in interaction free energy when two particles, covered by an adsorbed layer of polymer, approach each other. Despite its limitations, this simple model still provides a satisfactory description of trends observed by experimenters in sterically stabilized systems. According to the HVO model, when two flat plates, covered by adsorbed polymer, approach each other, the resulting rise in interaction free energy, ΔV_S , is due to the sum of two effects: (i) a volume restriction repulsion, ΔV_E , due to the decrease of configurational entropy of the adsorbed loops and tails on the approach of the second plate, and (ii) an osmotic or mixing effect, ΔV_M , due to the mixing of the adsorbed polymeric layers. The mixing effects can be either attractive or repulsive, depending on the solvent quality. In general, the total change in free energy will be given by

$$\Delta V_S = \Delta V_E + \Delta V_M \quad (19)$$

Meier³² was the first to recognize clearly the existence of both mixing (or osmotic) and volume restriction (or entropic) contributions to steric stabilization. In 1971, Hesselink et al.¹¹ following a mechanical statistical approach, modified the original model of Meier and developed a new equation for the calculation of the change of free energy per unit area when two interfaces, covered by adsorbed polymer, approach each other.

$$\Delta V_s = 2\nu kTQ(d, i) + 2\left(\frac{2\pi}{9}\right)^{3/2} \nu^2 kT(\alpha^2 - 1)\langle r^2 \rangle M(d, i) \quad (20)$$

where ν is the number of adsorbed loops or tails per unit area, d is the interaction distance, and i denotes the average number of segments per loop or tail, and is related to the mean end-to-end distance of a chain, $\langle r^2 \rangle$,

$$\langle r^2 \rangle = il^2 = \langle r^2 \rangle_\theta \alpha^2 \quad (21)$$

where l is the length of a segment, α is the expansion coefficient of the chains due to long-range interactions, and $\langle r^2 \rangle_\theta$ is the unperturbed mean square end-to-end distance in a Θ solvent. The expansion parameter α is given by Flory's equation³³:

$$\alpha^5 + \alpha^3 = \frac{27i^2 U_s^2 (\frac{1}{2} - \chi)}{(2\pi)^{3/2} U_1 (il^2)_\theta^{3/2}} \quad (22)$$

where χ is the Flory-Huggins interaction parameter, U_s is the segment volume, and U_1 is the volume of a solvent molecule. A basic requirement for calculating the expansion parameter from eq. (22) is a knowledge of χ . An estimate of the Flory-Huggins interaction parameter can be obtained from the Hilderbrand approximation,³⁴

$$\chi = 0.34 + \frac{U_1(\delta_1 - \delta_2)^2}{RT} \quad (23)$$

where δ_1 and δ_2 are the corresponding solubility parameters of monomer and solvent, calculated from the group contribution theory.

The first term in eq. (20) accounts for the loss of configurational entropy of the adsorbed loops and tails on the approach of a second interface. The second term refers to the change of free energy, caused by the mixing of polymer segments when the two surfaces approach each other. The exponential functions $Q(d, i)$ and $M(d, i)$ account for the rise in free energy per average loop or tail in units of kT and will depend on the chain configuration and the interaction distance, d . Hesselink et al.¹¹ considered three simplified cases of polymer segment configuration, namely, an equal loop distribution, an equal tail distribution, and a tail size distribution and for $d > (il^2)^{1/2}$, and they derived the following approximate expressions for the volume restriction term, $Q(d, i)$, and the osmotic term, $M(d, i)$.

Equal Loops

$$Q(d) \cong 2(4\beta d^2 - 1) \exp(-2\beta d^2) \quad (24)$$

$$M(d) \cong (3\pi)^{1/2} (2\beta d^2 - 1) \exp(-\beta d^2) \quad (25)$$

Equal Tails

$$Q(d) = 2 \exp\left(-\frac{\beta d^2}{2}\right) \quad (26)$$

$$M(d) \cong \left(\frac{6\pi}{5}\right)^{1/2} \left(\frac{4\beta d^2}{5} - 1\right) \exp\left(-\frac{2\beta d^2}{5}\right) \quad (27)$$

Tail Size Distribution

$$Q(d) \cong 2 \exp(-\beta d^2)^{1/2} \quad (28)$$

$$M(d) \cong 4[3 \exp(-6\beta d^2)^{1/2}]^{1/2} [(\beta d^2)^{1/2} - 1] + [\exp(-\beta d^2)^{1/2}] [(\beta d^2)^{1/2} + 2] \quad (29)$$

where

$$\beta = \frac{3}{\langle r^2 \rangle}; \quad d = H - 2L \quad (30)$$

H is the distance between the two flat interfaces and L is the thickness of the adsorbed layer. According to the HVO model, the main parameters determining the interaction energy of the two approaching surfaces, each covered by an adsorbed polymer layer, will be: (i) The molar weight and the amount of adsorbed polymer on the particle surface, (ii) The chain configuration of the adsorbed polymer, (iii) The quality of the solvent, (iv) The change of existing electrostatic and attractive van der Waals forces, due to the presence of adsorbed polymer, and (v) The presence of nonadsorbed polymer chains, which can increase or decrease the free energy of the colloidal system.

The interaction energy per unit area can be converted into a force, between two spherical primary particles, by using Derjaguin's transformation³⁵

$$\Delta V_S = \pi R_{ij} \int_{d_0}^{\infty} \Delta V_S dd \quad (31)$$

where R_{ij} is the effective particle radius (i.e., harmonic mean value) of the two particles and d_0 is the minimal interaction distance between particles.

The kinetics of primary particle coagulation are determined by the counteraction of the steric repulsive forces and the ever-existing van der Waals attractive forces. The overall potential of interaction, when two particles approach each other, will be given by the sum of the steric repulsive forces, ΔV_S , and the attractive forces, ΔV_A , (eq. 11).

$$\Delta V = \Delta V_S + \Delta V_A \quad (32)$$

Note that eq. (32) does not include the electrostatic repulsive forces, since, at short distances, these forces will be negligible in comparison with the steric forces. Furthermore, the presence of an adsorbed steric layer disturbs the electrostatic field so that eqs. (6) and (7) will not be strictly valid in this case. The calculated potential curves for sterically stabilized particles will be different from those obtained under electrostatic stabilization conditions. At large values of d , van der Waals attractive forces predominate. However, as d decreases, the osmotic repulsion forces become significant, and finally, at closer distances, the volume restriction forces appear. Actually, in a sterically stabilized system, due to the

presence of the adsorbed polymer layer, particle agglomeration can only occur at the secondary minimum, ΔV_{\min} , of the interaction potential curve, which is located at a large distance from the particle surface. At ΔV_{\min} , the van der Waals forces will be larger than the steric ones. The depth of the minimum determines the stability of the colloidal system. If the minimum is not protected by an energy barrier, agglomeration of the particles can be a reversible process. Otherwise, the particle agglomeration will be irreversible.

When the value of the interaction energy at the secondary minimum is less than the thermal energy of particles, $\Delta V_{\min} < kT$, the dispersion can be considered as thermodynamically stable. On the other hand, for $\Delta V_{\min} > kT$, particle agglomeration will take place. For these cases, the stability ratio, W_{ij} , can be approximated by³⁶:

$$W^{-1} = 1 - \exp\left(\frac{\Delta V_{\min}}{kT} - 1\right) \quad (33)$$

Note that for $\Delta V_{\min} > kT$, the stability ratio will tend towards zero and the particle agglomeration will follow Smoluchowski's kinetics of fast coagulation.

DISCUSSION AND RESULTS

In the following section, the stability of the PVC primary particles is quantitatively examined. First, the electrostatic stabilization of primary particles is investigated and the quantitative results are presented, showing the effect of ionic strength and temperature on the stability of the primary particles. Subsequently, the steric stabilization of primary particles is considered and the HVO theory is invoked to explain the experimentally observed increase of the primary particles' stability in the presence of a PMMA additive. Theoretical results are presented, which show the effect of molar weight, mass, and chain configuration of the adsorbed PMMA on the stability of PVC primary particles.

Results on the Electrostatic Stability of Primary Particles

The electrostatic nature of primary particle stability has been demonstrated by the ability of electrolytes to flocculate stable dispersions of primary particles in VCM. Indeed, Törnell and Uustalu³⁷ showed that, when VCM polymerization was carried out in the presence of completely dissociated quaternary salts

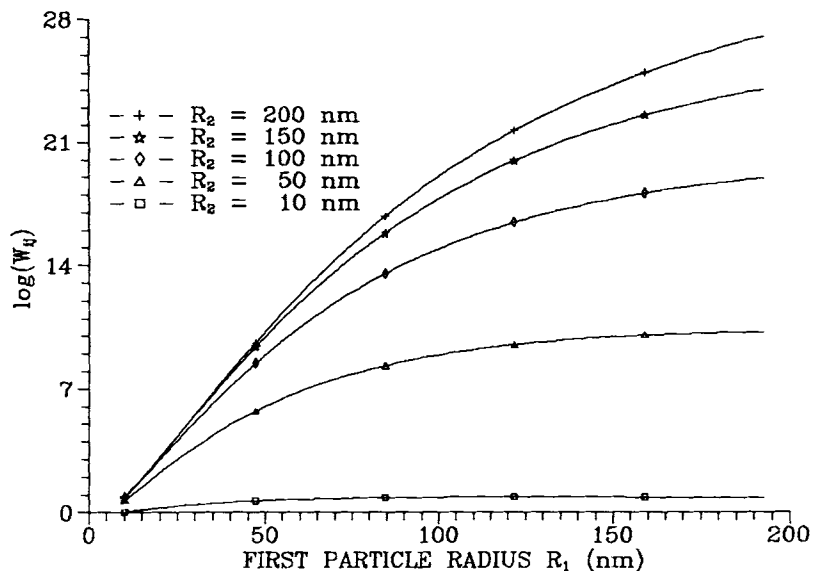


Figure 5 Variation of the stability ratio with respect to the radius of the first particle, R_1 ($K = 1 \times 10^7 \text{ m}^{-1}$, $T = 298 \text{ K}$, $p = 1.5$).

Figures 3 and 5 show the dependence of W_{ij} on the parameter p . Similarly, Figures 4 and 6 depict the corresponding variation of the particle coalescence rate constant. Note that for $p = 1$, the energy barrier for particle coalescence exhibits a maximum and, thus, the coalescence rate constant becomes minimal for particles of approximately equal size (Fig. 4). As the parameter p increases (i.e., $p = 1.5$), the interaction potential curves become smoother with no maxima and the stability of the particles increases with size (see Fig. 5). These calculations

show that particle agglomeration most readily occurs between small-small and large-small particles. Note that in all calculations, the harmonic mean radius [eq. (10)] was employed. It is important to point out that when the arithmetic mean value [eq. (9)] was used for the estimation of R_{ij} , the shape of the interaction potential curves was significantly different.

Figure 7 shows the effect of temperature on the coalescence rate constant. It can be seen that β_{ij} increases with temperature. Note that, as the tem-

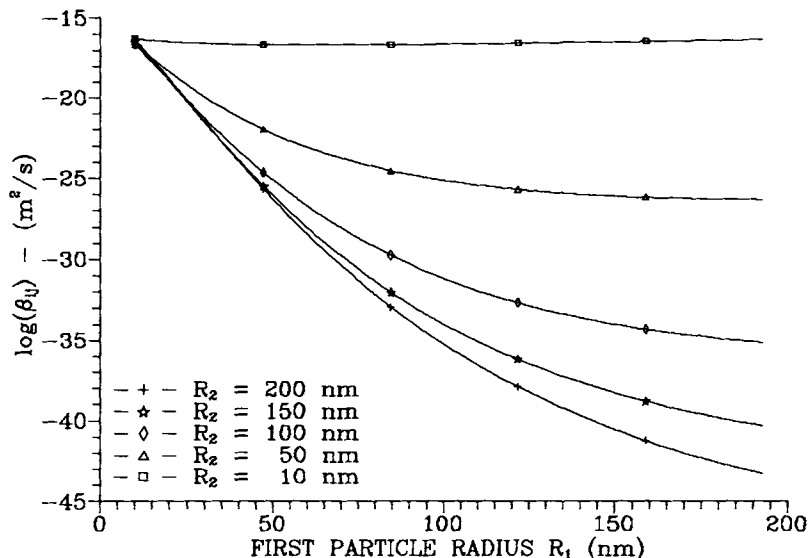


Figure 6 Variation of the coalescence rate constant with respect to the radius of the first particle, R_1 ($K = 1 \times 10^7 \text{ m}^{-1}$, $T = 298 \text{ K}$, $p = 1.5$).

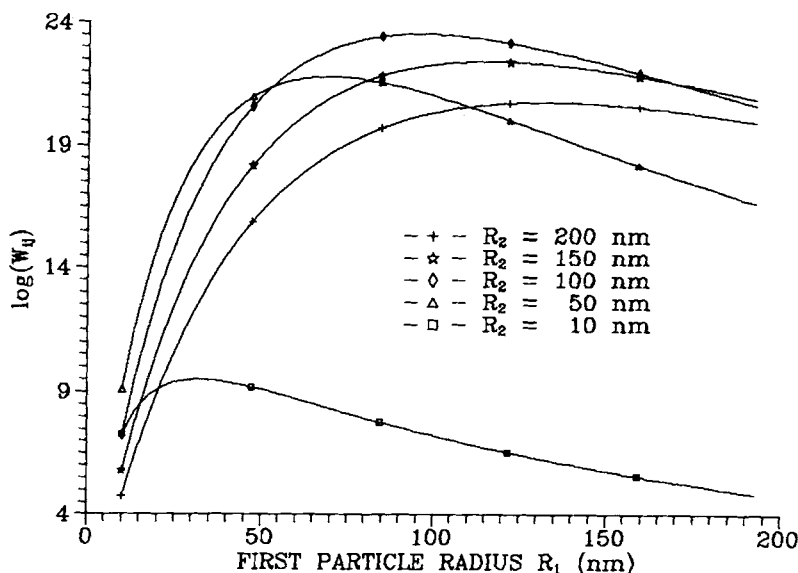


Figure 3 Variation of the stability ratio with respect to the radius of the first particle, R_1 ($K = 1 \times 10^7 \text{ m}^{-1}$, $T = 298 \text{ K}$, $p = 1.0$).

(i.e., Bu_4NBF_4 , Bu_4NCl), an early agglomeration of the primary particles was observed. They reported that smaller primary particles were obtained in the presence of salts than in additive-free polymerizations. Furthermore, they found that early agglomeration of smaller primary particles promoted the formation of porous PVC grains.

As mentioned previously, the parameter p , in eq. (17), was introduced in order to relate the total electric charge, Q_i , to the particle radius, R_i . In this

way, we can account for the variation of ψ_{oi} with the size of the primary particles. In Figures 3–6, the stability ratio, W_{ij} , and the coalescence rate constant, β_{ij} , are plotted for two values of the exponent p . In all simulated cases, the reciprocal Debye length was set equal to $1 \times 10^7 \text{ m}^{-1}$ and the temperature was set at 298 K. Different lines in Figures 3–6 represent the variation of the quantity of interest (i.e., W_{ij} or β_{ij}), when a particle of constant size, R_2 , approaches a second one of variable radius R_1 .

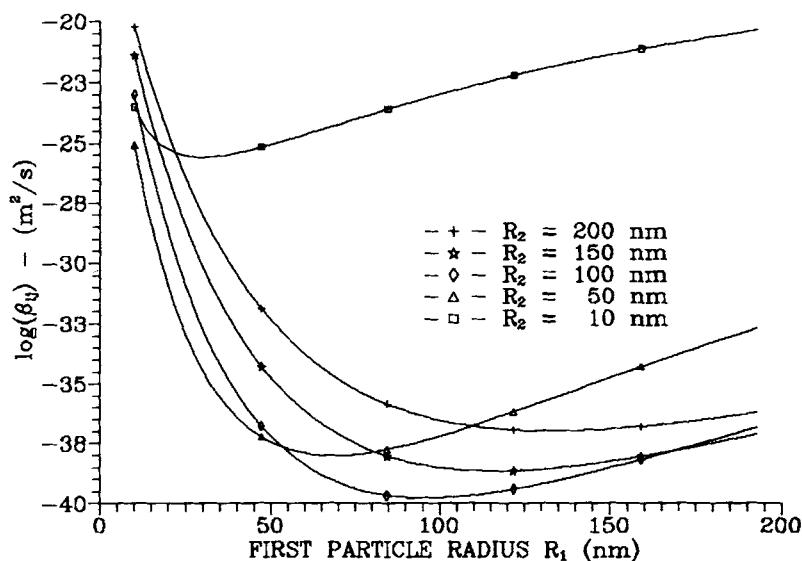


Figure 4 Variation of the coalescence rate constant with respect to the radius of the first particle, R_1 ($K = 1 \times 10^7 \text{ m}^{-1}$, $T = 298 \text{ K}$, $p = 1.0$).

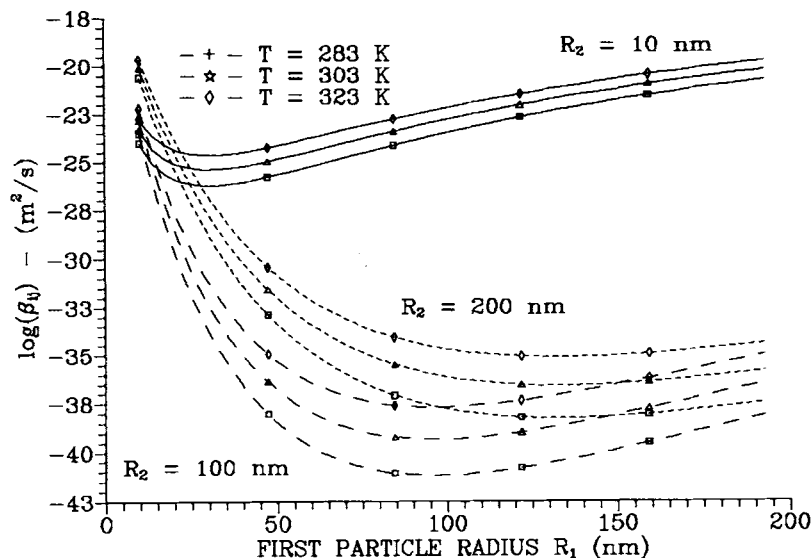


Figure 7 Effect of the temperature on the coalescence rate constant ($K = 1 \times 10^7 \text{ m}^{-1}$, $p = 1.0$).

perature increases, the maximum energy barrier decreases, while the Brownian movement of the particles increases. This results in an overall increase of the particle coalescence rate (Fig. 7).

The effect of the ionic strength (i.e., reciprocal Debye length, K) on the particle coalescence rate constant is shown in Figure 8 for $p = 1.0$. As K increases, the energy barrier, V_{\max} , decreases, which results in a decrease in the stability ratio and a corresponding increase of β_{ij} . Note that the coalescence

rate constant, β_{ij} , between basic and small primary particles, is large, which means that newly formed basic particles will rapidly be captured by the existing primary particles. From the results of these simulations, one can draw the following general conclusions:

1. The coalescence rate constant between small-small and small-large primary parti-

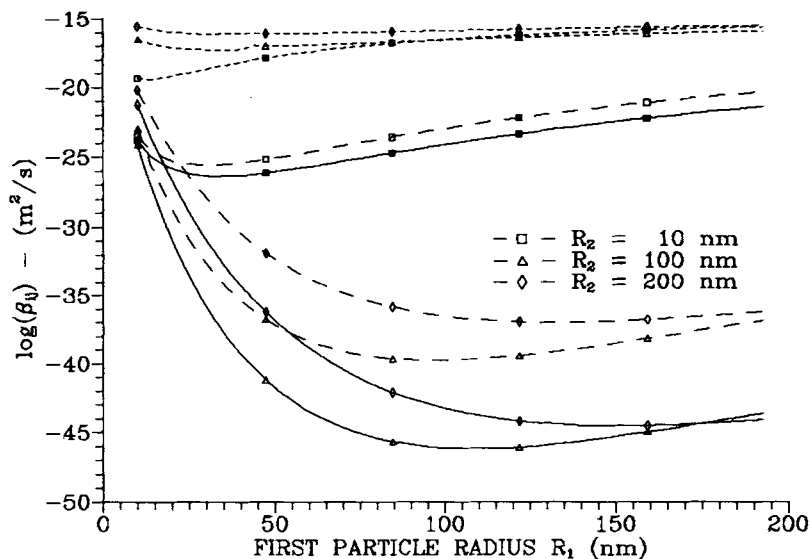


Figure 8 Effect of the reciprocal Debye length on the coalescence rate constant ($T = 298 \text{ K}$, $p = 1.0$, (—) $K = 8 \times 10^6 \text{ m}^{-1}$, (---) $K = 1 \times 10^7 \text{ m}^{-1}$, (....) $K = 5 \times 10^7 \text{ m}^{-1}$).

cles increases as the value of exponent p in eq. (17) increases.

- The coalescence rate constant between small-small primary particles will be larger than that between small and large primary particles for $p > 1$ (Fig. 6). This indicates that smaller primary particles will grow faster than larger ones. Such conditions will lead to the formation of narrow primary particle size distribution, in agreement with the experimental observations.^{2,5,6,10}
- It was found that, for particles carrying a constant electric charge (i.e., $p = 0$ in eq. 17), the calculated value of β_{ij} between basic-basic and basic-small primary particles was extremely small, due to the presence of high repulsive forces (see Fig. 1). Such conditions do not favor the coalescence of small particles, contrary to the experimental observations. Therefore, the assumptions of constant electric charge for all primary particles is not justifiable.
- In general, the coalescence rate constant increases with increasing temperature and increasing ionic strength of the medium. This can lead to an early agglomeration of primary particles, as shown by the results of Figure 8. Thus, primary particle aggregates, formed in the presence of dissociated electrolytes, will have a smaller initial size promoting the formation of a more porous PVC structure.³⁷

Results of the Steric Stabilization of Primary Particles

Törnell and Uustalu²¹ reported that the addition of EVA, PEVAc, and PMMA increased the stability of the primary particles. The largest increase was observed with high molecular weight PMMA. The increased primary particle stability was not followed by a significant increase in the particle size, because of the limited growth of the primary particles by coalescence. The increased primary particle stability, caused by steric stabilization forces, is thought to be the main reason for the observed increase of the resin porosity when a secondary dispersant is introduced into the VCM polymerization.

It is apparent that the presence of a polymeric additive changes the particle coalescence rate constant, due to the presence of steric stabilization forces. As discussed before, the main parameters determining the stability of a colloidal system are the configuration of the adsorbed polymer chains, the molar mass, the amount of the adsorbed polymer, and the quality of the solvent expressed by the value of the Flory-Huggins interaction parameter. The effects of these parameters on the stability of PVC primary particles in the presence of PMMA are discussed below.

In Figure 9, the effect of configuration of adsorbed polymer chains on the stability of primary particles is shown. Particles, stabilized by an adsorbed polymer layer, exhibiting a tail size distribution, show a

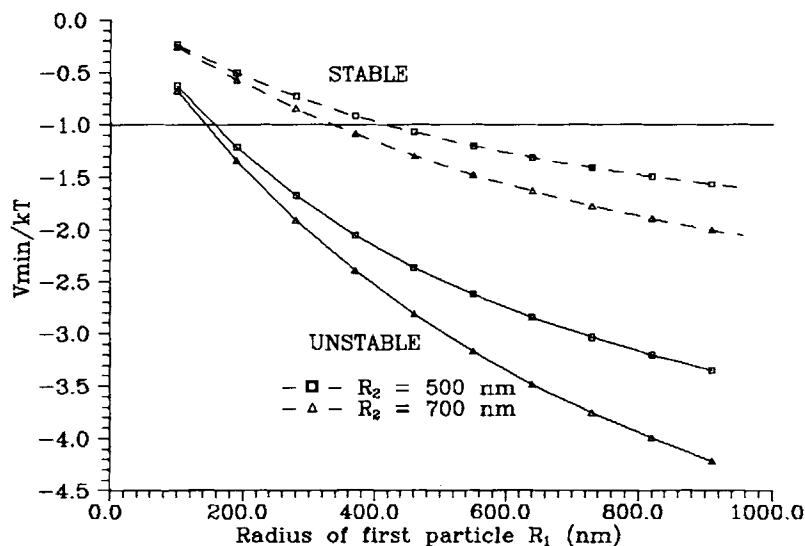


Figure 9 Variation of the minimum energy of interaction: Effect of polymer chain configuration [polymer mass = 0.01 mgr m⁻², MW = 69,000, $\chi = 0.5$, configuration: (—) equal loops, (---) tail size distribution].

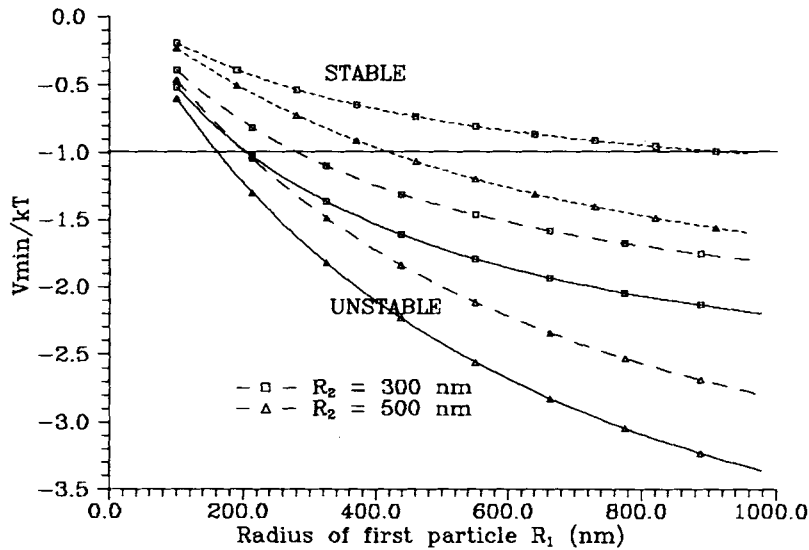


Figure 10 Variation of the minimum energy of interaction: Effect of adsorbed polymer mass [MW = 69,000, $\chi = 0.5$, configuration: tail size distribution, (---) mass = 0.01 mgr m^{-2} , (- - - -) mass = 0.005 mgr m^{-2} , (—) mass = 0.001 mgr m^{-2}].

higher stability than particles that are covered by a polymer with equal loops. Since both configurations will be present in a real system, a combination of loops and tails of adsorbed PMMA can stabilize primary particles in the range of 200–700 nm. The amount of adsorbed polymer will also affect the stability of the primary particles. This is clearly shown in Figure 10. It can be seen that the stability of particles increases as the mass of the adsorbed polymer

increases. Figure 11 depicts the effect of molar weight of polymer on the primary particle stability. An increase of the molecular weight of the polymer increases the thickness of the adsorbed polymer layer and, thus, the effective distance of the repulsive forces. Finally, Figure 12 illustrates the effect of the solvent quality, in our case VCM, on the stability of the primary particles. As the value of the interaction parameter for the VCM/PMMA system de-

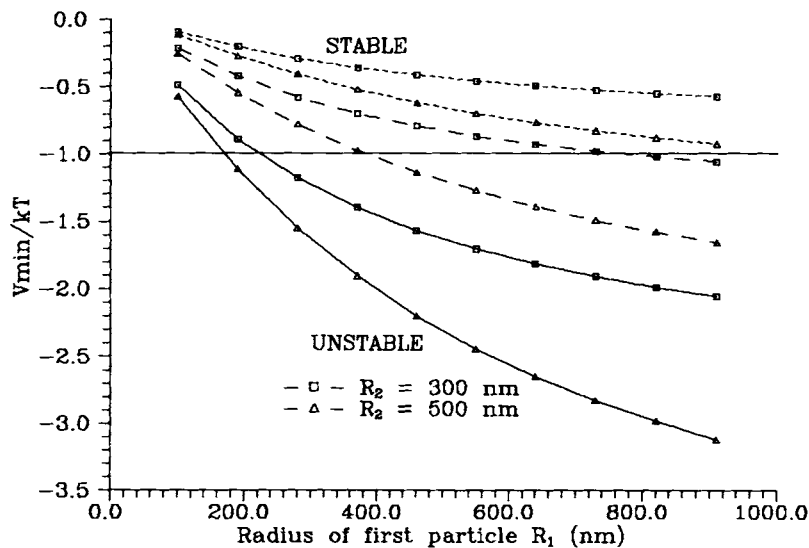


Figure 11 Variation of the minimum energy of interaction: Effect of molecular weight of adsorbed polymer [$\chi = 0.5$, polymer mass = 0.05 mgr m^{-2} , configuration equal loops, (---) MW = 500,000, (- - - -) MW = 200,000, (—) MW = 69,000].

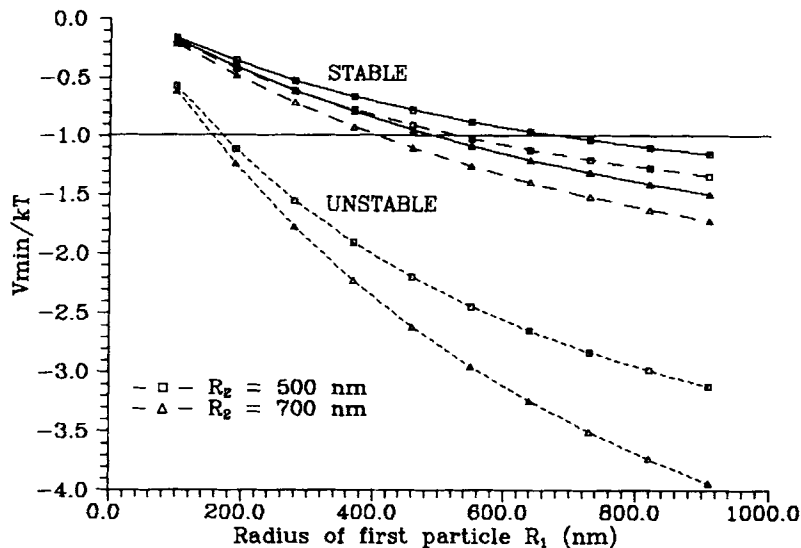


Figure 12 Variation of the minimum energy of interaction: Effect of solvent-polymer interaction parameter [MW = 69,000, polymer mass = 0.05 mgr m⁻², configuration: equal loops, (—) $\chi = 0.36$, (---) $\chi = 0.41$, (----) $\chi = 0.5$ (θ solvent)].

creases, that is, the solvent quality improves, the stability of the primary particles increases.

The results of Figures 10–11 are in qualitative agreement with the experimental observations of Törnell and Uustalu,²¹ who found that, as the molecular weight or/and the amount of PMMA increased, the formation of primary particle aggregates was delayed. Note that longer stabilization periods will not necessarily lead to an increase of the primary particle size, since particle growth is mainly controlled by particle coalescence. It is important to point out that other nonionic surfactants, such as Span 20 and Tween 21, will have similar stabilizing effects, leading to the production of small and uniform sized primary particles.^{21–23}

The present theoretical framework on electric and steric stabilization offers a quantitative explanation of experimental observations on primary particle stability and growth, and provides the means for controlling the structure and morphology of primary particles in a systematic way. Effective control over the shape, size of primary particles, and monomer conversion at which the primary particle network is formed, will eventually result in better control of PVC resin porosity, plasticizer adsorption, and monomer desorption rate.

APPENDIX: NOMENCLATURE

A Hamaker constant, (J)
 C_p parameter in eq. (17)

d distance between adsorbed polymer layers, (m)
 e electron charge, (Cb)
 H separation distance between the surface of two particles, (m)
 i number of segment per chain, dimensionless
 I_v rate of particle growth, (m³ s⁻¹)
 k Boltzmann constant, (J K⁻¹)
 K reciprocal Debye length, (m⁻¹)
 l polymer segment's length, (m)
 L thickness of adsorbed polymer layer, (m)
 M_i concentration of i type ions (greq m⁻³)
 $M(d, i)$ osmotic contribution to steric stabilization, dimensionless
 $n(v, t)dv$ number of primary particles in the size range v and $v + dv$, (m⁻³)
 N_A Avogadro's number
 p adjustable parameter in eq. (17), dimensionless
 Q_i charge of i particle, (Cb)
 $Q(d, i)$ volume restriction contribution to steric stabilization, dimensionless
 $r_0(t)$ rate of generation of basic particles, (m⁻³ s⁻¹)
 R universal gas constant (J mol⁻¹ K⁻¹)
 R_i radius of i particle, (m)
 R_{ij} arithmetic or harmonic value of particle radii, R_i and R_j , (m)
 $\langle r^2 \rangle$ mean end-to-end distance of a chain, (m)

t	time, (s)
T	temperature, (K)
U_s	volume of segment ($\text{m}^3 \text{mol}^{-1}$)
U_1	volume of solvent ($\text{m}^3 \text{mol}^{-1}$)
v	volume of primary particle (m^3)
V	total energy of interaction, (J)
V_A	London-van der Waals attraction energy, (J)
V_E	entropic energy of interaction, (J)
V_M	mixing energy of interaction, (J)
V_R	electrostatic repulsion energy, (J)
V_S	steric interaction energy, (J)
V_{\max}	maximum energy of interaction, (J)
V_{\min}	minimum energy of interaction, (J)
W	stability ratio, dimensionless
z_i	valence number of i particle, dimensionless

Greek Letters

α	Flory expanded parameter, dimensionless
β_{ij}	coalescence rate constant between particles i and j , ($\text{m}^2 \text{s}^{-1}$)
δ_i	solubility parameter, ($(\text{J m}^{-3})^{1/2}$)
ϵ	permittivity of the medium, ($\text{J}^{-1} \text{Cb}^2 \text{m}^{-1}$)
μ	viscosity, ($\text{kg m}^{-1} \text{s}^{-1}$)
ν	number of absorbed chains per unit area ($1/\text{m}^3$)
χ	Flory-Huggins interaction parameter, dimensionless
ψ_0	particle surface potential, (V)

REFERENCES

- D. G. Rance, *Colloidal Aspects of Poly(vinyl chloride) Production Processes*, in "Polymer Colloids," R. Buscall, T. Corner, and J. F. Stageman, Eds., Elsevier, Amsterdam, 289, 1985.
- D. G. Rance and E. L. Zichy, *Pure & Appl. Chem.*, **53**, 377 (1981).
- J. C. Wilson and E. L. Zichy, *Polymer*, **20**, 264 (1979).
- J. A. Davidson and D. E. Witenhafer, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 51 (1980).
- F. M. Willmouth, D. G. Rance, and K. M. Henman, *Polymer*, **25**, 1185 (1984).
- P. V. Smallwood, *Polymer*, **27**, 1609 (1986).
- C. Kiparissides, *Makromol. Chem. Macromol. Symp.*, **35/36**, 171 (1990).
- H. Müller, *Kolloid-Reih*, **26**, 257 (1928).
- N. Fuchs, *Z. Physik*, **89**, 736 (1934).
- B. E. Törnell, J. M. Uustalu, and B. Jönsson, *Colloid & Polym. Sci.*, **264**, 439 (1986).
- F. Hesselink, A. Vrij, and J. G. Overbeek, *J. Phys. Chem.*, **75**, 2094 (1971).
- H. Sonntag and K. Streng, *Coagulation Kinetics and Structure Formation*, Plenum, New York, 1987.
- B. E. Törnell and J. M. Uustalu, *J. Appl. Polym. Sci.*, **35**, 63 (1988).
- J. M. Uustalu, *J. Polym. Sci. Part A Polym. Chem.*, **24**, 1609 (1986).
- T. Hjertberg, Thesis, Chalmers University of Technology, Gothenburg, Sweden, 1982.
- R. J. Hunter, *Foundation of Colloid Science*, Clarendon, Oxford, 1987.
- D. G. Rance and E. L. Zichy, *Polymer*, **20**, 266 (1979).
- J. C. Prindle and W. H. Ray, *Emulsion Polymerization Model Development for Operation Below the CMC*, paper presented at the Annual AIChE Meeting, New York, November, 1987.
- J. Th. G. Overbeek, *Colloid Science*, H. R. Kruyt, Ed., Elsevier, Amsterdam, 1952.
- H. Reerink and J. Th. G. Overbeek, *Disc. Faraday Soc.*, **18**, 74 (1954).
- B. E. Törnell and J. M. Uustalu, *J. Vinyl Technol.*, **4**, 53 (1982).
- B. E. Törnell, *Polym. Plast. Technol. Eng.*, **27**, 1 (1988).
- E. J. Murray, U. S. Patent 4,579,923 (1986).
- D. H. Napper, *Polymeric Stabilization of Colloidal Dispersions*, Academic, London, 1983.
- T. Sato and R. Ruch, *Stabilization of Colloidal Dispersions by Polymer Adsorption*, Marcel Dekker, New York, 1980.
- P. G. de Gennes, *Macromolecules*, **13**, 1069 (1980).
- P. G. de Gennes, *Macromolecules*, **15**, 1637 (1981).
- J. M. H. M. Scheutjens and G. J. Fleer, *J. Phys. Chem.*, **83**, 1619 (1979).
- J. M. H. M. Scheutjens and G. J. Fleer, *J. Phys. Chem.*, **84**, 178 (1980).
- J. M. H. M. Scheutjens and G. J. Fleer, *J. Phys. Chem.*, **18**, 1882 (1985).
- H. J. Ploehn and W. R. Russel, *Macromolecules*, **22**, 266 (1989).
- D. J. Meier, *J. Phys. Chem.*, **71**, 1861 (1967).
- P. J. Flory, *Principles of Polymer Chemistry*, Cornell University, Ithaca, 1953.
- D. W. Van Krevelen and P. J. Hoftyzer, *Properties of Polymer*, Elsevier, Amsterdam, 1976.
- B. V. Derjaguin, *Kolloid Z.*, **69**, 155 (1934).
- L. M. Bagchi, *Adv. Chem. Ser.*, 143 (1975).
- B. E. Törnell and J. M. Uustalu, *Polymer*, **27**, 250 (1986).

Received February 12, 1992

Accepted May 14, 1992