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A Model for the Emulsion Polymerization of Vinyl Chloride

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ABSTRACT

Phenomena of emulsion polymerization of vinyl chloride have been analyzed on the molecular scale. A quantitative model is developed in which the polymerization is assumed to occur in a shell surrounding the dead core of the particles. The shell has the same composition as the entire particle, but it is assumed that the active species generated in the aqueous phase are not able to diffuse to the center of the particles and rather remain in a zone of limited thickness. Kinetic and geometric parameters are determined by fitting calculated values of rates and molecular weights to experimental data at 50°C.

INTRODUCTION

Many experimental data on the emulsion polymerization of vinyl chloride have been reported in the scientific literature. Up to now only one tentative model has been published, that of Ugelstad and coworkers [1, 2].

The Ugelstad model fits the experimental data well, but the basis of its formulation makes it suitable for the study of batch homopolymerization only, and only after the number of particles has become constant.

The purpose of this study is to establish new bases for a model able to describe nucleation phenomena, continuous runs, and copolymerizations.

THE APPROACH

Any chemical process should be analyzed with respect to the chemical steps and to the physical ones. Alternatives may be considered for describing some of the physical steps, resulting in different models. Moreover, assumptions may be made that some chemical or physical transitions are fast compared to other ones. Methods for model discrimination [3] are firstly qualitative, requiring self consistency of the results with the assumptions made before, and secondly, quantitative, through statistical tests based on comparison of aforedefined objective functions.

In this case, the chemical processes are well known, but we should insist that we do not confuse (as is often done [1]) the propagation reaction and the reinitiation reaction by a monomeric radical, the specific rate of the latter being considered lower as concluded from studies with transfer agents [4-6]. Several types of termination reactions are also distinguished: those involving two macroradicals, or two monomeric radicals, or one macro- and one monomeric radical.

Actually the first of these types of termination has not been considered because of the extremely low diffusivity of the polymer in the particles. The kinetic constants of the two other reactions are considered differently, the latter one being less than the former and assumed to decrease when the viscosity of the medium increases.

The physical steps are numerous but some of them may be neglected, being either unimportant parallel transitions, or fast ones in a series of transitions whose rate is governed by a slow chemical reaction. Diffusion in water of the initiator radicals and the further collision with soluble monomer molecules, the self-precipitation of soluble oligomeric radicals, the collision of soluble oligomeric radicals with existing particles, the escape of monomeric radicals out of particles, the capture by particles of soluble monomeric radicals, and the diffusion of surfactant molecules from one interface to another owing to affinity and surface ratios are considered.

The coalescence of existing particles and the exchange of active species with the gas phase are not considered in the model.

Very few of the elementary steps can be studied independently. On the other hand, it is inconceivable to embrace all the phenomena in the same study. Obviously, the elementary steps can be assembled into three different stages able to be analyzed independently from a theoretical and experimental point of view. The initiation stage has been discussed earlier [6, 7]. It comprises the decomposition of the initiator and the formation of a soluble oligomeric radical S° which further precipitates and is called then R°. The rate of formation of the macroradical R°, due to primary initiation, has been found to equal the rate of decomposition of the initiator with an efficiency factor of one.

The second stage comprises the first one and deals with the mechanism of growth when the number of particles is constant. The third stage to be studied concerns the nucleation phenomena, and thus its analysis requires the knowledge of the two others.

To discuss that stage of particle growth, different models have been tried. Differences were mainly those involving: the actual site of polymerization; the type of removal of the monomeric radicals from the particles, i.e., either physical desorption or molecular diffusion; and the relative importance given to chemical reactions involving the monomeric radicals in the aqueous phase.

The definition of the chemical species depends on the assumptions made, i.e., on the model. In the further discussion a shell model is retained after elimination of 12 other cases. The reactions to be considered are shown in Table 1 and illustrated in Fig. 1. It is seen how new particles can be formed and how termination can occur.

MODEL OF PARTICLE GROWTH

For the study of particle growth at constant number of particles, step 3 is not considered, and the rate of step 4 equals the sum of the rates of step 1 and of step 11.

Since every soluble oligomeric radical S° becomes a precipitated macroradical R°, monomer consumption through reaction 2 is considered to occur through reaction 5. There are indeed few propagation steps occurring in solution, so that eventual differences in rates of propagation will not affect the net rate of monomer consumption.

The steady-state equations are thus as given in Eqs. (1)-(3).

TABLE 1.

Equation	Constant	Reaction
1. $I/2 \longrightarrow \frac{1}{2} I^\circ \longrightarrow S^\circ$	k_{dec}	Initiation
2. $S^\circ + M_w \longrightarrow S^\circ$		Propagation in water
3. $S^\circ \longrightarrow R^\circ$ + Particle		Particle nucleation
4. $S^\circ \longrightarrow R^\circ$		Oligomer precipitation on existing particle
5. $R^\circ + M \longrightarrow R^\circ$	k_p	Propagation within particle
6. $R^\circ + M \longrightarrow M^\circ_p$ + Polymer	k_t	Transfer reaction
7. $M^\circ_p + M \longrightarrow R^\circ$	k_r	Reinitiation in particle
8. $M^\circ_p \longrightarrow M^\circ_s$	k_d	Escape of monomeric radical into the water phase
9. $M^\circ_s \longrightarrow M^\circ_p$	k_a	Trapping of soluble monomeric radical by particle
10. $M^\circ_p + R^\circ \longrightarrow$ Polymer	k_{trm}	Termination in particle
11. $M^\circ_s + M_w \longrightarrow S^\circ$	k_r	Reinitiation in water
12. $M^\circ_s + M^\circ_s \longrightarrow B$	k_{tmm}	Termination in water

$$d[R^\circ]/dt = 2\,k_{dec}[I] - k_t[R^\circ][M] + k_r[M^\circ_s][M_w] + k_r[M^\circ_p][M] - k_{trm}[M^\circ_p][R^\circ]\,(1/\phi) = 0 \qquad (1)$$

$$d[M^\circ_s]/dt = k_d[M^\circ_p] - k_r[M^\circ_s][M_w] - k_a[M^\circ_s] - 2\,k_{tmm}[M^\circ_s]^2 = 0 \qquad (2)$$

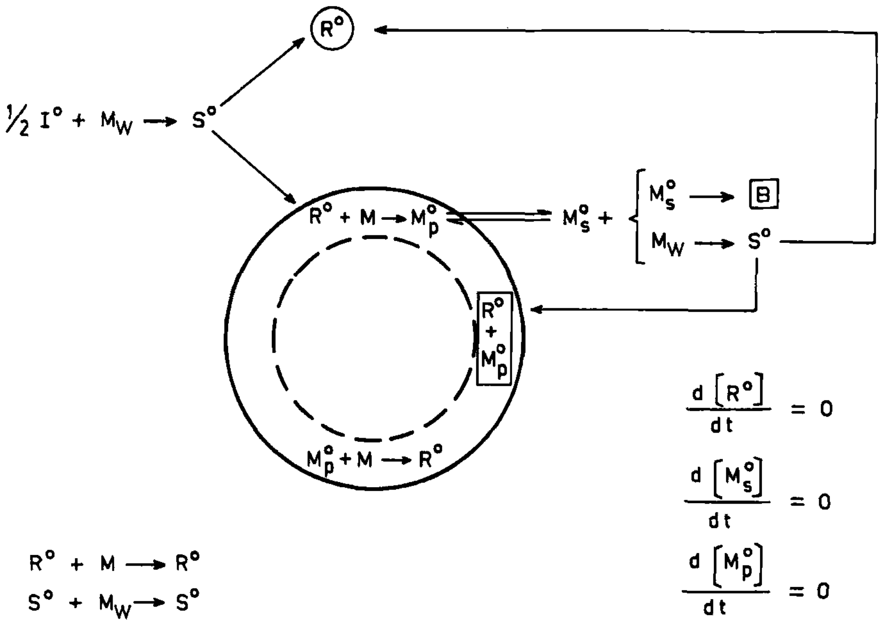

FIG. 1. Reactions in shell model.

$$d[M_p^\circ]/dt = k_t[R^\circ][M] - k_d[M_p^\circ] + k_a[M_s^\circ] - k_r[M_p^\circ][M]$$

$$- k_{trm}[M_p^\circ][R^\circ]\ (1/\phi) = 0 \qquad (3)$$

where

$$\phi = [(\pi/6)d_p^{\ 3} - (\pi/6)(d_p - 2f)^3]N_p \times 10^{-3} \qquad (4)$$

and where N_p is the number of particles per unit volume, d_p the particle diameter, and f the thickness of the shell. The validity of the use of the steady-state assumption for the radical species has been checked by comparison with other methods as Runge Kutta numerical integration or markovian analysis of the polymerization.

In case of very small particles, the specific rate of absorption is given [8] by:

$$k_a = 2D_{M/W} N_p d_p \pi \tag{5}$$

where $D_{M/W}$ is the diffusivity of vinyl chloride in water. On the other hand, the rate of escape of the monomeric radicals from the shell to water has been established with the aid of relations developed by Chandrasekhar on molecular diffusion from a random point to an absorbing barrier [9]. We consider indeed that a monomeric radical traveling in the shell is trapped by the aqueous phase when it reaches the particle-water interface, and this, owing to the great difference of diffusivities between the two phases.
Then:

$$k_d = 2D/\overline{E}^2 \tag{6}$$

with D being the diffusivity of the monomeric radical in the particle and $\overline{E}$ the average net distance such a radical has to cross before reaching the particle-water interface.

From geometrical considerations, we derive the serial expression for $\overline{E}$:

$$\overline{E} = r_p + f - \left(\frac{2}{\pi}\right) r_p - (r_p + f)\left[\left(\frac{1}{2}\right)^2 \left(\frac{K^2}{1}\right) + \left(\frac{1 \times 3}{2 \times 4}\right)^2 \left(\frac{K^4}{3}\right) + \ldots\right] \tag{7}$$

where

$$r_p = d_p/2$$

and

$$K = (r_p - f)/r_p \tag{8}$$

Equations (1), (2), and (3) are solved and the values of R°, M_s° and M_p° may be introduced in relations giving the rate of monomer consumption v_{Br} and the degree of polymerization DP.

FITTING OF THE PARAMETERS

The best fit should be found for the kinetic constants and the other parameters. The kinetic constant for the reaction 1 has been determined independently [6, 7] while values for the diffusivity of vinyl chloride in water [10] and its solubility in the particles [11, 12] have been found in the literature.

The parameters to be determined are the kinetic constants k_p, k_r, k_t, k_{trm}, and k_{tmm}, the diffusivity D, and a geometrical parameter defining the thickness of the shell. We tried two cases, one with a shell of constant thickness and the other with a thickness proportional to the particle diameter. With the available data, both were found satisfactory with respect to statistical tests, but the latter has the advantage of avoiding difficulties when one deals with very small particles as in the very beginning of the polymerization. Other laws of variation of the shell thickness should be tried.

If one deals with polymerizations performed at pressure p below the saturation pressure of vinyl chloride p_0, one defines three additional parameters (a_1, a_2, and a_3) relating some of the parameters to the vapor pressure or to the volume fraction v_2 of the polymer in the particles.

$$k_t = k_{t0} (p/p_0)^{a_1} \tag{9}$$

$$k_{trm} = k_{trm0} [(1 - v_2)/v_2]^{a_2} \tag{10}$$

$$D = D_0[(1 - v_2)/v_2]^{a_3} \tag{11}$$

Kinetic data on 11 classical batch polymerizations and on 10 experiments done at vapor pressure below saturation have been used to find the best fit of the parameters (Fig. 2). In those experiments, persulfate concentration ranges from 0.0025 to 0.04 mole/liter, the final particle diameter from 300 to 3000 Å, and the number of particles from 2×10^{15} to 10^{19} /liter. The objective function to be minimized is that shown in Eq. (12).

$$F = \sum_{i=1}^{k} \sum_{j=1}^{n} \left(\frac{v_{Br_{ij}} - v^*_{Br_{ij}}}{v^*_{Br_{ij}}} \times 100 \right)^2 + \frac{1}{2} (DP_{ij} - DP^*_{ij})^2 \tag{12}$$

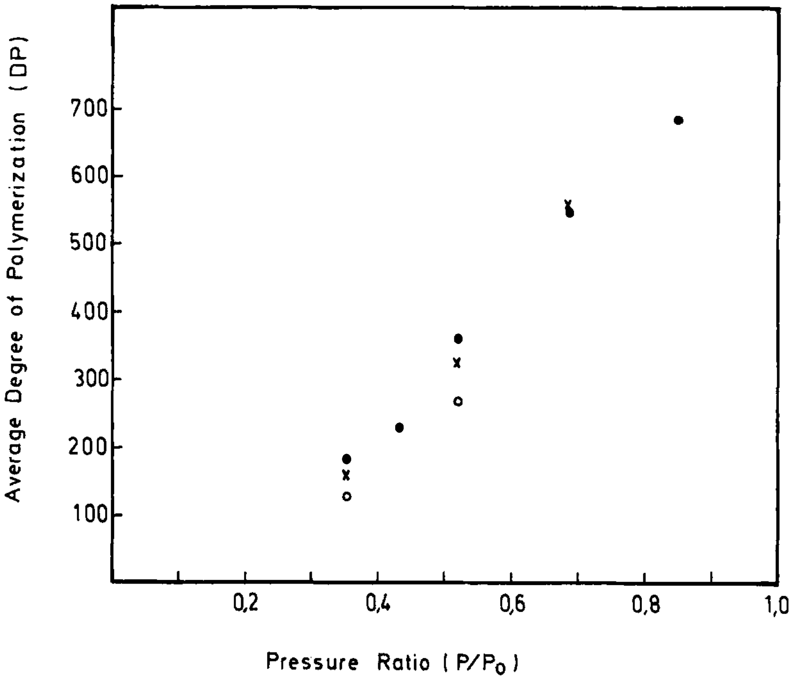

FIG. 2. Plots of pressure ratio vs. degree of polymerization obtained at various $K_2S_2O_8$ concentrations: (●) 0.0025 mole/liter; (×) 0.01 mole/liter; (○) 0.04 mole/liter.

where the subscript i refers to the i-th experiment, the subscript j to the j-th point in the i-th experiment, and the asterisks denote experimental values.

The values of the parameters at 50°C are obtained with a standard deviation of about 25% and are listed in Table 2. The value of a_1 is influenced mainly by results of molecular weights (Fig. 2), while a_2 and a_3 are related to the "max effect" mentioned for the first time by Ugelstad [1].

The application of this model to nucleation phenomena in order to calculate a priori the number of particles for a given recipe will be presented in a future paper.

TABLE 2. Values Found for the Parameters at 50°C

Parameter	Value
Propagation constant k_p	4675 liter/mole-sec
Reinitiation constant k_r	63 liter/mole-sec
Transfer constant k_t	5.5 liter/mole-sec
Termination constant k_{trm}	5.9×10^5 liter/mole-sec
Termination constant k_{tmm}	5.0×10^7 liter/mole-sec
Diffusivity in particles D	2.9×10^{-6} cm^2/sec
f/d_p	0.055
a_1	-1.3
a_2	1.84
a_3	0.91

NOTE

Readers who want to have details on the derivation of Eq. (7), or on the optimization technique used to minimize the function (12) may contact the author.

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