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Kinetic Models for Bulk Polymerization of Vinyl Chloride and Their Rate Expressions

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ABSTRACT

The various models and their rate expressions developed for the bulk polymerization of vinyl chloride are checked against carefully evaluated experimental data. Only Ugelstad's and Olaj's models yield rate expressions consistent with experiment.

The kinetics of bulk and suspension polymerization of vinyl chloride (VC), especially its nonlinear conversion-time behavior, have attracted the interest of the kineticists from the very beginning of kinetic investigations. In this contribution a survey is given of the various models which have been developed for the bulk polymerization of VC, giving special emphasis to the rate expressions which can be derived from these models.

Bengough and Norrish as early as in 1950 postulated a linear relationship between the instantaneous rate of conversion (dU/dt) and the conversion (U) to the 2/3 power, which suggests a correlation between rate and particle surface (which is assumed to be proportional to the 2/3 power of polymer mass, i.e., conversion) [1]:

$$dU/dt = a_1 + b_1 U^{2/3} \tag{1}$$

where a_1, b_1 are constants within a run.

Five years later Schindler and Breitenbach [2] introduced a conversion-dependent termination constant k_t into the kinetic scheme (a_2 = constant):

$$k_t = (k_t)_{U=0} (1 + a_2 U) \tag{2}$$

Their idea finally led to a linear relationship between the mean rate of conversion (U/t) and time t:

$$U/t = a_3 + b_3 t \tag{3}$$

In the mid-sixties Talamini and co-workers [3, 4] tried to give more specific consideration to the heterogeneous character of the polymerization system and developed a scheme which allowed for the occurrence of polymerization in both the phases, in the monomer-rich phase, which contains practically no dissolved polymer, as well as in the phase consisting of the precipitated polymer, which is swollen with monomer. The initiator is assumed to be distributed over both the phases according to some partition law, chains therefore may be initiated in either phase. However, the growing chains cannot change from one phase to the other during their life-time so that they will be terminated in that phase in which they have been initiated. This scheme, which has been further specified and developed by Hamielec et al. [5], in its simple form rather indicates a linear dependence of instantaneous rate on conversion itself:

$$dU/dt = a_4 + b_4 U \tag{4}$$

In its more elaborate form it necessarily contains additional parameters, so that at the first sight no such straightforward relationship between rate and conversion or time can be written as in the previous cases. The qualitative interpretation of the experimentally observed increase of rate with time (or conversion) here is that polymerization proceeds faster in the polymer-rich phase, so that an increase in the amount of that phase will–due to the increase in conversion–result in an increase in rate.

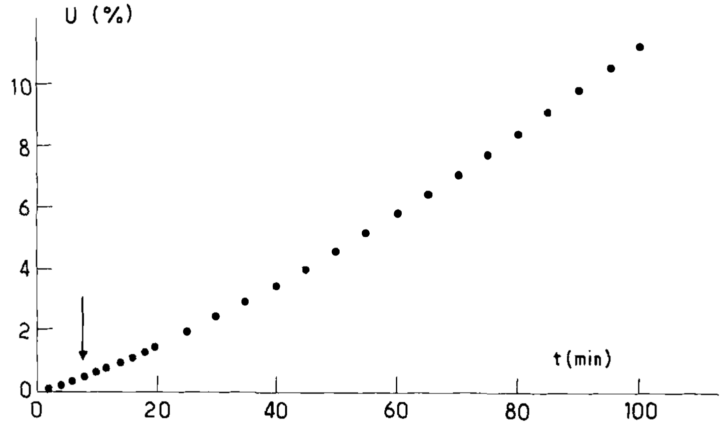

FIG. 1. Conversion as a function of time for polymerization of VC initiated by 2 × 10^{-2} mole/dm^3 2,2'-azobisisobutyronitrile at 50° C, measured by dilatometry. The arrow indicates the point of discontinuity.

If we at that point turn our attention to a typical conversion versus time curve of bulk polymerization of VC, which in this special case has been initiated by 2 × 10^{-2} mole/dm^3 2,2'-bisazoisobutyronitrile at 50° C, the conversion being carefully determined as a function of time by a dilatometric method (Fig. 1), and try to plot the experimental results after the instantaneous rate, dU/dt, has been evaluated, either by graphical or numerical differentiation, according to one of the equations derived from the kinetic models above, the outcome is not very satisfactory. None of these plots (Figs. 2-4) shows good linearity in the range of 1-10% conversion, although there seems to be a certain tendency towards linearity when going to higher conversions in the U/t versus t plot.

Although the two earlier models somehow have also taken into account the heterogeneity of the polymerizing system, the explicit assumption of two separate phases as put forward in the Talamini model, despite its shortcomings, offers the best platform for all attempts to develop an improved model for bulk polymerization of vinyl chloride.

The most vulnerable assumption inherent in the Talamini model seems to be the complete ignorance of the transport of radical chains from one phase to the other. Ugelstad et al. [6, 7]–most probably on the basis of such considerations–retained the explicit two-phase character of the polymerization system and in addition allowed for

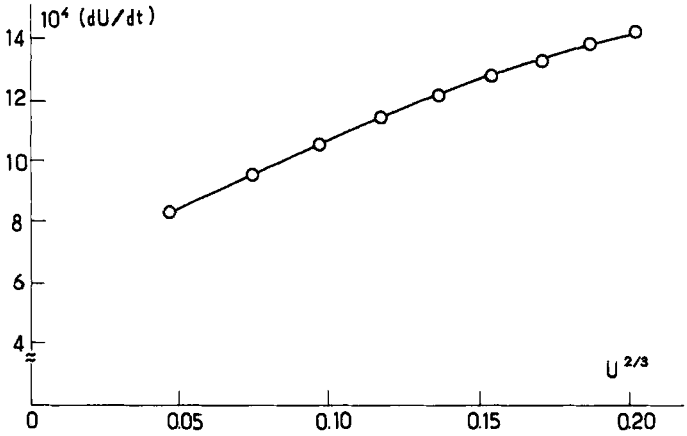

FIG. 2. Plot of the data originating from the run shown in Fig. 1 according to Eq. (1) (dU/dt vs. $U^{2/3}$).

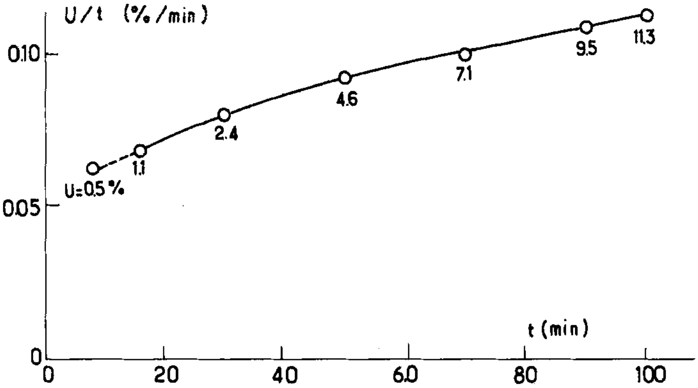

FIG. 3. Plot of the data originating from the run shown in Fig. 1 according to Eq. (3) (U/t vs. t).

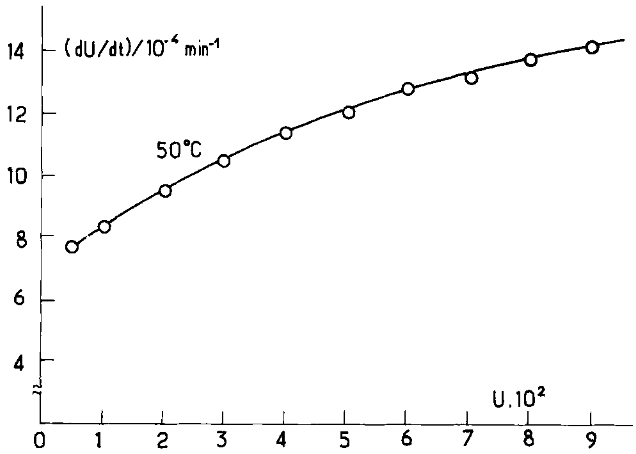

FIG. 4. Plot of the data originating from the run shown in Fig. 1 according to Eq. (4) (dU/dt vs. U).

radical absorption and radical desorption to and from the polymer phase (polymer particles), respectively. This led to an expression which implies a linear relationship between the instantaneous rate of conversion dU/dt and the square root of conversion $U^{1/2}$

$$dU/dt = a_5 + b_5 U^{1/2} \tag{5}$$

as an asymptotic law for high conversions, the actual behavior at low conversions being influenced by radical sorption and desorption processes to and from the polymer particles.

Practically at the same time we approached the problem of radical chain migration in a quite different way [8, 9]: We assumed that radicals may be formed by decay of the initiator in both the monomer-rich and the polymer-rich phases (see Fig. 5). Radicals formed in the monomer-rich phase will add monomer, thus being transformed into growing polymer chains. Due to the unfavorable thermodynamic conditions they soon will form tightly coiled chains and be finally incorporated into already existing polymer particles, where they may continue their growth and finally be stabilized by chain transfer or by mutual termination. On the other hand, the polymer radical chains, which have been initiated in the phase rich in polymer, will stay there

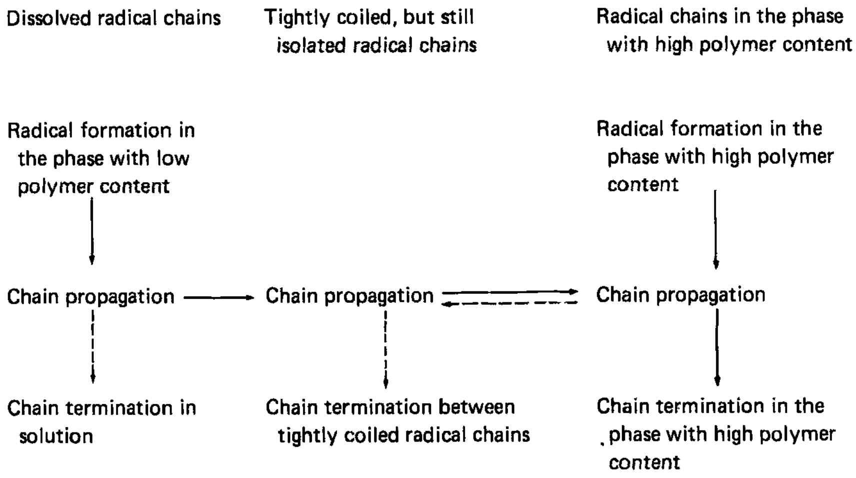

FIG. 5. Schematic representation of the reaction scheme for VC bulk polymerization as developed elsewhere [8, 9]. The thick arrows represent the most important paths of reaction.

until they are terminated. Thus we assume quantitative transport of the radicals which have been formed in the monomer-rich phase to the polymer-rich phase, which is the predominant site of polymerization, and assume all the termination to occur within the polymer particles. The main paths of the reaction corresponding to these assumptions are represented by the thick arrows of Fig. 5. According to this scheme, all radicals, irrespective of where they have been generated, finally contribute to the polymerization in the polymer particles. The rate expression, which can be extracted from this scheme, at least for not too high conversions, has the form

$$dU/dt = a_6 + b_6 U^{1/2} \qquad (6)$$

which is of the same general type as Eq. (5). The increase in rate with increasing conversion has to be understood as a consequence of the increase in kinetic chain length due to the volume expansion of the polymerization system in the actual sense, i.e., the polymer particles, at constant rate of initiation, while the constant term (a_6) may be looked upon as the contribution of the polymerization

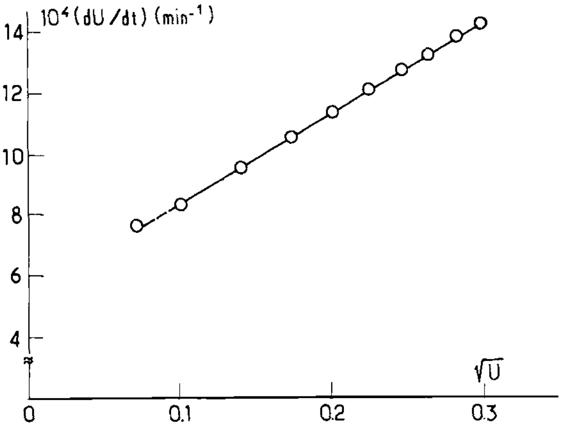

FIG. 6. Plot of the data originating from the run shown in Fig. 1 according to Eq. (6) (dU/dt vs. $U^{1/2}$).

occurring during the time lag which exists between the formation of the radicals in the monomer-rich phase and their incorporation into the polymer particles as growing polymer chains. Actually a plot of the data of Fig. 1 according to Eq. (6) [or Eq. (5)] shows a much better—if not a perfect—linearity (Fig. 6) compared to all former attempts (Figs. 2-4), thus favoring a model as Ugelstad's or ours over those described before.

An inspection of the physical meaning of b_5 and b_6 shows that these quantities are identical:

$$b_6 \equiv b_5 = k_p(f/k_t)^{1/2}(2k_o c_S)^{1/2}(\phi_M/\phi_P{}^{1/2})(\rho_M/\rho_P)^{1/2} \qquad (7)$$

where k_p, k_t are rate constants for chain propagation and bimolecular chain termination, respectively, within the particles. k_o is the first-order rate constant of initiator decomposition; f is initiator efficiency, c_S is the initiator concentration; ϕ_M, ϕ_P are volume fractions of monomer and polymer, respectively, within the monomer swollen polymer particles; and ρ_M, ρ_P are monomer and polymer density, respectively. This means that the Ugelstad model and ours yield the same expression for the so-called "autocatalytic term," $b_5U^{1/2}$

or $b_6U^{1/2}$, respectively. Accordingly, any argument in favor of one of the two models has to be derived from an inspection of the constant terms of Eq. (5) and Eq. (6), a_5 and a_6.

Ugelstad, on serious grounds has put forward the argument that radical desorption from the particles and bimolecular flocculation in solution should be important at low conversion, thus favoring his model over ours. However, one has to bear in mind what might be considered to be one of the most outstanding features of bulk polymerization of VC. From the work of Cotman et al. [10] it is known that at least for polymerization temperatures near 50° C in the very early stage of polymerization a large number of particles is formed (at least 25×10^{11}/g VC). Suddenly, at a conversion of a few tenths of a percent, this number drops to ca. 5×10^{11}/g VC (independent of initiator concentration), where it remains constant for at least that range of conversion which has been examinable by the electron microscope techniques employed. Parallel to this collapse in particle number there is a marked discontinuity in rate of polymerization (indicated by an arrow in Fig. 1); the rate which has increased with conversion before this drastic reduction of particle number suddenly drops at this point, too. An informatory calculation shows that, while before this discontinuity the number of particles exceeds the number of radicals, there are many more radicals than particles afterwards (approximately 5-10). We therefore may assume that at this discontinuity the system changes from polymerization conditions analogous to those to be encountered in emulsion polymerization (with the radicals well separated from each other) to a "pseudo-continuous" system where desorption processes and bimolecular flocculation are no longer of great importance. From these facts two important consequences may be derived: the first one, which has no direct relevance for the comparison of the kinetic models, is that the kinetic system after the discontinuity will be quite different from that before, so that it will make no sense at all to try to get insight into the polymerization behavior at higher conversions from measurements carried out in the very first stage before the drop in the particle number had occurred. The second is that most of Ugelstad's criticisms certainly will be valid for the state before the discontinuity has been reached (conversions below 0.5%). This state, however, completely differs from that at higher conversions. Our model—admittedly an oversimplification of the true situation—claims to be valid only from conversions onward which are well above the discontinuity ($U \geq 1\%$).

Now, from the fact that there is good linearity of the dU/dt versus $U^{1/2}$ plot from conversions as low as 1% upward (Fig. 6), some preference for our description of the situation in the bulk polymerization of VC in this range of conversions may be derived; Eq. (6) should be valid already at comparatively low conversions (i.e., after the discontinuity has been passed) while Eq. (5) which follows from the Ugelstad scheme is a limiting law for higher conversions and most probably should not be valid down to conversions as low as 1%.

Another possibility of comparison of the two models (Ugelstad's and ours) could be based upon an examination of the reaction order of the quantities a_5 and a_6 with respect to the initiator concentration. a_5, which is a complicated expression containing all parameters involved in the Ugelstad scheme, should be proportional to $c_S^{1/2}$, while a_6 is given by

$$a_6 = k_p(2fk_oc_S/k_{aggl})\,\phi_M^* \tag{8}$$

where k_{aggl} is the formal (first-order) rate constant of "agglomeration" of the radical chains initiated in the monomer-rich phase, to the polymer particles and ϕ_M^* is the volume fraction of monomer at the site of reaction of the radical chains in the monomer-rich phase. Accordingly, a_6 should vary with c_S itself. Actually, we have found that the intercepts of the plots of dU/dt versus $U^{1/2}$ are proportional to $c_S^{0.67}$ [11], so that the truth seems to lie somewhere in the middle. This conclusion probably may be generalized for the comparison of the two models in all.

It remains to emphasize that from the theoretical expression obtained for the "autocatalytic term" the characteristic ratio of rate constants $k_p/k_t^{1/2}$, multiplied by the square root of the efficiency f, can be calculated for the polymerization within the particles, i.e., the polymer-rich phase, provided the monomer concentration within the particles is known. With the aid of careful swelling measurements [12, 13], the volume fractions of monomer and polymer have been determined for quite a few precipitation polymerization systems with VC as a monomer, further consisting of precipitants for the polymer (such as cyclohexane) or solvents (such as 1,2-dichloroethane) in amounts insufficient for rendering the polymerization homogeneous. Although no independent check of this quantity $k_p(f/k_t)^{1/2}$ is available, it must be stated that it behaves fully reasonably on any change in composition, volume fraction of polymer in the polymer particles, temperature, etc. It would appear, therefore, that k_t is governed by a marked Trommsdorff effect (gel effect), the extent of which is uniquely determined by the volume fraction of PVC in the swollen polymer particles at constant temperature of polymerization, whatever the polymerization system might be, thus reflecting the properties of the polymer particles as the predominant site of polymerization [8, 9, 11]. This view is further supported by the highly negative overall energy of activation measured for this quantity [14] (-4.5 kcal/mole), which indicates an energy of activation of ca. 23 kcal/mole for k_t. Such a high value is incompatible with polymerization in a "normal" medium as the monomer-rich phase, but is highly reasonable for a polymerization system which consists approximately 70% of polymer, as it is the case in the monomer swollen polymer particles in bulk VC polymerization.

As the physical meaning of the autocatalytic term is the same for Ugelstad's model and ours, the reasonable variations which we observed for k_t with composition and temperature of course will lend equal support to both the models, distinctly favoring them over all previous ones.

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