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Bulk Polymerization of Vinyl Chloride: Nucleation Phase

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ABSTRACT

Techniques are presented to follow the formation of the first polymer structures. The instrumentation is based on the use of a turbidimetric device equipped with a 1-liter glass autoclave and special sampling procedures. First particles appear as conversion reaches a value of approximately 10^{-5}; they are spherical at 50 or 60°C, but somewhat more complex at lower temperatures. Their number, related with the free radical formation rate, remains constant up to a critical conversion rate, which depends strongly on stirring speed. Above this critical rate, a second nucleation begins and simultaneously the submicronic primary particles ("granules") agglutinate to form "grains," the size of which is not lower than 20-30 μm. Some kinetic data, as well as molecular characteristics, are indicated.

INTRODUCTION

The bulk polymerization of vinyl chloride has already been the subject of a large number of publications; a substantial bibliography can be found in the article by Kuchanov and Bort [1]. These authors stress the important role played by phenomena occurring at the start of polymerization, as had been pointed out by Mickley [2], Cotman [3], Ravey [4], and Behrens [5]. However, a critical survey of these publications shows that this important stage of the polymerization has not yet been investigated exhaustively, perhaps because of the technological problems encountered.

The purpose of this publication is to bring a contribution to the study of the nucleation phase in the bulk polymerization of vinyl chloride (VC), by presenting techniques designed to follow as closely as possible the formation of the first polymer structures.

EXPERIMENTAL

Figure 1 shows the 1-liter glass autoclave. The stirring device includes a continuous speed variator and a shaft which has been equipped with different stirrers (Pfaudler impellers and Lightnin flat-bladed turbines).

Figure 2 presents the turbidimetric device. A white light source (1) is located, on an optical bench, at the focus of a converging lens (2). The parallel light beam thus obtained is directed, through a total reflection prism (3), into a vertical glass rod (4) inserted in the flat bottom part of the autoclave. Then it crosses over the reaction medium, the optical path being preselected (about 60 mm). It is received by an optical fiber (5) situated upright in the axis of the glass rod, which conducts the light, through the upper part of the autoclave, to an electric photo cell (8). The electric signal is amplified (9) and recorded (10). Figure 3 shows an example of typical curve obtained.

Sampling

Sampling is made by means of a manual valve, which opens a tube located at the bottom of the autoclave. Samples are received in glass aerosol bottles, equipped with a clack adaptable to the end part of the tube. For each polymerization run, two samples are taken: one for conversion ratio determination, the other for morphological examination.

In following the course of polymerization, one can observe successively three different types of samples (Fig. 4). First, a turbid liquid, in which turbidity is caused by the presence of very small particles (submicronic granules) in stable suspension; second, a

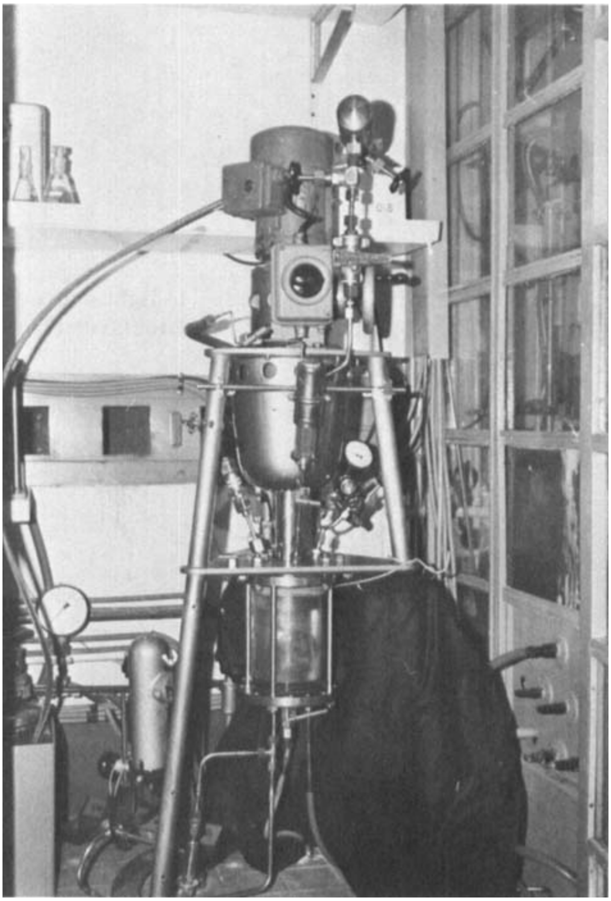

FIG. 1. View of the 1-liter glass autoclave.

turbid liquid supernatant over a layer of white product at the bottom of the bottle (this layer is formed of grains, larger than 10 μm); third, a clear liquid, with the white product layer at the bottom, indicating the absence of granules.

The submicronic granules are observed in detail by means of electronic microscopy, after direct pulverization of the contents of the aerosol bottle onto a metallic grid. A quick expansion of VC is

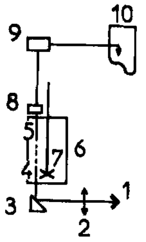

FIG. 2. Scheme of turbidimetric device: (1) light source; (2) lens; (3) prism; (4) glass rod; (5) optical fiber; (6) autoclave; (7) stirrer; (8) photocell; (9) amplifier; (10) recorder.

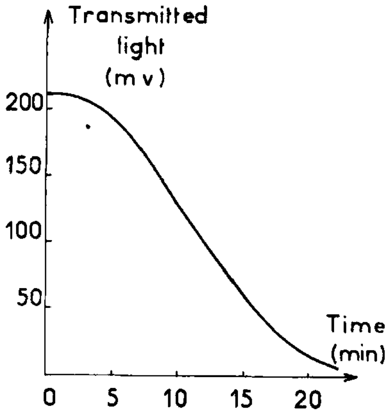

FIG. 3. Example of experimental turbidimetric curve.

necessary to avoid the plasticization that takes place when VC is degassed slowly.

The "grains"–here described as particles of size higher than 10 μm–are transferred, together with the liquid monomer, into a large excess of methanol, and VC is then slowly degassed. The methanol slurry is observed by optical microscopy, and used for granulometric analysis.

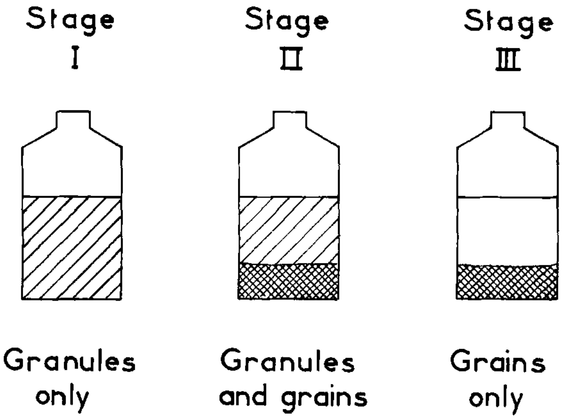

FIG. 4. Evolution of samples during a polymerization run.

Interpretation of Turbidimetric Curves

The measurement of electric intensity I recorded as a function of time permits the calculation of the optical density D:

$$D = \log I_0/I$$

where I_0 is the intensity measured before the start of polymerization. Three assumptions will enable us to interpret these curves: first, the number of particles remains constant throughout the polymerization, second, all the particles have the same growth rate, third, light absorption follows the same law as in the case of polymer lattices. Accepting these assumptions, one can write:

$$\tau/\phi^3 = \tau_f/\phi_f^3 \tag{1}$$

where τ denotes polymer concentration (i.e., conversion ratio), ϕ denotes average diameter of particles, and the subscript f refers to final values as experimentally measured at the end of the polymerization run, and

$$D = kD_0\tau \tag{2}$$

where D_0 denotes specific optical density of the PVC particles in liquid VC and k is a constant.

From Eqs. (1) and (2), one can infer

$$D = D_f\,(\phi/\phi_f)^3\,D_0/D_{0f} \tag{3}$$

The formula empirically established for PVC latices is

$$D_0 = A\phi^2 + B\phi \tag{4}$$

where A and B are constants.

The system of Eqs. (3) and (4) can be reduced to a fifth-degree equation

$$D = D(\phi) \tag{5}$$

Resolution of this equation makes it possible to calculate ϕ for each point of the curve, and then Eq. (1) leads to the value of τ (conversion ratio): so the recorded curve $I = I(\tau)$ finally yields the kinetic curve $\tau = \tau(t)$.

Furthermore, the number of particles N created (per cm^3 of liquid monomer) can be calculated by the relation

$$N = 1.2 \times 10^{10}\,\tau_f/\phi_f^3 \tag{6}$$

Complementary Runs

Complementary tests were performed in a 16-liter stainless steel-lined autoclave, in order to follow the same polymerization run by repeated samplings; this was not possible in the 1-liter autoclave, owing to the perturbations they would cause.

RESULTS AND DISCUSSION

Solubility of PVC in VC

An examination of the turbidimetric curves shows that the poly(vinyl chloride) (PVC) formed at the start of polymerization has a solubility in its monomer less than 10^{-5} (10^{-3}%). This value is significantly lower than those given by Kuchanov and Bort [1], who mentioned 0.5%, and by Ravey [4], who gave 0.03% (3×10^{-4}). These authors investigated the solubility in VC of samples of "normal" PVC, in other words, polymer obtained after a conversion ratio exceeding 70%. One cannot exclude the possibility that, during the final stage of polymerization, PVC chains of a special structure are formed, the solubility of which is higher in VC than that of the first chains formed.

Nature of First Particles Formed

The first particles observed in polymerization runs at 50 and 60°C occur in the form of substantially spherical granules which appear to remain below 0.25 to 0.35 μm (after removal of VC). Figure 5 shows a picture of typical particles.

When the polymerization temperature is 30 or 40°C, the pictures obtained appear to indicate the presence of a substructure in the particles, which are no longer spherical (Fig. 6).

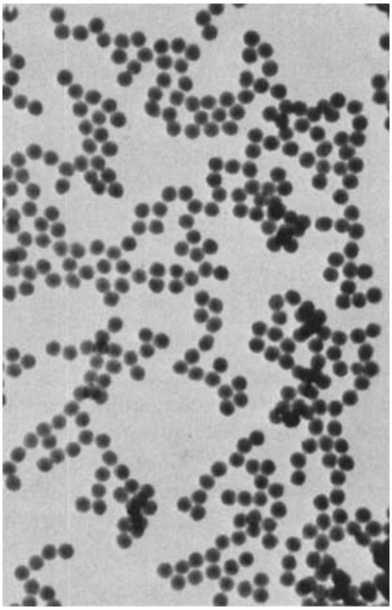

FIG. 5. Particles first formed at 50° C (agitation 0.7 m/sec). × 10,000.

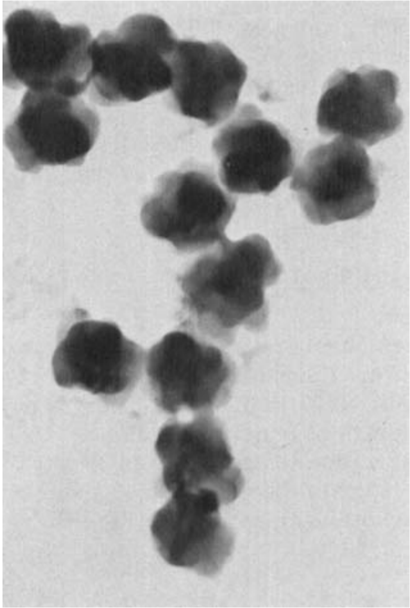

FIG. 6. Particles first formed at 40°C (agitation 0.7 m/sec). ×50,000.

A polymerization run at 20°C yielded particles which look like a crystalline product (Fig. 7).

These granules form suspensions infinitely stable in the monomer, as the flocculation described by Mickley [2] only occurs in other conditions. During a specific run, and up to a critical conversion ratio τ_c, the number of granules remains constant (hence it is determined from the start), and the granules grow in a uniform manner, while the size distribution remains remarkably uniform (Fig. 8). Thus, we can say that two of our assumptions are verified. The number of granules created per unit volume of VC monomer depends on free-radical formation rates. In the region investigated, which covers a range of free-radical formation rates in a ratio of 1 to 500, a relationship of the type shown in Eq. (7) is observed:

$$N = 2.7 \times 10^{10}(R \times 10^{13})^{\beta} \tag{7}$$

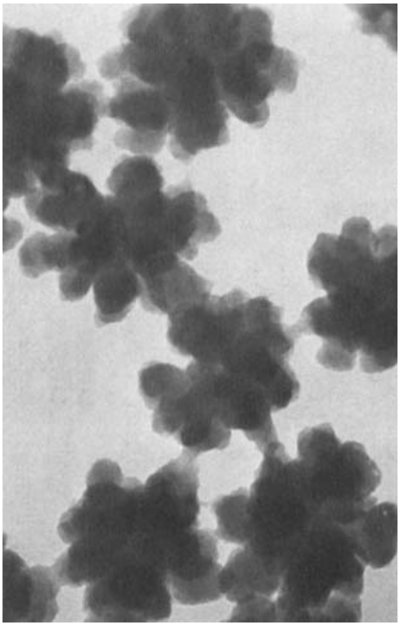

FIG. 7. Particles formed at 20°C (nonagitated medium). ×50,000.

where R denotes rate of formation of free radicals and the exponent β varies as a function of temperature (θ) in accordance with a formula of the type shown in Eq. (8):

$$\log(1 - \beta) = a + b\theta \tag{8}$$

It can be seen that for any given free-radical formation rate, the number of particles created decreases with increasing temperature (Figs. 9 and 10).

Particle Diameters

The homogeneous growth of particles with time is illustrated by Fig. 11, in which the results of a series of tests conducted with the

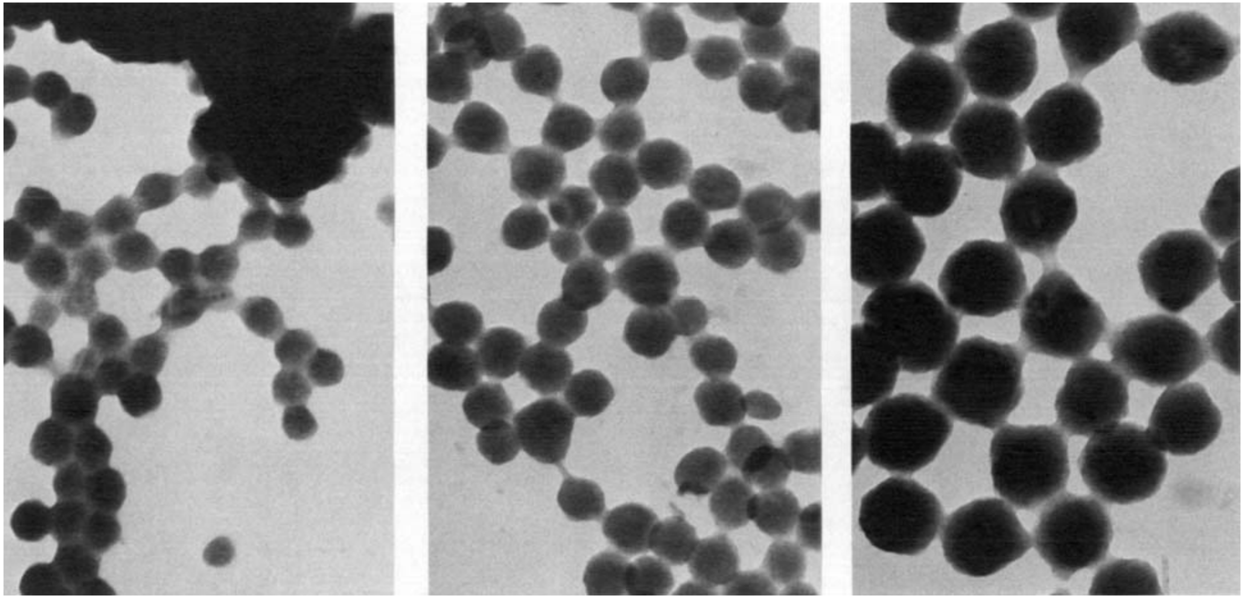

FIG. 8. Evolution of first formed particles during a polymerization run at 50°C (agitation 0.7 m/sec): (a) after 15 min (conversion 0.015%); (b) after 30 min (conversion 0.029%); (c) after 80 min (conversion 0.121%). ×50,000.

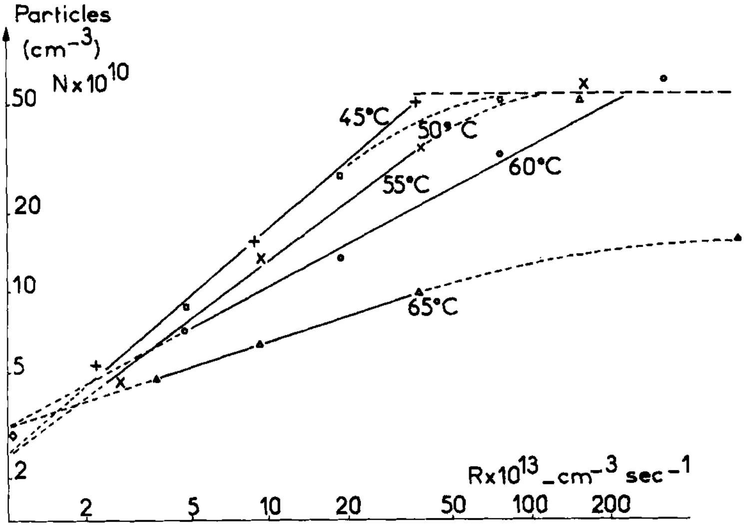

FIG. 9. Effect of rate of formation of radicals R on the number of generated particles N. Initiator: lauroyl peroxide.

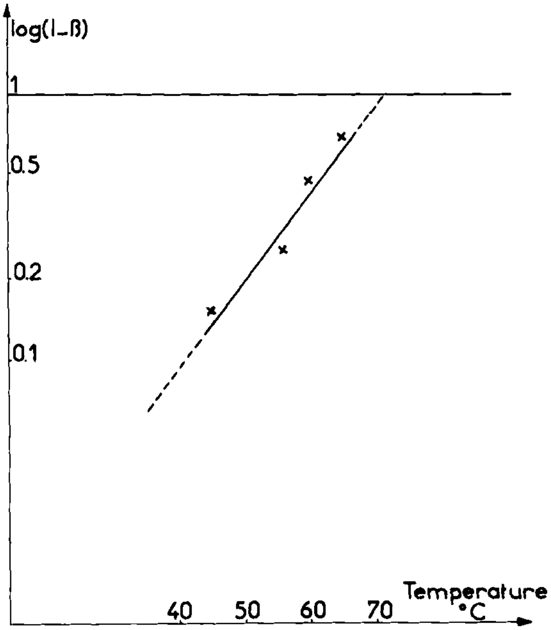

FIG. 10. Effect of temperature upon exponent β of the relation: $N = 2.7 \times 10^{10} . (R \times 10^{13})^{\beta}$. Initiator: lauroyl peroxide.

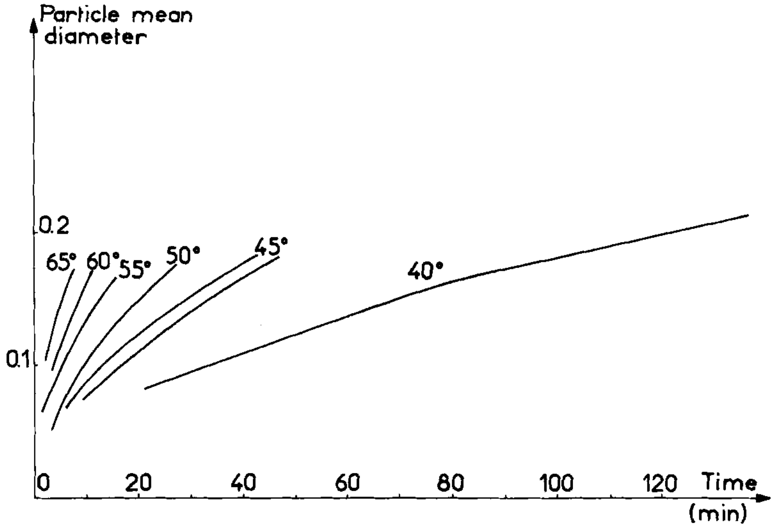

FIG. 11. Evolution of particle size with time and temperature. Initiator: lauroyl peroxide, mole fraction 7.82 × 10^{-6}.

same rate of initiator and different temperatures are compared. One cannot observe the linear relation indicated by Behrens [5] which should relate to particular kinetics.

Effect of Agitation

Above a critical conversion ratio τ_c, the particle size distribution ceases to be uniform. A second, far smaller population of granules appears, indicating a second nucleation (Fig. 12); simultaneously, some of the granules begin to agglutinate to form granules of a complex structure as well as grains with a minimum size of 20 to 30 μm, in other words, about 100 times larger than the granules. The value of this critical conversion ratio depends strongly on agitation. Hence, in the experimental conditions employed, a value of τ_c is observed close to 0.12%, with a peripheral agitation speed of 0.7 m/sec, whereas with a speed of 2m/sec, the value of τ_c is lower than or equal to 0.05%.

This point is of major importance, as it makes it possible to explain

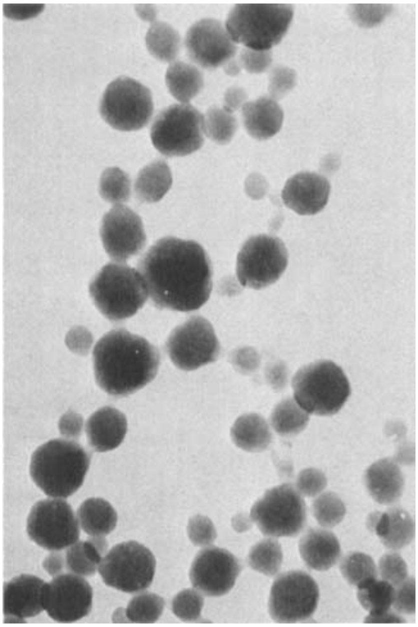

FIG. 12. Sample observed after the second nucleation ($\tau > \tau_c$). ×50,000.

the main differences between hitherto published data, especially those of Mickley [2], Cotman [3], Ravey [4], Bort [1] and other publications mentioned in the latter and the experimental results obtained during this investigation.

Actually, the experiments described in these publications are based on polymerization in a nonagitated medium (sealed tube or dilatometer) with low volumes limiting the influence of thermal convection currents which may agitate the reaction medium. In these conditions, it is certainly true that the critical conversion ratio is likely to be very high, which explains why the authors were able to observe uniform spherical granules at conversion rates far greater than 0.1%.

The different stages of the start of polymerization may be summarized as follows. The macromolecules formed initially are grouped in packs of 5 to 10, according to Behrens [5], which form particles of about 0.01 μm (10 nm), called granules here, that remain in stable suspension in the monomer. These granules subsequently grow

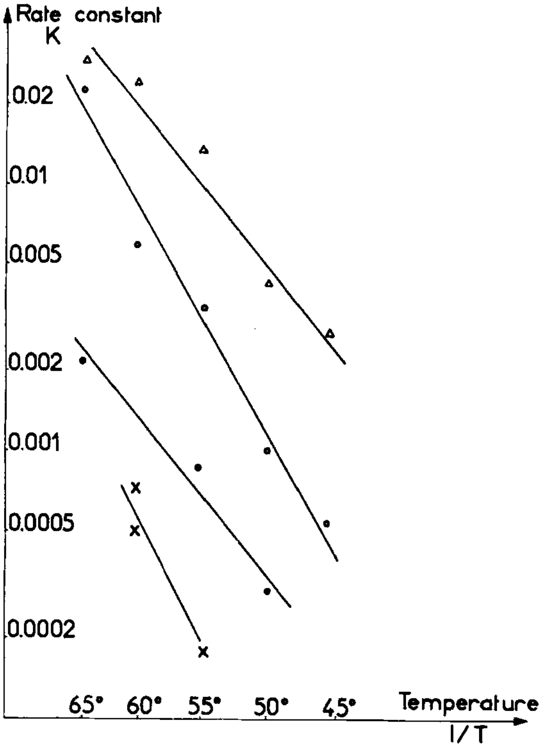

FIG. 13. Variation of rate constant K ($\tau = Kt^{1.5}$) with reciprocal absolute temperature at various mole fractions of lauroyl peroxide: (×) 1.95×10^{-6}; (●) 7.82×10^{-6}; (○) 3.13×10^{-5}; (△) 1.25×10^{-4}.

uniformly, without any formation of new particles, up to a critical conversion ratio τ_c which depends on agitation and decreases when the intensity of agitation rises; in this stage, the size of these granules does not exceed 1 μm, according to Mickley [2], in the absence of agitation and 0.2 to 0.3 μm in a highly agitated medium. Starting from the critical conversion ratio, there occurs a second nucleation, and the granules begin to aggregate, forming grains, the size of which is not lower than 20-30 μm in strongly agitated medium; these grains do not form a stable suspension and settle immediately as soon as agitation is stopped.

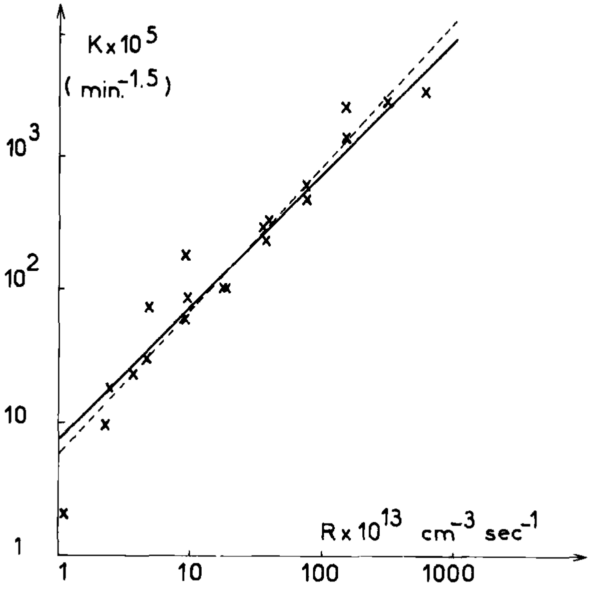

FIG. 14. Variation of rate constant K (τ = $Kt^{1.5}$) with radical formation rate: (—) linear relation; (--) regression calculation (slope = 1.076), correlation coefficient 0.969.

Kinetics of Polymerization

In the region of conversion ratios below the critical rate, namely, as long as polymerization occurs with the growth of a constant number of uniform granules, the study of kinetic curves obtained by means of the turbidimetric device leads to the following conclusions.

The kinetics may be described by Eq. (9):

$$\tau = Kt^{1.5} \tag{9}$$

where t denotes the time of polymerization and K designates a constant depending on the temperature and on the initiator. The constant K in Eq. (9) varies as a function of temperature in accordance with an Arrhenius law with a heat of activation of about 30 kcal/mole (Fig. 13). For a given initiator (lauroyl peroxide), the constant K depends biunivocally on the rate of formation of free radicals (independently

TABLE 1. Effect of Agitation on Initial Kinetics of Polymerization

Polymerization temperature (°C)	Stirrer speed						
	Stirrer type	Axial (t/min)	Linear (m/sec)	Reaction time (min)	Conversion (%)	Mean polymerization rate (%/hr)	Granulometry
50	Impeller	250	0.71	30	0.103	0.206	Homogeneous; no grain
	Turbine	250	0.42	29	0.078	0.161	
50	Impeller	700	1.97	28	0.063	0.135	Heterogeneous; granules and grains
	Turbine	1200	2.01	29	0.046	0.095	
60	Impeller	250	0.71	52	0.536	0.62	Granules and grains
	Impeller	1200	1.97	52	0.261	0.30	No granule
	Impeller	1200	1.97	105	0.518	0.295	No granule

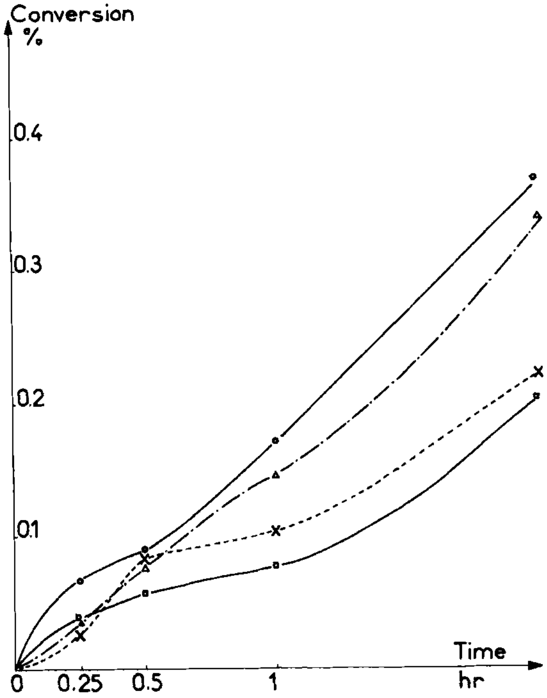

FIG. 15. Examples of slow kinetics exhibiting characteristic inflection at various mole fractions lauroyl peroxide: (□) 3.12×10^{-6}; (×) 7.82×10^{-6}; (○, △) 15.64×10^{-6}. Temperature 50°C.

of temperature), in accordance with a substantially linear relationship (Fig. 14). The foregoing results correspond to tests conducted under moderate agitation (peripheral speed 0.7 m/sec).

If polymerization is performed in the same conditions with more intense agitation, it is observed that the mean polymerization rate decreases (Table 1). The results presented reveal that the effect recorded does not depend only on the peripheral agitation speed, but also on the type of stirrer, namely the agitation system. As the turbidimetric device fails to provide any further usable information in these conditions (we are now above the critical conversion rate and the particle size distribution is heterogeneous), the investigation was performed by means of successive samplings during polymerizations in a 16-liter autoclave. The curves thus obtained (Fig. 15) exhibit a characteristic accident (slowdown followed by reacceleration), similar to that observed by Cotman [3]; this slowdown is perhaps the cause of the drop in mean polymerization rate observed when increasing the intensity of agitation (Table 1). It should be noted that this accident does not appear on the curves plotted in the region of uniform particle size distribution. It appears only during tests which exceed the critical conversion ratio (and when this passage is sufficiently slow to enable observation). Hence it may be surmised that the kinetic slowdown observed is associated with the passage from granules to grains.

When polymerization (or agitation) is sufficiently rapid for the critical conversion ratio τ_c to be exceeded before any observation, the kinetics have an autoaccelerated aspect and no longer follow Eq. (9), which is valid in the region of conversions below τ_c.

Molecular Characteristics of the PVC Formed

Several distribution analyses of molecular weights by gel-permeation chromatography were carried out on samples polymerized at 50° C with lauroyl peroxide (7.82 × 10^{-6} mole/mole PVC), up to conversion rates of about 0.06%.

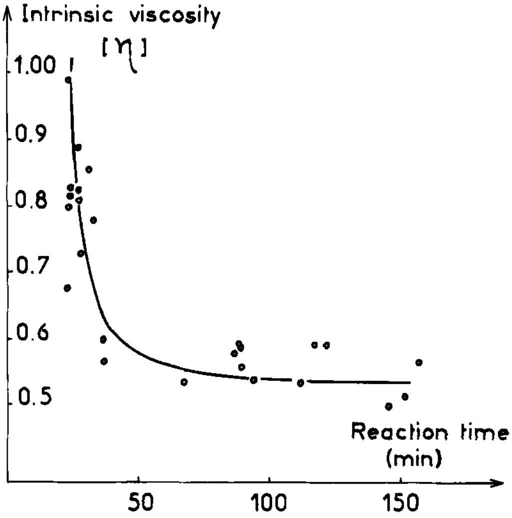

FIG. 16. Intrinsic viscosity vs. reaction time in presence of added impurities. Temperature, 50° C; mole fraction lauroyl peroxide, 7.82 × 10^{-6}.

TABLE 2. Molecular Characteristics of Some PVC Samples

Polymerization conditions[a]			Molecular characteristics of PVC		
Time (min)	Conversion (%)	Mean rate (%/hr)	$\overline{DP}_n$	$\overline{M}_w/\overline{M}_n$	IVA[b]
31.5	0.047	0.090	705	1.82	110
31	0.050	0.097	625	1.78	100
29	0.064	0.132	590	1.78	95
21	0.069	0.197	520	1.81	85
300/360	75/85	12/17	865	1.9	130

[a] Polymerization temperature, 50° C.
[b] Afnor viscosity index (0.5% cyclohexanone).

The results lead to make the following observations. The molecular weights of these samples are significantly below those of the products obtained after a high conversion ratio; this had been considered by Danusso [7] and Abdel Alim and Hamielec [8]. The spread of the molecular weight distribution, evaluated in terms of the ratio $\overline{M}_w/\overline{M}_n$, remains highly comparable to that observed for standard PVC (approximately 2). A number of compounds liable to exert an effect on the polymerization of vinyl chloride were added to the monomer at a uniform concentration of 10^{-4} (by weight). It was observed that, when these impurities increased, the reaction time (period required for the optical density to reach a given value), they cause a drop in molecular weight (Fig. 16).

For a small number of reference tests, which do not appear to have been disturbed by the presence of impurities (Table 2), it was observed that the molecular weight increases with decreasing polymerization rate (Fig. 17). This observation, which is contrary to the previous one, makes it possible to compare the case of polymerization of VC to free-radical vinyl polymerizations in homogeneous phase, where this correlation is the rule; combined with the first observation, which indicates a tendency of molecular weight to increase with conversion ratio—a tendency which is also generalized in homogeneous polymerization—this enables us to state that, in a very small

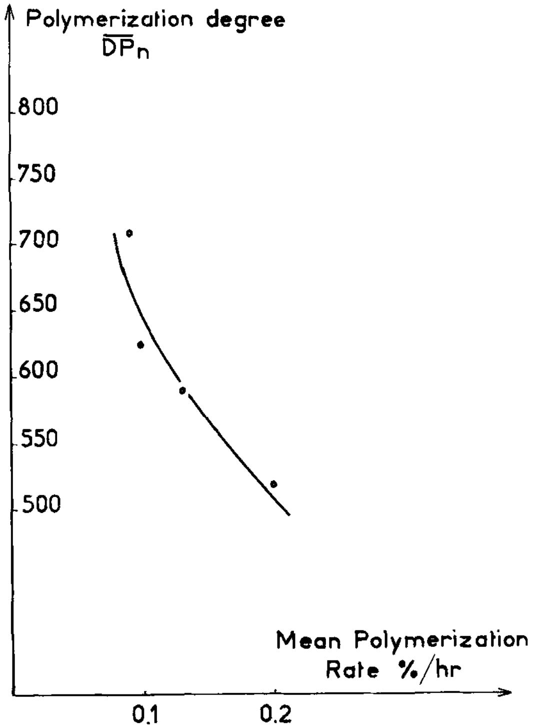

FIG. 17. Molecular weight vs. polymerization rate. Temperature, 50° C; mole fraction lauroyl peroxide, 7.82×10^{-6}.

TABLE 3. Double Bond Content

Polymerization conditions				Double bond content	
Time (hr)	Conversion (%)	Temperature (°C)	Degree of polymerization $\overline{DP}_n$	Per 1000 VC units	Per macromolecule
2.0	3.04	50	726	2.1	1.55
5.0	80	56	720	1.7	1.2
8.0	63	46	1055	1.35	1.4

region of conversion ratios, the polymerization of VC starts by following standard rules of vinyl polymerization in homogeneous phase and deviates from this rule as the heterogeneity of the medium increases.

Double Bond Content

Titration of double bonds by the liquid-phase bromination method described by Morikawa [9, 10] indicates a double-bond content somewhat higher than in the case of usual PVC samples (obtained at high conversion rate, 60-80%). Results are presented in Table 3.

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