Polymerization of Vinyl Chloride at Reduced Monomer Accessibility. IV. The Effect of Diffusion Control on Polymerization Rate, Molecular Weight, and Thermal Stability

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Synopsis

The effect of diffusion control on the polymerization of vinyl chloride has been studied by observing the rate as well as the molecular weight and the thermal stability of the polymer formed. The polymerizations were performed at 97% of saturation pressure in a water-suspended system at 55°C, using emulsion PVC latex as seed and a water-soluble initiator. The monomer was charged as vapor from a storage vessel kept at a lower temperature. Characterization included determination of molecular weight distribution by GPC and viscometry, and thermal dehydrochlorination. The gas–liquid contact was varied by changing the speed of agitation and the design of the stirrer. With a propeller the polymerization rate increased with the agitation up to ca. 1000 rpm, where after it became almost constant. Simultaneously, the molecular weight and the thermal stability increased. This indicates diffusion control, and thus decreased monomer concentration, at low agitation speeds, while the polymerization becomes reaction controlled at higher speeds. By a comparison with earlier data, obtained at different pressures and under reaction control, the actual monomer concentration could be calculated, which allowed an evaluation of the mass transfer constant. The possibilities to encounter problems with diffusion control in commercial polymerization of vinyl chloride is discussed. It is demonstrated that diffusion control is utilized in continuous polymerization of vinyl chloride, which explains the lower thermal stability of such materials.

INTRODUCTION

The production of poly(vinyl chloride) (PVC) is dominated by suspension polymerization.[1] As PVC is insoluble in vinyl chloride, precipitation occurs at a very early stage, and the major part of the propagation takes place within the polymer phase[2] swollen with monomer. The polymer gel is surrounded by liquid monomer, maintaining a constant monomer concentration, until the "pressure drop" at 70–75% conversion. Commercial polymerizations are normally continued to somewhat higher conversion, e.g., 85–95%.

In emulsion polymerization, which accounts for 10–15% of the PVC production, the reaction takes place in much smaller particles, typically 0.1–2 μm. These are swollen with monomer but not in contact with a free liquid monomer phase. The monomer is present in small droplets (10 μm) and must diffuse through the water phase to the locus of polymerization. The very short diffusion paths insures, however, a very rapid equilibrium.

Although monomer diffusion thus normally can be ignored in commercial batchwise polymerization of vinyl chloride, there are techniques where it might be of importance. An example is emulsion polymerization with multiad-

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ditions of monomer. The gentle agitation used in emulsion polymerization might then cause uneven distribution of the liquid monomer initially after each addition.

In a number of articles we have discussed the effect of decreased monomer concentration on polymerization kinetics and molecular weight,[3-5] as well as on the formation of labile defects and the subsequent consequences on the thermal stability.[6-9] We perform these polymerizations at pressures below the saturation pressure ("subsaturation"), i.e., without liquid monomer present, and the system is thus a model for the later stages in an ordinary batch polymerization of vinyl chloride. To keep a constant concentration, monomer is continuously added to the gas phase, and the technique can be regarded as a semicontinuous batch polymerization. The diffusion paths in the water might be longer than in an emulsion polymerization, and, in addition, the monomer must pass over the gas–water interface. To avoid diffusion control, we have found that we must use a much more intense agitation compared to that usually encountered.[5] In this article we discuss diffusion control of subsaturation polymerization of vinyl chloride in more detail.

EXPERIMENTAL

Polymerizations

The subsaturation polymerizations of vinyl chloride were performed with the polymerization technique described earlier.[3-5] The monomer was continuously charged as vapor from a storage vessel kept at a lower temperature (54°C) than the reactor (55°C). The ratio between the actual pressure (P) and the saturation pressure (P_0) was accordingly $P/P_0 = 0.97$. The polymerizations were performed in a 5-L stainless-steel reactor with an inner diameter of 155 mm, using distilled water as suspending agent and ammonium peroxydisulfate (0.25 g/dm^3) as initiator. The seed particles had a diameter of ca. 30 nm, and 5 g/dm^3 was added (25% dry content). Vinyl chloride of polymerization grade was kindly supplied by Norsk Hydro Plast AB, Sweden. After water had been charged to the reactor, air was removed by 5 cycles of evacuation and purging with extra pure nitrogen (< 2 ppm O_2). All additions were made under a nitrogen blanket. The procedure to calculate the weight of consumed monomer and to correct for the amount of monomer swelling the polymer has been given earlier.[5]

Two kinds of stirrer have been used. Most experiments were performed with a propeller having three blades. The diameter was 52 mm, and the angle between the blades and the horizontal plane 40°. A U-shaped anchor with two blades was used in some experiments. The outer diameter was 91 mm, the inner 73 mm, and the height 90 mm.

Characterization

Gel chromatography and viscometry were used to determine the molecular weight distribution. Details of the GPC analysis and dissolution procedure have been given earlier.[10] A Waters Associated GPC Model 200 operating at 25°C with tetrahydrofuran as solvent was used. The column combination consisted of five Styragel columns with permeabilities ranging from 10^3 to 10^7

Å, giving good separation in the molecular weight range of interest. The setup also contained a SEPEMA on-line viscometer of the Ubbelohde type including a syphon with a volume of 4.57 mL (V_s). The effluent time of pure solvent (t_0) was 113.75. The variations in t_0 were less than ± 0.01 s. To calculate the intrinsic viscosity ($[\eta]$), eq. (1) was used:

$$[\eta] = \frac{\sum \Delta t \cdot V_s}{t_0 \cdot c_0 \cdot V_i} \tag{1}$$

where Δt is the time difference between solution and pure solvent for each fraction, c_0 the concentration of polymer in the injected solution, and V_i the injected volume. To calculate MWD and molecular weight averages, the computer program devised by Drott and Mendelson[11] was used, assuming trifunctional branch points. The calibration curve for linear PVC was obtained via the universal calibration curve as described earlier.[10]

The degradation experiments were performed in a specially designed apparatus described earlier.[12] Bulk samples (150 mg) were heated at 190°C in nitrogen atmosphere (< 5 ppm O_2). The rate of dehydrochlorination was followed conductometrically, and the rate is expressed as evolved HCl, in percent of the theoretical amount, per minute.

RESULTS

In our earlier work with subsaturation polymerization of vinyl chloride, we found it necessary to add some PVC as seed to obtain reasonable polymerization rates.[3,4] We have tested both suspension PVC[3] and uncoagulated PVC latex[4,5] as seed. With respect to diffusion problems, the much larger number of particles for a given amount of PVC certainly favors the latter alternative. A typically monomer consumption curve using emulsion PVC as seed is given in Figure 1.

At first the gas volume of the reactor is filled, and both water and seed are saturated according to the applied pressure. The reaction rate increases until a critical conversion, at which the rate suddenly decreases and becomes constant. Samples taken before this point consist of dispersed primary particles. The number of particles is that given by the addition of seed, whereas the size increases according to the conversion.[5] We have found that the kinetics of subsaturation polymerization of vinyl chloride, at least qualitatively, can be described by the expressions for ordinary emulsion polymerization given by Ugelstad et al.[13] and Friis and Hamielec[14] (see below). The increased rate is due to the unavoidable increase in the polymer volume, i.e., an increase in the active polymerization volume.

Samples taken after the break, on the other hand, consist of porous aggregates with a mean diameter in the range 100–200 μm. Within these aggregates the monomer transport cannot be influenced by agitation. It is therefore reasonable to assume that the low and constant polymerization rate after the aggregation is due to diffusion control. As a consequence, the monomer concentration should be reduced relative to the equilibrium concentration at the applied pressure. Indeed, we found that the molecular weight as well as the thermal stability decreased substantially after aggrega-
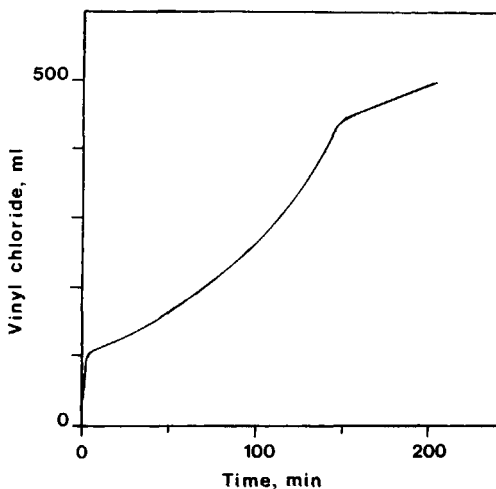
Fig. 1. Monomer consumption curve in a subsaturation polymerization of vinyl chloride with emulsion PVC latex as seed.

tion,[5] similar to what is observed before the aggregation if the monomer pressure is decreased. Although the system thus becomes influenced by diffusion, the rather uncontrolled aggregation makes it unsuitable for an investigation of the importance of diffusion. The present work has therefore been restricted to the conditions prevailing before the aggregation.

To introduce diffusion control, we have instead changed the degree of agitation. Figure 2 shows how the agitation speed influenced the polymerization rate in subsaturation polymerization of vinyl chloride using a propeller. This kind of stirrer is used in ordinary suspension polymerization of vinyl chloride. The speed in a commercial reactor might be 2–300 rpm, but in the small scale used in the present investigation 5–700 rpm is typical. The normal
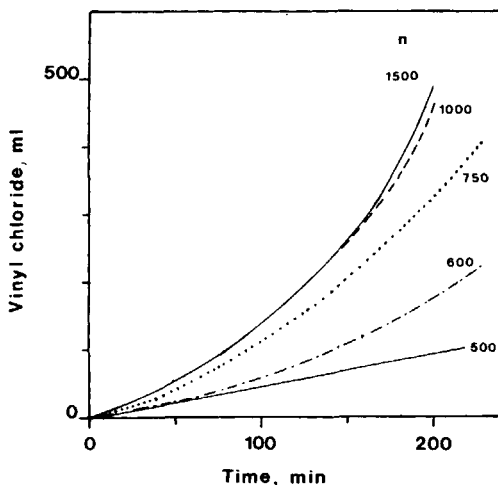

Fig. 2. Monomer consumption curves corrected for initial filling of the reactor and obtained at different speed of agitation, n, using a propeller.
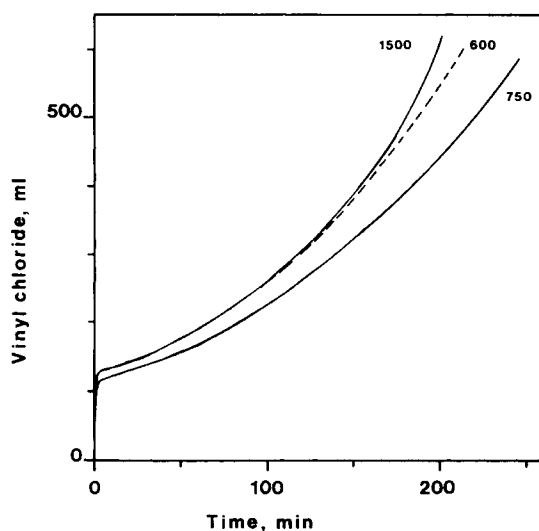
Fig. 3. The influence of the design of the stirrer on the polymerization rate: (—) propeller; (---) anchor.

purpose of the agitation system is, however, not to give a good gas–liquid contact, but to disperse the monomer into droplets of wanted size. Obviously, conventional agitation is insufficient in a subsaturation polymerization. The dependence of the polymerization on the agitation speed instead clearly indicates diffusion control. Above 1000 rpm, however, further increase in agitation does not have any large influence. Above this limit, it is therefore plausible to assume that the polymerization is reaction controlled.

Besides the speed of agitation, the design of the stirrer can also influence the contact between the gas and the liquid phase. Some experiments were performed with an anchor as well. This type is often used in ordinary emulsion polymerization of vinyl chloride at 1–200 rpm. The much larger area should lead to a higher input of energy compared to the propeller, i.e., a lower tendency of diffusion control. As demonstrated in Figure 3, the rotation speed necessary to obtain reaction control is considerably lower for the anchor compared to that of the propeller, 600 and 1000 rpm, respectively.

TABLE I
Molecular Weight and Dehydrochlorination Data
of Polymers Obtained Using the Propeller

n^a (rpm)	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$[\eta]$ (dL/g)	$(de_{HCl}/dt) \times 10^3$ (%/min)
1500	145	55.0	1.05	13.1
1000	138	53.1	1.02	13.6
750	136	39.5	0.96	20.7
600	118	35.5	0.80	28.1
500	92.5	22.0	0.60	43.7

[a]Speed of agitation.

The lower polymerization rate observed below the limit of reaction control is accompanied by decreased monomer concentration. In accordance with our earlier work on subsaturation polymerization of vinyl chloride under reaction controlled conditions,[5] decreased molecular weight and thermal stability are observed as well (see Table I). The decreased stability is due to increased formation of tertiary chlorine connected to ethyl, butyl, and long chain branches, as well as internal allylic chlorine.[7-9] The values observed for the samples obtained with 1500 and 1000 rpm using the propeller, and with 600 rpm using the anchor, are similar to those of an ordinary emulsion PVC prepared under corresponding conditions.

DISCUSSION

The data presented above are thus in agreement with diffusion control below a certain level of agitation. The insufficient transport of monomer will tend to decrease the concentration of monomer within the polymer gel. As a consequence, the polymerization rate will decrease until it balances the rate of monomer transport. Apart from the nominal pressure, the behavior of a diffusion-controlled polymerization is thus similar to that of a well-agitated subsaturation polymerization performed at a lower pressure.

In fact, it is possible to estimate the effective concentration of monomer in the polymer phase by comparing the molecular weight and the rate of dehydrochlorination with data of polymers obtained under reaction control, but at different pressures. As reference data we have used the values given in an earlier paper.[5] To avoid problems due to differences in recipes and GPC calibrations, we only compare relative values, normalizing to the conditions giving the highest monomer concentration, i.e., $P/P_0 = 0.97$ and 1500 rpm. In Figures 4 and 5 the relative molecular weight (M_n) and the relative rate of dehydrochlorination, respectively, obtained with a well-agitated system, are
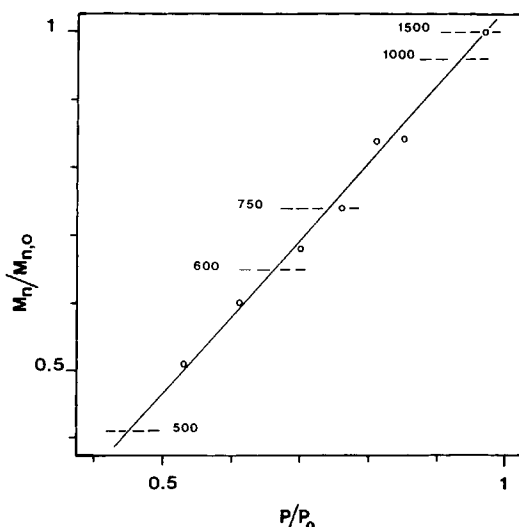

Fig. 4. The relation between relative molecular weight and relative monomer pressure. As reference the values obtained at $P/P_0 = 0.97$ and $n = 1500$ rpm are used: (○) data from Ref. 5.
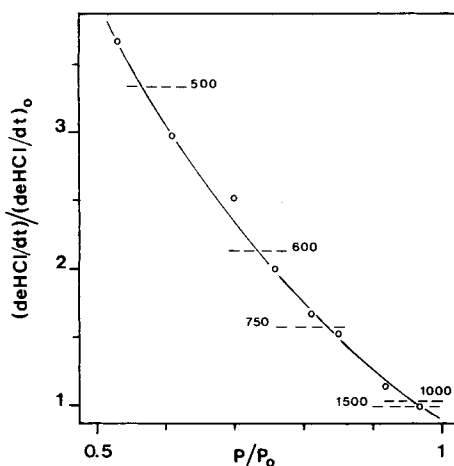
Fig. 5. The relation between relative rate of dehydrochlorination and relative monomer pressure. As reference the data obtained at $P/P_0 = 0.97$ and $n = 1500$ rpm are used: ($\circ$) data from Ref. 5.

plotted against the relative monomer pressure. The values obtained in the present investigation at $P/P_0 = 0.97$, using the propeller at different agitation speeds, are indicated by the broken lines.

The actual concentration of monomer in the polymer gel in a diffusion-controlled polymerization is reasonably equal to the equilibrium value given by the value of P/P_0, producing a similar polymer in a reaction-controlled system. The corresponding values, obtained from M_n as well as the degradation rate, are plotted in Figure 6. Although there are some discrepancies, especially at lower concentrations, both curves very clearly demonstrate the
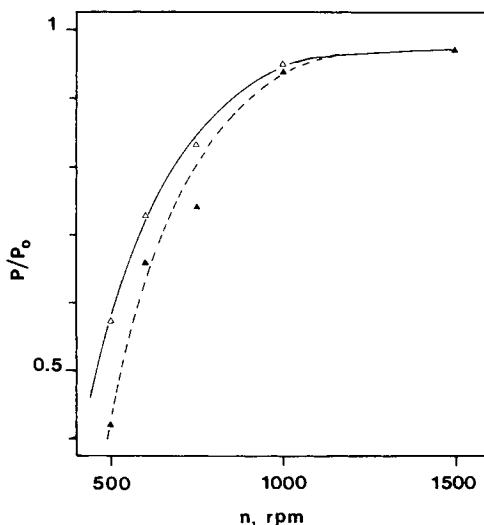

Fig. 6. The relation between the speed of agitation, n, and the apparent relative monomer pressure, P/P_0, as determined from Figures 4 and 5: ($\blacktriangle$) from relative molecular weight; ($\triangle$) from relative rate of dehydrochlorination.

TABLE II
Apparent P/P_0 Values as Determined from Figure 6

n (rpm)	P/P_0	$[M]^a$ g VC/100 g PVC
1500	0.97	25
1000	0.94	22
750	0.80	13.6
600	0.70	10.2
500	0.52	6.1

[a]According to Ref. 15.

effect of diffusion control. Decreasing the pressure from $P/P_0 = 0.97$ to 0.53, or the agitation speed to about 500 rpm, causes a decrease in monomer concentration with a factor of 3, using the equilibrium values given by Berens.[15] Furthermore, the independence on agitation at higher speeds is a clear evidence that the system becomes reaction controlled in agreement with our earlier assumption.[5]

The apparent P/P_0 values, as well as the corresponding concentrations of monomer in the polymer gel, related to the different agitation speeds, are given in Table II. By using these data and the curves of monomer consumption, the mass transport of monomer can be determined according to

$$N_{VC}a = k_L a(c^* - c) \tag{2}$$

where $N_{VC}a$ is the mass flow of vinyl chloride, $k_L a$ the mass transfer constant, c^* the concentration of monomer at the water–polymer interface, and c the actual concentration in the bulk of the gel.

The total mass flow of monomer, as measured by the monomer consumption, consists of two parts: First, the monomer is consumed by the polymerization reaction, and second, the polymer formed will absorb additional monomer according to the apparent P/P_0 value. It must be remembered that the polymerization rate (R_p), i.e., the "driving force" for the monomer transport, depends on the number of particles as well as the volume of the monomer swollen particles of polymer, $V_p^{5,13,14}$:

$$R_p = \frac{k_p[M_p]}{N_A}(2fk_i[I])^{1/2}\left(\frac{V_p N_A}{2k_{tp}} + \frac{N^{1/3}V_p^{2/3}}{2k'_d}\right)^{1/2} \tag{3}$$

where k_p = propagation rate constant, $[M_p]$ = monomer concentration within the polymer particles, N_A = Avogadro number, f = initiator efficiency factor, k_i = initiator decomposition rate constant, $[I]$ = initiator concentration, V_p = total volume of the monomer-swollen polymer particles, k_{tp} = termination rate constant, N = total number of particles, and k'_d = specific desorption rate constant.

An important aspect of eq. (3) is that R_p will increase with V_p and N in a reaction-controlled system. The number of particles is easily kept constant as N is given by the addition of the seed. However, to be able to compare values of $k_L a$ calculated according to eq. (2) at different degrees of diffusion control,

data obtained at the same V_p should be used. The original data were therefore treated in the following way. The curves of monomer consumption were first converted to curves of conversion to polymer by correcting for the degree of monomer swelling, whereafter R_p was calculated at several different times. These values were plotted against the corresponding values of V_p (considering the degree of swelling) in a log–log plot. From this plot R_p was determined at three different levels of V_p: 0.01, 0.05, and 0.1 dm³/dm³ H_2O. Finally, the mass transport of monomer, $N_{VC}a$, could be calculated by adding the additional flow of monomer necessary to maintain the degree of swelling for the experiment in question.

The value of c^* should be the concentration of monomer at the particle surface at $P/P_0 = 0.97$. This concentration corresponds to the equilibrium value obtained in a nonpolymerizing system at the same pressure. According to the results discussed earlier, the monomer concentration in the experiment performed at 1500 rpm should be very close to the equilibrium value, i.e., $c^* - c$ can be approximated to zero. At the lower levels of agitation, $c^* - c$ will be positive according to Table II. To facilitate a calculation according to eq. (2) the concentrations have been recalculated to the amount of monomer per volume water (g VC/dm³ H_2O), which compares with the expression normally used for R_p (g VC/h dm³ H_2O). The relevant data together with the values of k_La (h⁻¹) as calculated according to eq. (2) are presented in Table III.

It is obvious that the mass transfer constant strongly depends on the agitation speed n. Figure 7 is a log–log plot between k_La and n. At all levels of V_p linear relations are obtained, and the exponent β in the relation

$$k_La \propto n^\beta \tag{4}$$

increases from 4.3 to 5.6 with increasing V_p (see Table III). By extrapolation in Figure 7 it is also possible to obtain k_La for $n = 1500$ rpm and calculate a

TABLE III
Mass Transfer Data

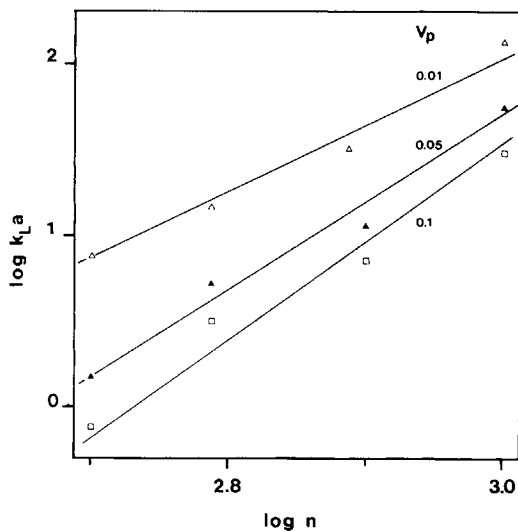| V_p (dm³/dm³ H_2O)	n (rpm)	R_p (g/h dm³ H_2O)	$N_{VC}a$	c (g/dm³ H_2O)	$c^* - c$	k_La (h⁻¹)	β
0.01	1500	24.1	30.2	2.47	(0.04)	(741)	4.3
	1000	24.0	29.3	2.25	0.22	133	
	750	23.9	27.2	1.56	0.91	29.9	
	600	16.2	17.7	1.23	1.24	14.3	
	500	12.0	12.7	0.78	1.69	7.5	
0.05	1500	53.0	66.4	12.4	(0.17)	(398)	5.2
	1000	49.1	59.8	11.3	1.1	54.4	
	750	43.3	48.9	7.78	4.6	10.6	
	600	28.9	32.0	6.19	6.3	5.1	
	500	12.1	12.7	3.88	8.5	1.5	
0.10	1500	71.2	89.0	24.7	(0.23)	(389)	5.6
	1000	66.0	80.5	22.5	2.20	29.8	
	750	54.2	61.4	15.6	9.1	6.8	
	600	36.5	40.1	12.3	12.4	3.2	
	500	11.9	12.7	7.7	17.0	0.75	

Fig. 7. The relation between the mass transfer constant $k_L a$ and the speed of agitation, n, at different volumes of polymer gel, V_p.

corresponding value of $c^* - c$. These values are given in parentheses in Table III, and it is obvious that the starting approximation is almost correct.

The value of β is unusually high. In a recent paper Stenberg and Andersson[16] discussed a number of models for the gas–liquid mass transfer constant in agitated vessels. Admittedly, the reactor systems (size, stirrer, etc.) were quite different compared to that used in the present investigation. However, according to their results, β should be expected to be much lower, in the range 1–1.5. This is also in accordance with results of other investigations cited in Ref. 16.

Flat-blade impellers with the blade perpendicular to the agitation plane are normally used in investigations dealing with the mass transfer constant. For the standard propeller used in this work, the angle is instead 40°. The strong dependence on the agitation speed can most likely be explained by slip of the gas bubbles at the edge of the blades. This would imply that the propeller speed is too low to cause effective dispersion of the gas into the liquid. It is further likely that the critical agitation speed for creating small enough bubbles has been reached at 1500 rpm. The flat-blade anchor would, on the other hand, give higher shear forces at the edge and should thus more effectively disperse the gas into the liquid. The larger diameter also implies a much higher tip speed. These are probably the main reasons for the much lower speed needed to obtain reaction control with the anchor compared to the propeller (see Fig. 3).

Although not nominally used in practice, subsaturation polymerization offers some advantages. We have, e.g., shown that it is possible to obtain agglomerated emulsion PVC without adding metal salts[5] (cf. Fig. 1). The adverse effect of decreased monomer concentration on thermal stability necessitates such polymerizations to be performed as close as possible to $P/P_0 = 1$. Furthermore, the results discussed in this article clearly demonstrate that the

agitation must be sufficient in order to avoid diffusion control. It is doubtful if this can be achieved with an ordinary reactor used for commercial production of PVC.

Liquid monomer is present in most commercial polymerizations of vinyl chloride. Even with a stirrer of propeller type, this would ensure an effective dispersion, which is further improved by the presence of colloid stabilizers or surface active agents. Normally, diffusion control should thus not be a problem. Polymers obtained by emulsion polymerization in which the monomer is added in several portions might, however, exhibit somewhat lower thermal stability than ordinarily observed.[17] In such polymerizations a certain pressure drop is taken as indication for each addition. A larger part of the reaction will thus take part under subsaturation conditions, resulting in more labile structures. The mixing of the new liquid monomer with the bulk of the reactor content may also take some time as relatively gentle agitation is used, causing further decrease in monomer concentration due to limited diffusion rate. This would be most obvious in reactors with a high L/D ratio.

Besides the dominating batch techniques, continuous polymerization of vinyl chloride has been in commercial use for over 40 years,[18, 19] mainly in Germany. Berens[20] has derived a mathematical model for continuous polymerization of vinyl chloride. According to this model, the steady-state concentration of PVC would increase exponentially with the residence time, and reach infinity at a certain critical time. In reality this is impossible, but the conclusion implies that the degree of conversion should be very sensitive, even to small changes in residence time, feed rates, and so on. This is in accordance with the observed difficulties to control continuous reactors.[18, 19]

However, if the reactor is operated at a residence longer than the critical, the monomer polymerizes as fast as it is fed.[20] For a given time this can also be obtained by increasing the initiator concentration above a certain level. In this way the conversion is controlled by the monomer feed rate, but another problem then occurs. The reaction would be diffusion controlled; i.e., the monomer concentration in the polymer gel would decrease. According to the results presented in this paper, as well as earlier,[3-9] this should also lead to decreased heat stability, which is indeed observed[19] for continuous processes for emulsion PVC. In another investigation,[21] we have studied a commercial product obtained by continuous polymerization. Compared with a corresponding batch-polymerized sample, the former must have experienced a lower monomer concentration: rate of dehydrochlorination at 190°C, 23.5×10^{-3}, and 12.2×10^{-3} %/min; tertiary chlorine, 1.4 and 0.8 per 1000 monomer units; internal double bonds, 0.5 and 0.1 per 1000 monomer units for the polymer obtained by the continuous and the batch processes, respectively. Although not large, these differences are significant. A comparison with the data discussed earlier implies that the actual monomer concentration in the polymer gel should have corresponded to $P/P_0 = 0.9$. This is a clear indication that diffusion control might have been utilized in the production of the continuous-process polymer.

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