

# Kinetics of High Conversion Polymerization of Vinyl Acetate. Effects of Mixing and Reactor Type on Polymer Properties

W. BAADE, H. U. MORITZ, and K. H. REICHERT, *Institut fuer Technische Chemie, Technische Universitaet Berlin, Berlin, Federal Republic of Germany*

## Synopsis

In the present article the kinetics of polymerization of vinyl acetate in suspension up to high conversion was studied. The molecular weight distribution and the side chain branching of polyvinyl acetate produced were examined with respect to micro and macro mixing as well as to reactor type. The following results were achieved: the time-activity curves of the polymerization can be described up to high conversions considering the exponential increase in viscosity of the polymerizing system and combining the viscosity with rate constants of the polymerization. The change of volume of the polymerizing system has no significant influence on kinetics. The narrowest molecular weight distribution of the poly(vinyl acetate) produced was achieved when polymerizing in the homogeneous continuous stirred tank reactor while the broadest molecular weight distribution was observed in the segregated continuous stirred tank reactor. The batch reactor and the flow tube reactor produce polymers with molecular weight distributions lying in between. Considering the side chain branching, another order was found. The batch reactor and the tube reactor show the lowest side chain branching, the homogeneous continuous stirred tank reactor shows a larger one and the segregated continuous stirred tank reactor shows the largest. Possible reasons for the different behavior of the different reactors are discussed. The degree of segregation was determined by experiments.

## EXPERIMENTAL

Vinyl acetate (Hoechst AG, polymerization grade) used for the polymerization was rectified in a large column and stored at low temperature. Dicyclohexyl peroxidicarbonate (P1652, Peroxid Chemie) was used as initiator and 2,2-diphenyl-1-pikryl-hydrazyl (DPPH) (Fa. Fluka) was used for stopping the reaction after sampling. The dispersion agent utilized was partly saponified poly(vinyl acetate) (Mowiol 18-88, Hoechst AG). Tertiary butanol (Bayer AG) was used as solvent for the polymerization in solution because this solvent has the smallest transfer constant of a poly(vinyl acetate) radical to a solvent molecule.

Unless mentioned otherwise, the volume fraction of vinyl acetate to water was 0.12 to 0.25, and the initiator concentration was 0.5 wt % related to the monomer. For the polymerization in solution, 15 wt % monomer was solved in tertiary butanol and the same monomer to initiator ratio was chosen.

For polymerization, a 1.5 l thermostatic stirred tank reactor (ratio height/diameter = 2.5) with a blade stirrer (stirrer diameter to reactor diameter 1:3, centrosymmetrically arranged one-third away from the bottom of the vessel) of 600 rpm for the polymerization in suspension was used. During the continuous process, feeding was put in through an injector at the bottom of the vessel. Outlet and sampling took place in the upper part of the reactor. All experiments were

carried out under an inert atmosphere of nitrogen. Unless mentioned otherwise, the reaction temperature was  $61^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ . The mean residence times ranged between 10 and 75 min in the continuous experiments. Here the steady state in relation to the molecular weight distribution (MWD) was obtained generally after six times the mean residence time.

For measurement of the MWDs the gel permeation chromatography (GPC) with a differential refractometer as detector was used. The dispersion index  $D$  calculated from the MWD with the aid of a computer program was taken as a measure of characterization of the breadth of the MWD:

$$D = \frac{\bar{M}_w}{\bar{M}_n} = \frac{Q_2 Q_0}{Q_1 Q_1}$$

where  $\bar{M}_w$  is the weight average molecular weight,  $\bar{M}_n$  is the number average molecular weight, and  $Q_n$  is the  $n$ th moment of the distribution.

The GPC was carried out with  $\mu$ -styragels (Waters Co.) and tetrahydrofuran as elution medium. Calibration was made with polystyrene standards (High Pressure Co.). The calibration curve obtained was corrected in the usual way according to the absolute values of the number-average molecular weight of poly(vinyl acetate). The absolute values of the number-average molecular weight was determined by membrane osmosis. As the main chain branching of poly(vinyl acetate) is hardly accessible, only the side chain branching was studied, particularly since this mainly produces the long chain branching which is of interest here. Main chain branching of poly(vinyl acetate) is said to constitute a small part only.<sup>1,2</sup> The difference of the molecular weight before and after removal of the hydrolyzable side chains at roughly the same molecular weight of the branched samples was regarded as a relative size for the description of the side chain branching. Removal was carried out in accordance with an article by Cane and Capaccioli<sup>3</sup> whereby the washing process needed to be modified in order not to wash out the low-molecular-weight components of the polymer.

The experimental arrangement for the kinetic measurements (Fig. 1) was built up following the studies of Gunesch and Schneider<sup>4,5</sup> and technically improved and optimized according to present-day possibilities of data gathering and data processing. Here, the experimental data was determined by gravimetric measurements. By the following method of operation the polymerization temper-

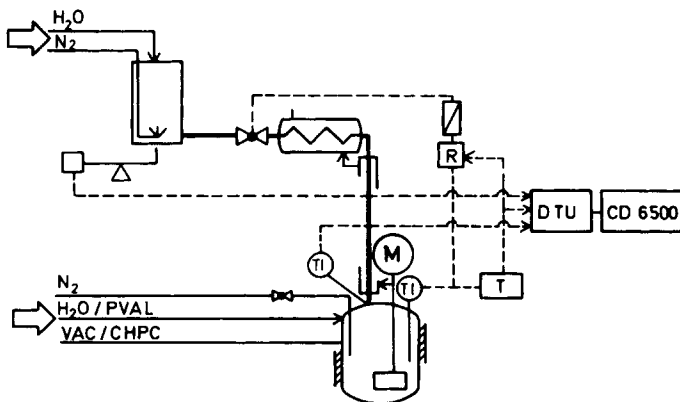


Fig. 1. Schematic flowsheet of the kinetic measuring arrangement.

ature, which is tuned in a few seconds after the feed of the cooled vinyl acetate with the initiator, is given to control system as set point. If the temperature increases by the released heat of polymerization, water with a temperature of  $0.5^{\circ}\text{C}$  flows in until the desired value is attained again. The mass of the water is thereby measured by an electric balance. With consideration of the losses of heat, the time-activity curve can be calculated from the mass flow of the water and the difference in temperatures.

The present caloric method of measurement allows the determination of kinetic data during the isothermal polymerization in stirred suspension. The measurement carried out shows a great accuracy so that maximum differences of  $0.1^{\circ}\text{C}$  from the set point temperature can occur during the experiments.

### Dependence of Kinetics in Initiator Concentration

Figure 2 shows the time-activity curves of different initiator concentrations at a temperature of  $60.2^{\circ}\text{C}$ . The overall initial rate of polymerization results from the slopes of the individual curves. The influence of temperature and initiator concentration  $[I]$  on initial polymerization rate is examined. An overall activation energy of  $19.5 \pm 0.5$  kcal/mole results for the examined temperature range of  $40^{\circ}\text{C}$ – $63^{\circ}\text{C}$ .

The overall initial rate is shown in Figure 3 as a function of the initiator concentration at polymerization temperatures of  $50^{\circ}\text{C}$  and  $60^{\circ}\text{C}$ . For low initiator concentrations from 0.3 to 10 mmole/L, curves with a slope of 0.5 result on double-logarithmic paper as expected from the standard kinetics of radical polymerization. On the other hand, in the range of higher initiator concentrations, the overall initial rate increases.

In view of this the decomposition of the initiator concentration was studied in detail by measuring the concentration of initiator in ethyl acetate by iodometric methods. Figure 4 shows the logarithm of the relative initiator concentration  $[I]/[I]_0$  as a function of time at a temperature of  $60^{\circ}\text{C}$  for various initial concentrations from 4 to 140 mmole/L.

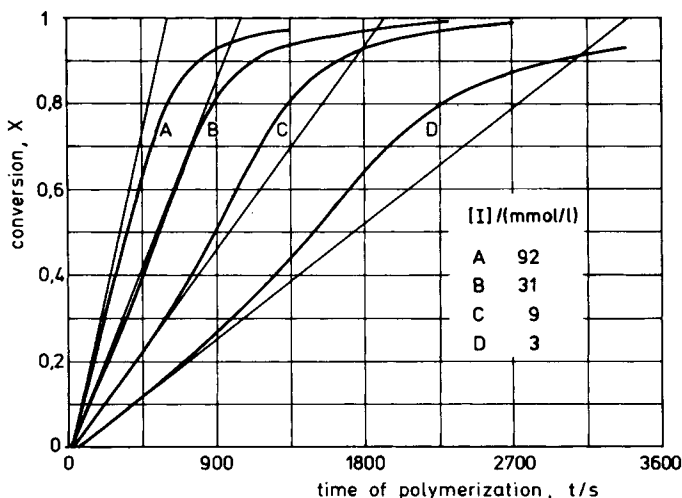


Fig. 2. Conversion-time curves for various initiator concentrations (in mmol/L): A,  $[I] = 92$ ; B,  $[I] = 31$ ; C,  $[I] = 9$ ; D,  $[I] = 3$ .

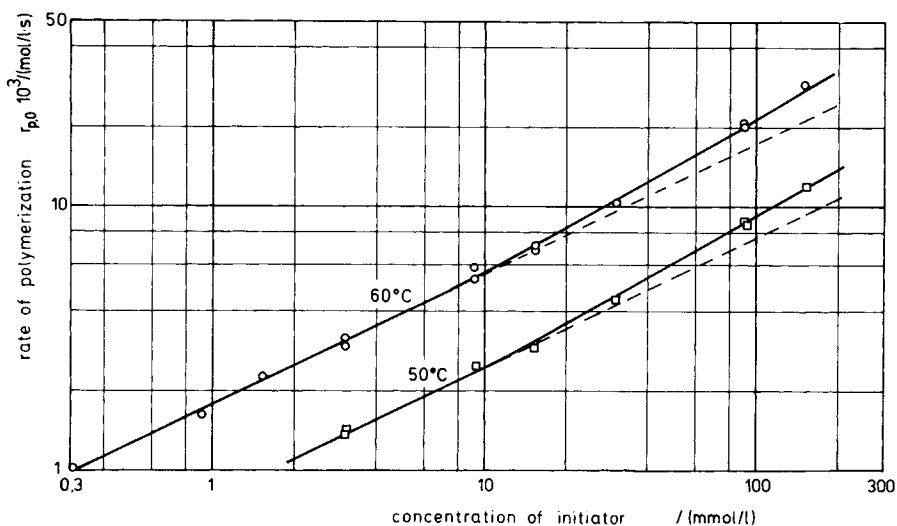


Fig. 3. Initial rate of polymerization with respect to the initiator concentration at 50 and 60°C.

The ratio of decomposition rate to the initiator concentration versus the initial concentration of initiator  $[I]_0$  is plotted in Figure 5. The resulting straight lines show that the decomposition of initiator can formally be described by the equation:

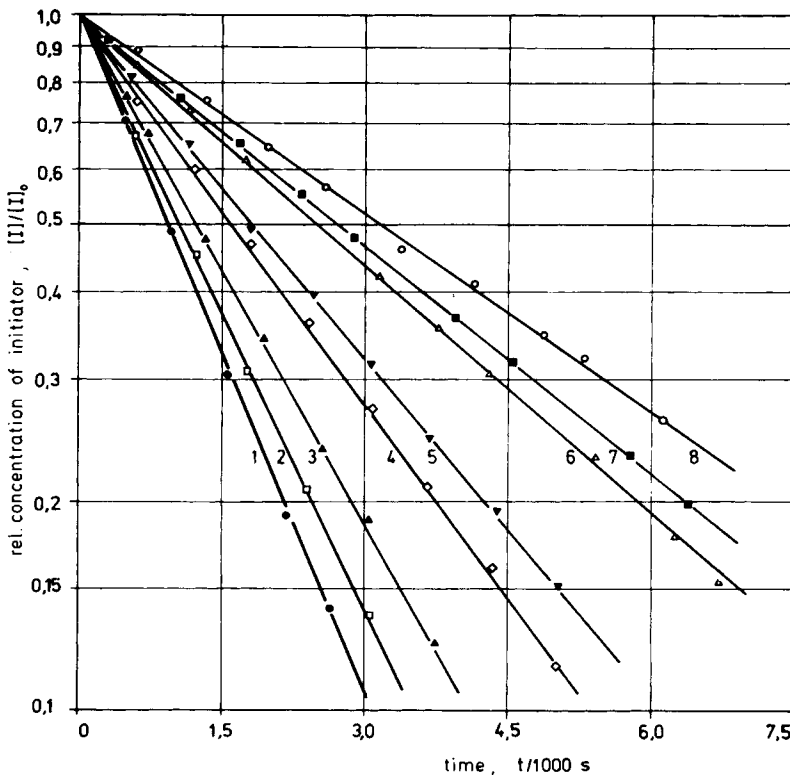


Fig. 4. Relative initiator concentration  $[I]_0$  (in mmole/L) vs. time of initiator decomposition: 1 = 137, 2 = 103, 3 = 80.0, 4 = 46.6, 5 = 32.4, 6 = 12.9, 7 = 8.0, 8 = 4.2.

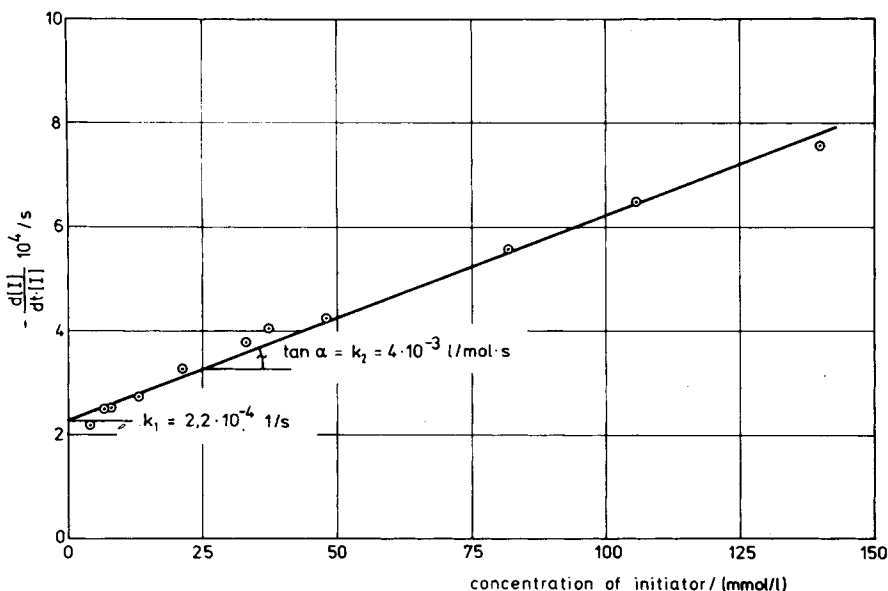


Fig. 5. Rate of decomposition related to initial initiator concentration vs. initial initiator concentration.

$$-(d[I]/dt) = (k_1 + k_2 \cdot [I]_0)[I]$$

with the intercept  $k_1 = 2.2 \times 10^{-4} \text{ s}^{-1}$  and the slope  $k_2 = 4 \times 10^{-3} \text{ L/mole s}$ . This simple expression does not permit any conclusions to be drawn on the reaction mechanism. A decay mechanism suggested by van Sickle<sup>6</sup> that could be verified by gaschromatographic analysis of our own of reaction products leads to two coupled differential equations whose numerical solution, however, shows no better matching of the experimental values. Therefore the more simple formal kinetic equation is preferred in this case because this equation describes satisfactorily the increase of the order of reaction in relation to the initiator concentration even for higher initial concentrations.

If the logarithm of the decomposition constant combined as shown is plotted versus the reciprocal temperature  $T$  in an Arrhenius plot (Fig. 6), two approximately parallel lines and an overall activation energy about 30 kcal/mole result.

### Specification of the Kinetic Model

The questions arise if a termination by radicals in the aqueous phase takes place for the kinetics of polymerization in suspension and what are the influences of the size of the specific phase surface area between the polymerizing particles and the aqueous phase and thereby the stirrer speed on the termination reaction. Figure 7 shows the time-activity curves of different stirring rates from 200 to 600 rpm, where for the sake of clarity only every fifth measuring point is plotted. The specific phase surface area is enlarged by a factor of 13 from the lowest to the highest stirring rate. Gunesch and Schneider<sup>4</sup> measured for the vinyl acetate-dibenzyl peroxide system for doubling of the stirring rate almost half the polymerization rate. Contrary to these studies, no significant influence of the stirring rate can be stated in this case. Even with the addition of ammonium

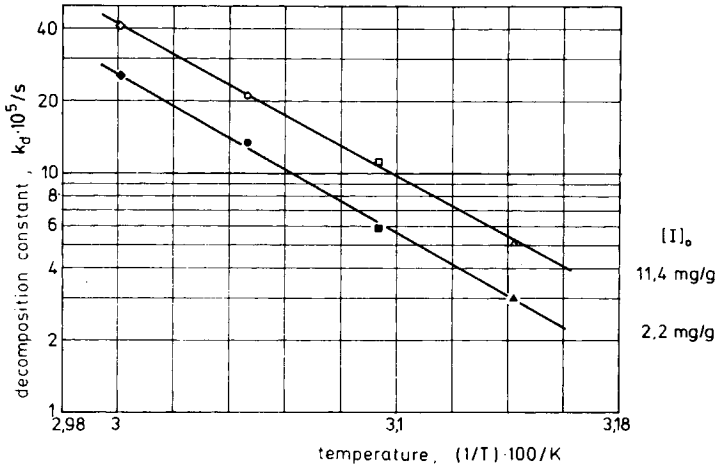


Fig. 6. Decomposition constant with respect to the reciprocal temperature.

thiocyanate as inhibitor to the aqueous phase the polymerization rate was independent of the stirring rate.

The kinetics of the polymerization of vinyl acetate is determined by the appearance of the gel effect which is illustrated in Figure 8. The overall polymerization rate  $r_p$  which was standardized on the actual initial value is plotted as a function of the conversion  $X$  for various initiator concentrations and temperatures of 50°C and 60°C. For low initiator concentrations the polymerization rate increases by a factor of 1.6 of its initial value; even with higher initiator concentrations a nearly constant reaction rate is measured up to a conversion of 50%. It is remarkable that the gel effect is already beginning during the initial

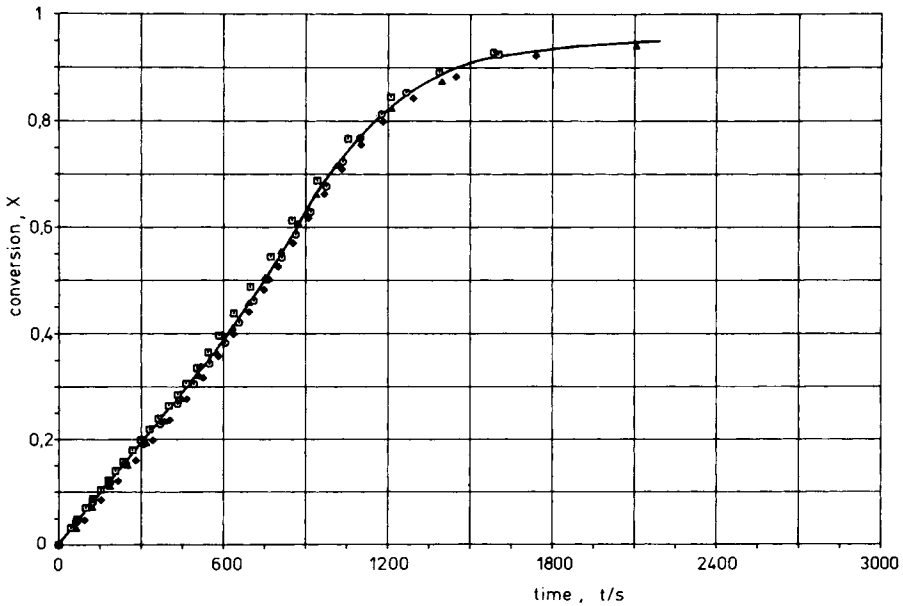


Fig. 7. Time-activity plot for different stirring rates (in rpm):  $\square = 200$ ,  $\diamond = 400$ ,  $\circ = 500$ ,  $\triangle = 600$ .

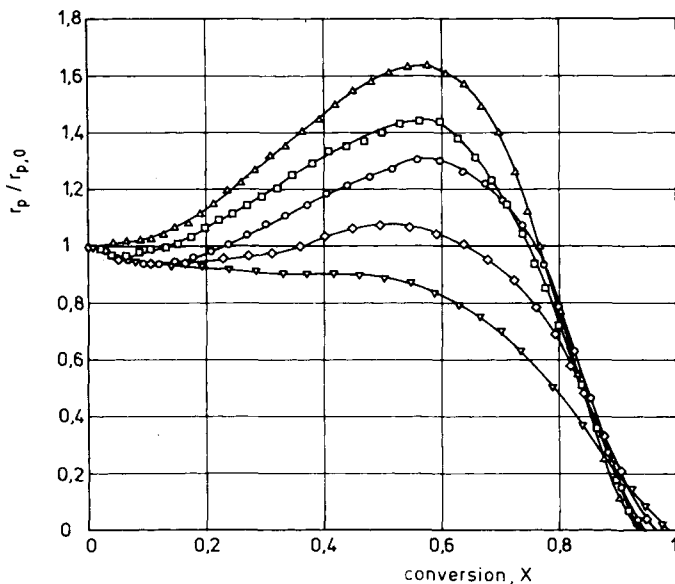


Fig. 8. Relative reaction rate vs. conversion  $[I]_0$  (in mmole/L):  $\Delta = 3.1$  ( $T = 50^\circ\text{C}$ ),  $\square = 3.1$  ( $T = 60^\circ\text{C}$ ),  $\circ = 9.2$  ( $T = 60^\circ\text{C}$ ),  $\diamond = 30.7$  ( $T = 60^\circ\text{C}$ ),  $\nabla = 92$  ( $T = 60^\circ\text{C}$ ).

phase of polymerization and occurs from the start of the reaction at low initiator concentrations so that the termination reaction has to be regarded as controlled by mass transfer from the onset of polymerization.

Referring to the Einstein–Stokes definition of the diffusion coefficient,<sup>7</sup> the effective viscosity of the polymerizing phase is of great significance for the description of kinetics. Therefore vinyl acetate was polymerized in bulk in a double slit rotational viscosimeter and the increase in viscosity was measured as a function of time. Figure 9 shows the logarithmic plot of the zero shear rate dynamic viscosity of the polymerizing vinyl acetate versus polymerization time for different initiator concentrations. The increase in viscosity could be observed over six decimal powers in the measuring arrangement chosen and could be matched to the proportionality

$$\eta \sim e^{at}$$

With respect to the Einstein–Stokes relation mentioned above for the termination constant,  $k_t$ , the following equation applies:

$$k_t \sim 1/\eta \text{ respectively } k_t \sim e^{-at}$$

so that  $k_t = k_{t,0} e^{-at}$  could be approximated, where  $k_{t,0}$  is the value of the termination constant at the beginning of the reaction.

Considering that the efficiency factor  $f$  and the propagation  $k_p$  for high conversions can also be functions of viscosity, the simple correlation

$$\frac{k_p^2 f k_d}{k_t} \sim e^{\bar{a}t}$$

is obvious. Integrating the general kinetic expression with  $X = [M]_0 - [M]/[M]_0$ , leads to

$$X = 1 - \exp \left[ - \frac{2k_p}{\bar{a} - k_d} \left( \frac{2fk_d[I]_0}{k_{t,0}} \right)^{0.5} \left( \exp \left[ \frac{\bar{a} - k_d}{2} t \right] \right) - 1 \right]$$

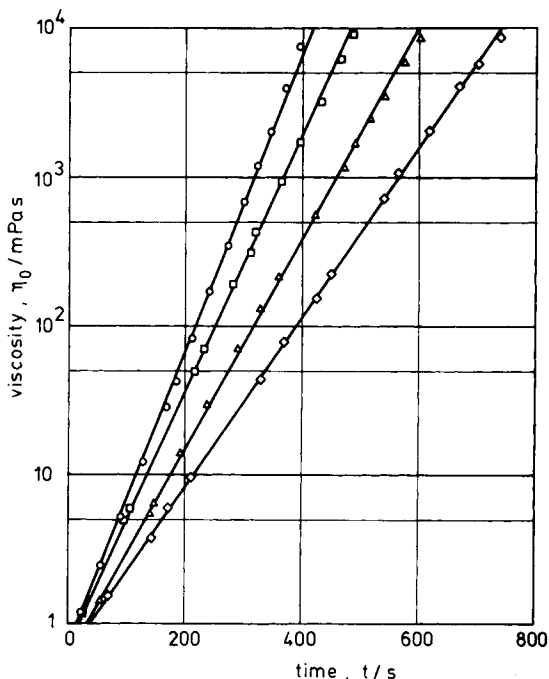


Fig. 9. Zero shear rate viscosity with respect to the time of reaction of  $[I]_0$  (in mmole):  $\blacksquare = 154$ ,  $\square = 92$ ,  $\Delta = 31$ ,  $\diamond = 9$ .

where for the description of the time-activity curve,  $\bar{a}$  is the only additional parameter that has to be matched. In this equation  $[M]$  is the monomer concentration,  $[M]_0$  the monomer concentration at the beginning of the reaction, and  $k_t$  the decomposition constant of the initiator. Good agreement between values calculated and those obtained by experiments is achieved for the following proportionalities:

$$k_t \sim \eta^{-1}$$

and

$$k_p^2 \cdot f k_d \sim \eta^{-0.8}$$

Beyond this, the volume contraction, which in the case of vinyl acetate amounts to 34% related to the monomer, and a polymerization temperature of 60°C were considered. As during integration of the rate expression, an expression is obtained which is not separable for the conversion; the conversion has to be determined by iteration.

$\bar{X}$  therefore is the conversion, taking into account the volume contraction, whereby the following expression results:

$$\bar{X} = \frac{[M]_0 V_0 - [M] V}{[M]_0 V_0}$$

where  $V_0$  is the volume of the reaction at the beginning of the reaction and  $V$  the volume of the reaction at time  $t$ . Figure 10, for example, shows the comparison of the calculated curves with the experimental measuring values in a time-activity plot. For all curves the standard rate expression of the radical polymer-



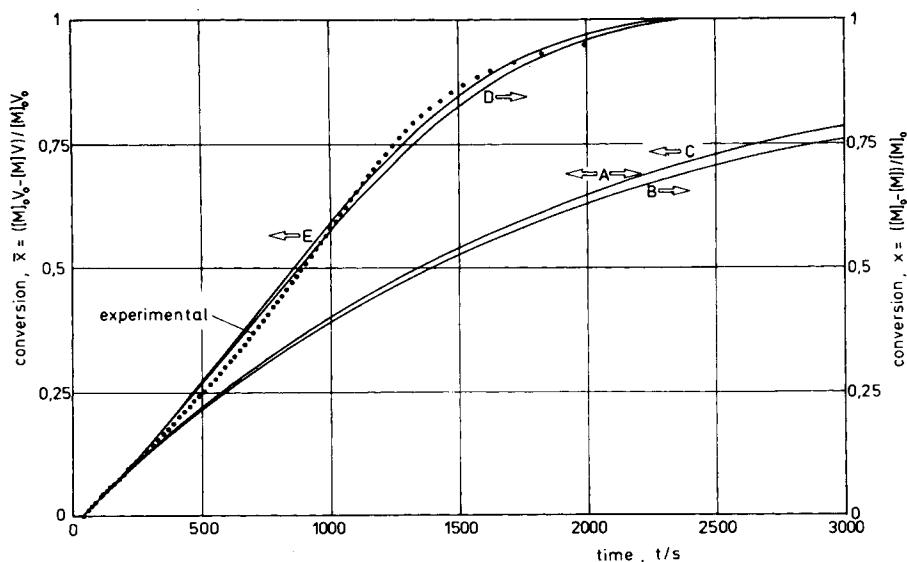


Fig. 10. Time-activity curves of vinyl acetate polymerization with and without regard to the volume contraction.

ization is used and the constants as far as they are not measured by experiments are chosen in the scope of the ranges cited in literature<sup>8</sup> such that the measured initial rates result. The time-activity curve A which is described following the standard kinetic by the equation

$$\bar{X}, X = 1 - \exp(-Kt)$$

where

$$K = \left( \frac{2k_p^2 f k_d [I]_0}{k_t} \right)^{0.5}$$

results from the simplified assumption that the initiator concentration remains constant during the reaction. Consideration of volume contraction has no influence on the shape of the curve. For obtaining curve B with

$$X = 1 - \exp\left(\frac{2}{k_d} K \left[ -\exp\left(\frac{k_d}{2} t\right) - 1 \right]\right),$$

the decrease of the initiator following the previously determined rate expression is taken into account. For curve C which is described by the expression

$$N(\bar{X}) = \frac{k_d}{2} K \left( 1 - \exp\left[-\frac{k_d}{2} t\right] \right)$$

with

$$N(\bar{X}) = a \cdot \ln \frac{(a+b)(a-1)}{(a-b)(a+1)} - 2(b-1)$$

where

$$a = (1 + \epsilon)^{0.5}, \quad b = (1 + \epsilon \cdot X)^{0.5}$$

Furthermore the additional decrease of the volume is considered. In general

the conversions become similar to those of pattern A. It must not be concluded from the picture, however, that A and C show the same conversion on principle. It is essential that this model describes the real polymerization process only for conversions up to 15%. When considering the viscosity which increases during polymerization in the way described, however, the model leads without any volume contraction to the time-activity curve D with the following equation:

$$X = 1 - \exp\left(-\frac{2}{\bar{a} - k_d} \left[ K \exp\left(\frac{\bar{a} - k_d}{2} t\right) - 1 \right]\right)$$

and having regard to the change of volume to the curve E:

$$N(\bar{X}) = \frac{2}{\bar{a} - k_d} K \left[ \exp\left(\frac{\bar{a} - k_d}{2} t\right) - 1 \right]$$

The variances of the experimental values are at most 4% during the entire polymerization process. The existing course of polymerization reaction, which is considerably influenced by the characteristic gel effect, can already at the beginning of polymerization be described up to high conversions with sufficient accuracy by the present model. This model considers the experimentally measured exponential increase of viscosity.

### Effect of Mixing on MWD and Branching

For determining the influence of the so-called micro and macro mixing on the MWD and the branching of poly(vinyl acetate), the dependence of these two parameters on the mixing efficiency (possible maximum mixedness or complete segregation) and on the reactor type was investigated. The following reactor types were compared: batch reactor (BR), the tube reactor (FTR), segregated continuous stirred tank reactor (SCSTR), and homogeneous continuous stirred tank reactor (HCSTR).

Denbigh<sup>9</sup> mentioned first that for radical polymerization the BR shows a broader MWD than the HCSTR. These results were extended by Biesenberger<sup>10</sup> and Biesenberger and Tadmor<sup>11,12</sup> by considering the influence of segregation during continuous processing. According to their results the breadth of the MWD increases in the order of HCSTR, BR, and SCSTR. Contrary to the theoretical results of Biesenberger and Tadmor, Graessley et al<sup>13-17</sup> calculated for branched poly(vinyl acetate) the narrowest MWD for the BR, a broader MWD for the SCSTR, and the broadest MWD for the HCSTR. Graessley tried to explain these results by the large extent of branching in continuous reactors.

In order to obtain a system that is highly micromixed and therefore satisfies the conditions of a HCSTR, the polymerization of vinyl acetate was carried out in dilute solution by powerful mechanical mixing (stirrer speed 1600 rpm). In order to find out how intensively micromixed the polymerizing solution is, the degree of segregation  $J_S$  was determined following the method of Truong and Methot<sup>18</sup> and Vollmerhausen<sup>19</sup> for homogeneous systems according to the equation:

$$J_S = \frac{c_{m,MM} - c_{m,EXP}}{c_{m,MM} - c_{m,SEG}}$$

where  $c_{m,MM}$  is the calculated concentration of the monomer at the outlet of the reactor at maximum mixedness,  $c_{m,SEG}$  is the calculated concentration of the monomer at the outlet of the reactor at complete segregation, and  $c_{m,EXP}$  is the experimental concentration of the monomer at the outlet of the reactor.

An average value of the degree of segregation of 0.15 was measured in the range of conversion from 20 to 60%. A value of zero corresponds to maximum mixedness and a value of 1 corresponds to complete segregation.

The completely segregated state and thereby the conditions for a SCSTR are gained by a polymerization in suspension with 4 wt % dispersion agent. With this high concentration of dispersion agent there is no coalescence.<sup>20</sup> A comparison of the experimental values with the theoretical dependence of the conversion on the 1. Damköhler number  $Da_1$  shows good agreement in the case of the SCSTR (Fig. 11). This demonstrates that the polymerization in suspension without coalescence may be regarded as being completely segregated, too. The theoretical dependence of the conversion on the 1. Damköhler number was calculated in accordance with the equation:

$$X = Da_1[1 - \exp(-1/Da_1)]$$

where the conditions were chosen in accordance with the results of the two former sections of this article so that a formal kinetics of 0. order was obtained in good approximation up to 80% conversion. The 1 Damköhler number is determined for 0. order reaction by the equation

$$Da_1 = \frac{k \cdot \tau}{[M]_0}$$

where  $k$  is the overall rate constant of the polymerization,  $\tau$  is the mean residence time, and  $[M]_0$  is the initial concentration of the monomer.

The dispersion indices  $D$  of the polymer samples that result from the batch polymerization in solution and suspension are comparable, given the same monomer to initiator ratio. For conversions up to 95%, no essential differences could be noted. In general the dispersion index shows slightly lower values in

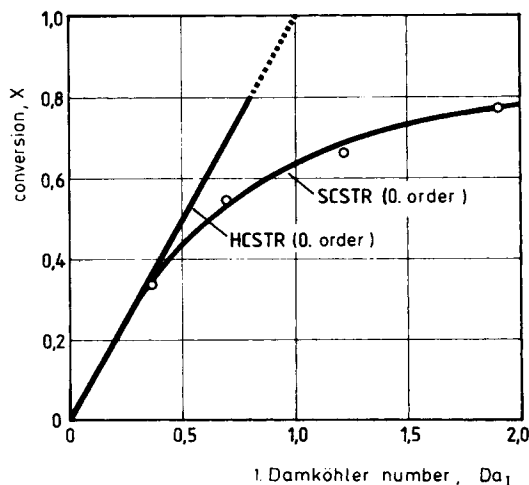


Fig. 11. Conversion as function of the 1. Damköhler number for 0 order reaction (O = experimental data).

the case of polymerization in solution. The differences, however, are always smaller than the measuring errors of the system, which are assumed to be 10–15%. Thus it appears justified to compare the data of the dispersion indices obtained in solution and suspension. Figure 12 shows the change of the difference in molecular weight  $\Delta \bar{M}_n$  as a relative index of the side chain branching versus the conversion in the three reactor types considered. Since only the side chain branching is recorded here, for consideration of the whole branching the amount of the main chain branching also has to be considered, which is however considerably smaller. Owing to this as well as to the measuring errors of the membrane osmosis, the present results can only be specified with a major error of up to 20%. Taking into account this tolerance, there are practically no differences between the branching up to a conversion of 40% in the reactor types considered. Only for higher conversions considerable differences occur. In consequence of the relatively great measuring errors mentioned above, the dependence of the product properties from mixing and reactor type are essentially specified only qualitatively.

[In Figure 18, the dependence of the number averages and weight averages of the molecular weight on conversion is shown in the three reactor types—HCSTR, BR, and SCSTR. The number averages of the molecular weight  $\bar{M}_n$  have about the same values by receipt guaranteeing comparability of the results in the different reactor types. For clarity, they are gathered up in a band.]

The change of the dispersion indices with conversion in the three reactor types considered—BR/FTR, HCSTR, and SCSTR—is shown in Figure 13. In the SCSTR, only samples up to 80% conversion could be measured, as the exclusion limitation of the existing GPC columns were exceeded for samples of higher conversions. In the HCSTR, only samples up to 60% conversion could be in-

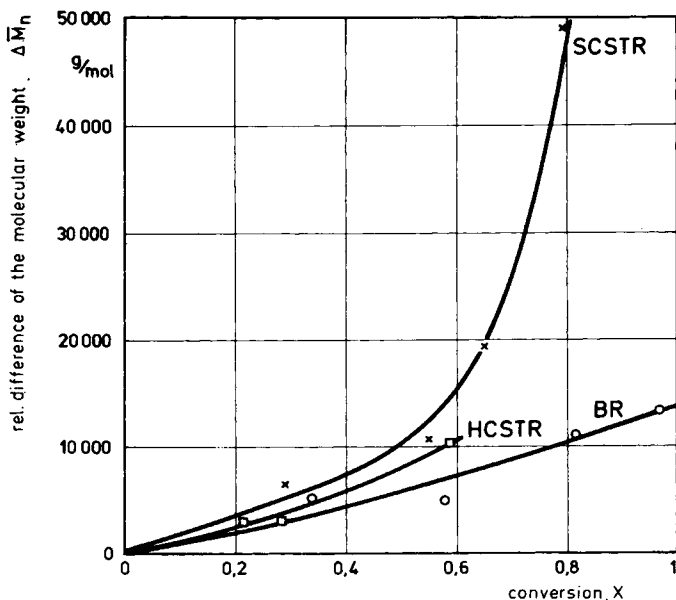


Fig. 12. Relative difference of the number average of the molecular weight of poly(vinyl acetate) before and after hydrolysis and reacetylation with respect to the conversion [ $\bar{M}_n$  of the poly(vinyl acetate) before hydrolysis ca. 90,000 g/mole].

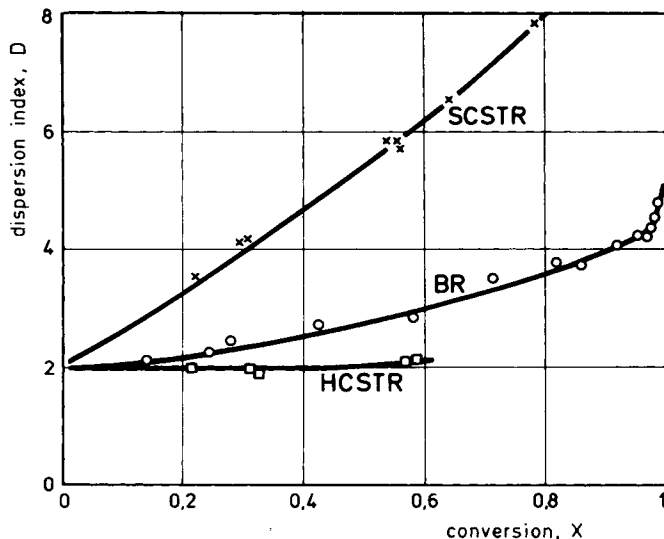


Fig. 13. Experimental determined dispersion index of poly(vinyl acetate) as function of the conversion in the three regarded reactor types.

investigated because for higher conversions the present system could no longer be considered as being sufficiently micromixed. The plot shows that in the HCSTR the dispersion index hardly increases with conversion. Up to 60% conversion, it practically has a value of 2 which is given by the termination mechanism of disproportionation.

A comparison of the MWDs in the three reactor types considered for a conversion of 57% is shown in Figure 14. The weight fraction  $W_r$  related to 1 g polymer is plotted versus the degree of polymerization.

Comparing the change of the dispersion indices with conversion of the poly(vinyl acetate) samples after removal of the hydrolyzable side chains (Fig. 15) to the same branched poly(vinyl acetate) samples, the dispersion indices with exception of HCSTR (where approximately the same values prevail) have es-

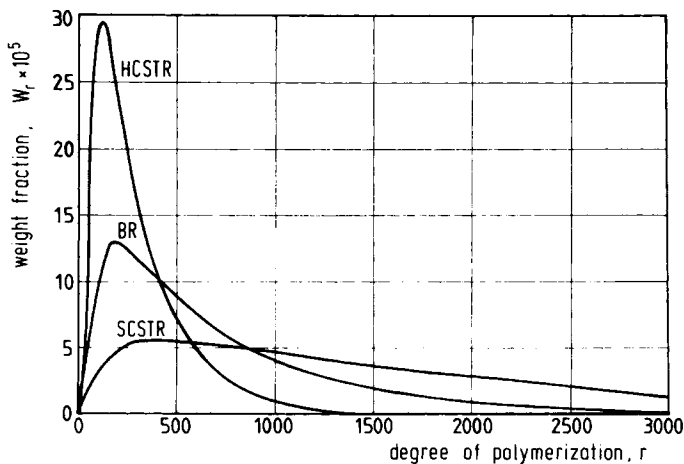


Fig. 14. Experimental molecular weight distribution of poly(vinyl acetate) with respect to the degree of polymerization at 57% conversion.

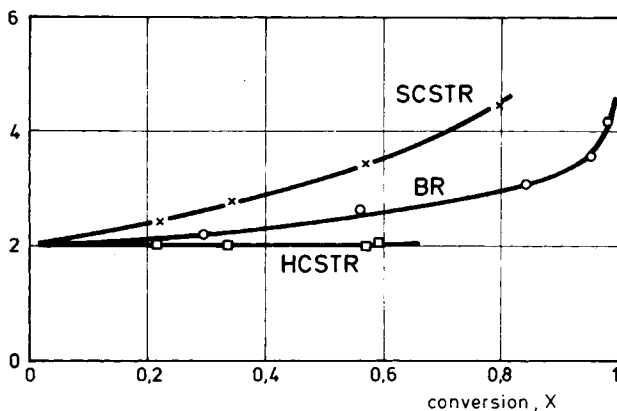


Fig. 15. Experimental determined dispersion index of poly(vinyl acetate) without side chain branching vs. conversion.

entially smaller values. This shows the broadening of the MWD by side chain branching. A comparison of results obtained in BR with those obtained in a tube reactor for conversions up to 95% produces the same values in the scope of the tolerances.

### Theoretical Calculations and Discussion of the Influence of Reactor Type on MWD and Branching

For comparison with the experimental MWDs, we tried to calculate the MWD in the three reactor types.

For calculation of the MWD in HCSTR, the method of Bamford and Tompa<sup>21</sup> was used as the basis of the kinetic scheme of the polymer process. The scheme they used was modified for the radical polymerization of vinyl acetate in the following manner:

1. The initiation step was substituted by the decomposition of the initiator used (dicyclohexyl peroxidicarbonate).

2. The transfer reaction of a polymer radical to the terminal double bond of a polymer molecule was considered. For polymerization in very dilute solution, however, this is significant only for the calculation of the probability of propagation.

3. As shown by the calculations, the transfer reaction to molecules of the solvent could be neglected on account of the very small value of the transfer constant of tertiary butanol compared to the other rate constants.

Table I shows the kinetic scheme for poly(vinyl acetate) including the previously mentioned limitations. Following the calculations of Bamford and Tompa with constant concentration of the monomer which is present in HCSTR, the following equation of the dependence of the weight fraction from the degree of polymerization results:

$$W_r = \frac{r P_r}{M X} = \frac{1}{\bar{r}} \exp[-\rho \cdot (1 + \Omega)] \frac{2 + \Omega}{\Omega} I_1[\rho \cdot \Omega^{0.5}(2 + \Omega)^{0.5}]$$

where

$$\Omega = k_{tr,2}(k_d I / k_t)^{0.5} \bar{r} \tau$$

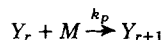
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TABLE I  
Kinetic Scheme for Poly (vinyl Acetate)<sup>a</sup>

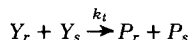
(1) Decomposition of the initiator;



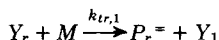
(2) Propagation reaction;



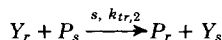
(3) Termination reaction by disproportionation:



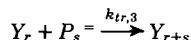
(4) Transfer reaction of a polymer radical to a monomer molecule:



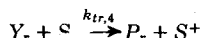
(5) Transfer reaction of a polymer radical to a polymer molecule:



(6) Transfer reaction of a polymer radical to the terminal double of a polymer molecule:



(7) Transfer reaction of a polymer radical to a solvent molecule:



<sup>a</sup> *M* notes the monomer, *S* notes the solvent, *I* notes the initiator, *P<sub>r</sub>* notes the polymer with the degree of polymerization *r*, *P<sub>r</sub><sup>=</sup>* is the polymer with terminal double bond, *Y<sub>r</sub>* is the polymer radical, *r* and *s* are, respectively, the number of monomer units for each polymer molecule or polymer radical, and *k<sub>i</sub>* is the rate constant of single reaction steps.

$$\rho = r/\bar{r}$$

*I*<sub>1</sub> is the Bessel function of first kind and first order and  $\tau$  is the mean residence time. *P<sub>r</sub>*, *M*, and *I* are the molar concentrations of the symbols explained above in Table I.

The rate constants used were taken from the literature<sup>1,8,22</sup> as average rates with the exception of the decomposition constant which was applied according to the results of part three of this study. Therewith the termination constant *k<sub>t</sub>* was considered as being constant for all conversions in the present dilute solution. The values of the rate constants used are shown in Table II.

A comparison of the measured and the calculated MWD mentioned above for a conversion of 59% is shown in Figure 16. Regarding this a satisfactory agreement can be noted. A calculation of the MWD in BR and SCSTR following the same method has not been successful so far because in this case the concentration of the monomer does not remain constant. Consequently, a calculation with the aid of the moments of the distribution becomes necessary. Because for this calculation the transfer constant to the terminal double bond can no longer be partly neglected, a system of differential equations is obtained that is no longer uniquely solvable. In our opinion none of the six present kinetic equations can

TABLE II  
Rate Constants of the Single Reaction Steps of Vinyl Acetate Polymerization (All at 60°C)

$k_d = 2.2 \times 10^{-4} + 4 \times 10^{-3} [I]_0 \text{ s}^{-1}$
$k_p = 9500 \text{ L/mol}\cdot\text{s}$
$k_t = 355 \times 10^6 \text{ L/mol}\cdot\text{s}$
$k_{tr,1} = 2.38 \times 10^{-4} k_2 \text{ L/mol}\cdot\text{s}$
$k_{tr,2} = 3.4 \times 10^{-4} k_2 \text{ L/mol}\cdot\text{s}$
$k_{tr,3} = 0.66 k_2 \text{ L/mol}\cdot\text{s}$

be neglected. Therefore, the calculation method developed by Nagasubramanian and Graessley<sup>13,14</sup> was not applied, particularly since this method shows no agreement with the experimental results of this study. This may be attributed to the fact that single kinetic parameters have been neglected. Other calculations, for example those by Hamielec,<sup>23</sup> only enable calculation of the first three moments of the distribution to be carried out.

Furthermore, we tried to calculate the dependence of the dispersion index from the conversion in SCSTR. This was done from the values of the dependence of the dispersion index on the conversion which were experimentally measured in BR and from the function of the residence time distribution in SCSTR. The residence time distribution was determined by delta function input and measurement of the conductivity. This can be done if the discrete values of the dispersion index-conversion-dependence and the values of the function of the residence time distribution are known:

$$D(\tau) = \frac{1}{\tau} \lim_{i \rightarrow \infty} \sum_{i=1}^{\infty} D(t_i) f(\theta_i) \Delta t$$

In this equation  $t$  is the time and  $\theta$  the dimensionless residence time. When comparing the dependence of the dispersion index on conversion (Fig. 17), which was obtained by calculations with the experimental results in SCSTR, it is shown that the theoretical calculated curve is similar to the experimental curve only by the shape but the absolute values are about 20% lower. This can be explained

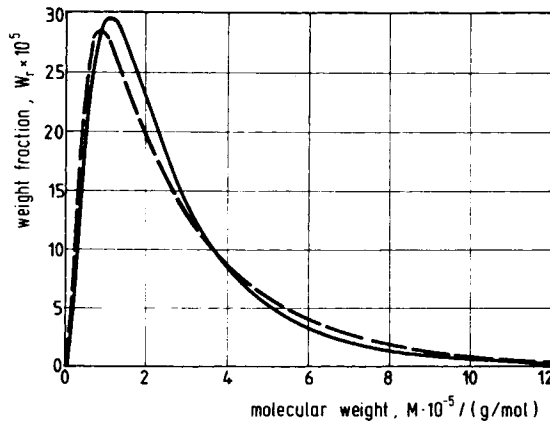


Fig. 16. Molecular weight distribution of poly(vinyl acetate) in HCSTR at 59% conversion: (---) theoretical; (—) experimental.



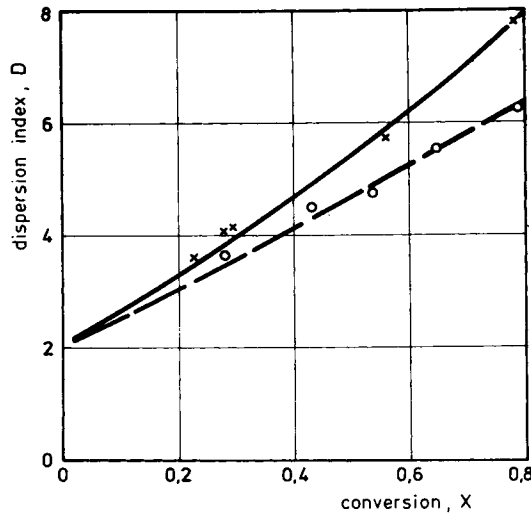


Fig. 17. Dispersion index of poly(vinyl acetate) with respect to the conversion in SCSTR (---) theoretical; (—) experimental.

by the fact that for the calculations the different increases of the branching has to be considered in the two reactor types, BR and SCSTR. This has, however, not been done, because it has not been possible to calculate up till now.

Considering branching, it was found that branching fundamentally increases with increasing conversion (Fig. 12) which is attributed to the increase in concentration of the polymer with increasing conversion. Consequently transfer reactions to the polymer will take place to a greater extent.

Larger branching during continuous processing than in BR can be explained

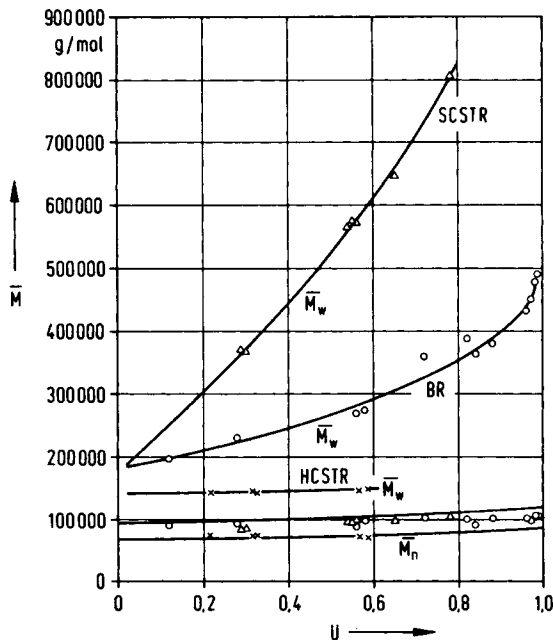


Fig. 18. Molecular weight of poly(vinyl acetate) vs. conversion for different reactor types.

by the fact that in continuous tank reactors polymer molecules can have a residence time which is larger than the reaction time in BR. Therefore, molecules are available considerably longer for transfer reactions, causing a greater branching probability. The much larger side chain branching in SCSTR as compared with HCSTR may be attributed to the higher local average concentration of the polymer in a completely segregated system. This again accounts for an accelerated transfer probability.

With regard to MWD one can observe that the smallest MWD results in HCSTR, a broader one in BR, and the broadest in SCSTR. This corresponds with the theory of Biesenberger and Tadmor<sup>10-12</sup> specified for linear polymers in these reactor types. The width of the MWD, however, increases much faster with conversion for branched poly(vinyl acetate) than for linear polymers, which is essentially caused by the intense long chain branching of poly(vinyl acetate). This becomes particularly noticeable when comparing the change of the dispersion index of polymer samples without side chain branching with the data published in literature by Biesenberger.<sup>10-12,24</sup> These curves (Fig. 15) are similar in shape to those calculated by Biesenberger, with differences still recognizable on account of main chain branching.

The experimental results for the HCSTR which were obtained in this study are different than those in refs. 13-17. It should be noted, however, that the dispersion indices of poly(vinyl acetate) for HCSTR were calculated theoretically only in refs. 13-17. The results of BR are in good agreement with Graessley's results. For SCSTR, slightly larger dispersion indices than those published by Graessley were found in this study, which in our opinion can be explained by the fact that a complete segregation with polymerization in solution in contrast with polymerization in suspension can hardly be achieved.

The amount of the gel effect on the broadening of the MWD is relatively low<sup>24</sup> compared to the influence of branching and temperature on the width of the distribution. The difference in the order of distribution and branching in BR and HCSTR may possibly be explained by different values of the termination constants. Furthermore, just in these two particular reactor types, the influence of the concentration gradient of the monomer is obviously greater than the influence of branching, since branching is almost the same in both reactor types.

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