

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Estimation of the Characteristic Ratio $k_p(f/k_t)^{1/2}$ and Its Temperature Dependence in Bulk Polymerization of Vinyl Chloride

O. F. Olaj^a; J. W. Breitenbach^a; K. J. Parth^a; N. Philippovich^a

^a Institute of Physical Chemistry, University of Vienna, Vienna, Austria

To cite this Article Olaj, O. F. , Breitenbach, J. W. , Parth, K. J. and Philippovich, N.(1977) 'Estimation of the Characteristic Ratio $k_p(f/k_t)^{1/2}$ and Its Temperature Dependence in Bulk Polymerization of Vinyl Chloride', Journal of Macromolecular Science, Part A, 11: 7, 1319 – 1331

To link to this Article: DOI: 10.1080/00222337708061328

URL: <http://dx.doi.org/10.1080/00222337708061328>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Estimation of the Characteristic Ratio $k_p(f/k_t)^{1/2}$ and Its Temperature Dependence in Bulk Polymerization of Vinyl Chloride

O. F. OLAJ, J. W. BREITENBACH, K. J. PARTH, and
N. PHILIPPOVICH

Institute of Physical Chemistry
University of Vienna
A-1090 Vienna, Austria

ABSTRACT

According to a reaction scheme which as its main features assumes that polymerization is predominantly in the interior of the monomer swollen poly(vinyl chloride) particles and that all the decaying initiator finally contributes to the polymerization within the polymer particles, the ratio $k_p(f/k_t)^{1/2} = K$

(where k_p, k_t are rate constants for chain propagation and chain termination, respectively, within the particles and f is initiator efficiency) has been calculated for bulk polymerization of vinyl chloride at three temperatures. K is found to be markedly larger than the corresponding quantity for homogeneous solution polymerization; e.g., at 50°C it is seven times this latter quantity. The characteristic ratio K shows a marked negative temperature dependence, which corresponds to approximately -4.5 kcal/mole for $E_p - (E_t/2)$, when f is assumed to

be independent of temperature. This behavior is quite consistent with a strong gel effect being operative at the site of reaction, i.e., the swollen polymer particles can be taken as equivalent to a homogeneous polymerization system at high conversion.

INTRODUCTION

The free-radical polymerization of vinyl chloride in bulk or suspension at normal reaction temperature (around 50°C) is distinguished by an early nonlinear conversion-time behavior. In the course of time, quite a number of kinetic models have been developed to account for this increase in the instantaneous rate of conversion dU/dt , with time or conversion U . Bengough and Norrish [1], as early as 1950, postulated a linear relationship between dU/dt and $U^{2/3}$ which should suggest a connection of rate to particle surface (which is assumed to be proportional to the 2/3- power of polymer mass, i.e., conversion). Five years later, Schindler and Breitenbach [2] introduced a conversion-dependent termination constant into the kinetic scheme. Their idea finally led to a linear dependence of the average rate of conversion, U/t , on time. 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 phases, the one rich in monomer and containing practically no dissolved polymer, the other consisting of the precipitated polymer swollen with monomer. This scheme, which later was further specified by Ugelstad et al. [5, 6] as well as by Hamielec et al. [7], at least in its basic form, favors a linear variation of dU/dt with U :

$$dU/dt = a + bU \quad (1)$$

where a and b are constants for a specific run. The qualitative interpretation of the increase in 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 (due to an increase in conversion) will result in an increase in rate.

It should be noted, however, that this steady increase in rate, which is the subject of all these theories, is given only after a certain critical conversion (at about 0.5%), where a marked discontinuity in rate of polymerization has been observed [2]. This is not the only important change which happens in this very range of conversion.

As has been discovered by Cotman et al. [8], not only does the rate drop very sharply, but there is also (at a polymerization temperature of 47°C) a sudden decrease in the number of polymer particles from at least 25×10^{11} to 5×10^{11} per gram of monomer, independent of initiator concentration; the latter number remains constant during the subsequent stage of polymerization. An informatory calculation will show that the radical/particle ratio, which is probably less than unity before the discontinuity, will be of the order of 5 afterwards [9]. The coincidence of rate and particle number change therefore strongly indicates that the polymerization system passes from emulsion polymerization-like characteristics to a system where the polymer particles may be treated as a "pseudo-continuous" phase. As a consequence, all considerations and kinetic deductions in some way making use of this pseudo-continuous character of the polymer particle phase can be applied to the later stage of the vinyl chloride polymerization only (above ca. 1% conversion). On the contrary, measurements carried out at conversions lower than 0.5% refer to a fully different kinetic system and can cast no light at all on the kinetic behavior at higher conversions.

In the course of a careful analysis of the conversion-time curves of the bulk polymerization of vinyl chloride (and a large number of other polymerization systems with vinyl chloride as the monomer showing the characteristics of precipitation polymerization) at a polymerization temperature of 50°C [9, 10] we have invariably found that the instantaneous change of conversion with time is a linear function of the square root of conversion, i.e.,

$$dU/dt = \text{const} + \kappa \sqrt{U} \quad (2)$$

κ being a constant for each run. This law which held from conversions of 0.5-1% (after the critical conversion mentioned above has been passed) up to conversions of at least 20-30%, clearly differs from the predictions of the simple Talamini scheme [Eq. (1)].

In order to cope with our findings, [Eq. (2)], a reaction scheme has been established [9] which allows for a rapid transport of the growing chains originating from the decay of initiator outside the monomer swollen particles into the particles so that—apart from a short time lag for these radicals, which finally leads to the conversion-independent term in Eq. (2)—essentially all the initiator decaying in the system, irrespective of whether the decomposition takes place inside or outside the polymer particles, will contribute to the initiation of polymerization within the particles. Under these conditions, the volume growth of the particles with conversion (the degree of swelling

being independent of conversion) in view of the bimolecular termination will lead to a continuous increase in kinetic chain length. This may be regarded as the genuine reason for the so-called autoacceleration observed at this temperature. Clearly enough, on these grounds the rate of polymerization must be governed by the conditions prevailing in the interior of the polymer particles swollen with monomer.

According to this concept, the physical meaning of the quantity κ is

$$\kappa = k_p (f/k_t)^{1/2} (2k_0 c_S)^{1/2} (\phi_M/\sqrt{\phi_P}) (\rho_M/\rho_P)^{1/2} \quad (3)$$

where k_p , k_t are rate constants for chain propagation and bimolecular chain termination, respectively, within the particles; k_0 is the first-order rate constant of initiator decomposition; f is initiator efficiency; c_S is the overall 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. Equation (3) offers direct access to the most interesting quantity $k_p (f/k_t)^{1/2} \equiv K$, which with respect to k_p and k_t refers to the conditions of polymerization within the particles. As k_0 , ρ_M , and ρ_P usually are known with sufficient accuracy, aside from careful rate measurements necessary for the determination of κ itself, the crucial quantities for the evaluation of κ will be ϕ_M and ϕ_P . A short description of a method of obtaining ϕ_M and ϕ_P from swelling measurements has already been given [11].

Apart from the fundamental importance of the quantity K mainly relative to the corresponding value for the homogeneous (solution) polymerization of vinyl chloride, a more detailed insight into the reaction scheme is expected if, in addition to evaluating the characteristic ratio K for a single temperature (50°C), its temperature dependence is also estimated. This, however, necessitates a check of the validity of Eq. (2) for temperatures other than 50°C.

EXPERIMENTAL

Kinetic Measurements

Kinetic measurements were carried out dilatometrically with purified, prepolymerized, and degassed vinyl chloride monomer

(Halvic) by use of sealed vessels with a high surface/volume ratio to ensure rapid transport of the heat of polymerization evolved to the thermostat bath. Readings were taken with the aid of a cathetometer with an accuracy of 0.02 mm. The dilatometric curves were converted into conversion-time curves by using the appropriate contraction factors. Differentiation of the conversion time curves was carried out graphically with the help of a modified mirror ruler. The slopes obtained by this procedure in many cases were checked by numerical differentiation. No significant deviations could be detected.

2,2'-Azobisisobutyronitrile (AIBN) was used as initiator in the 35 and 50°C experiments, while 1,1'-azobis(1-cyanocyclohexane) (ACHN) was chosen in the 60°C experiments because of its comparatively low rate of decomposition. k_0 values of 2.6×10^{-7} and 2.6×10^{-6} sec⁻¹ for AIBN at 35 and 50°C, respectively, have been inserted into the calculations [12, 13] while for k_0 of ACHN at 60°C a value of 4.75×10^{-7} sec⁻¹ based on the equation [14] of Olaj has been chosen.

Evaluation of ϕ_M and ϕ_P

Cylindrical polymer rods with sharp boundaries, prepared from solid annealed extruded poly(vinyl chloride), were used. Care had been taken that the polymer contained a minimum of additives only. The rods were placed vertically into monomer in sealed vessels and their increase in length followed by means of a cathetometer until a final equilibrium value characteristic for the temperature of the experiment had been reached. Assuming isotropic swelling behavior, the increase in volume due to swelling was calculated according to

$$V/V_0 = (\ell/\ell_0)^3 \equiv 1 + \beta \quad (4)$$

where V , ℓ are equilibrium volume or length, respectively, of the rod after swelling, V_0 , ℓ_0 are initial volume or length, respectively, of the rod, and β is the relative increase in volume due to swelling. Two different samples were used: sample A, having $[\eta] = 116$ cm³/g in cyclohexanone at 25°C, and sample B, with $[\eta] = 68$ cm³/g in cyclohexanone at 25°C. Actually, sample B, probably as a consequence of the difficult extruding conditions due to its extremely low content

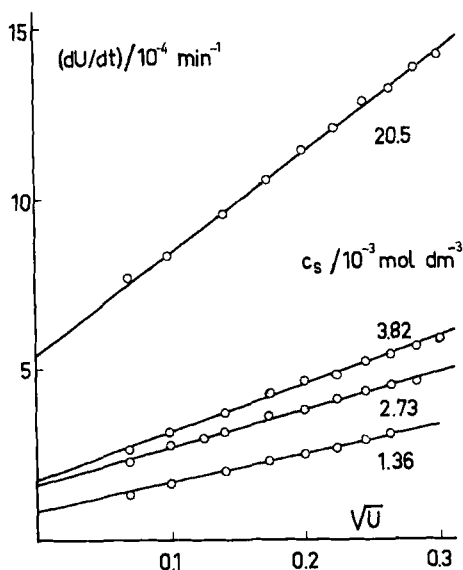


FIG. 1. Plot of dU/dt vs. $U^{1/2}$ [according to Eq. (2)] for the AIBN-initiated bulk polymerization of vinyl chloride at 50°C .

of lubricant, showed a slight deviation from isotropic swelling for which an appropriate correction has been made. Assuming additivity of volume in the swelling process (only a negligible volume change of the overall system occurred during the swelling procedure), ϕ_M and ϕ_P may be equated to $\beta/(1 + \beta)$ and $1/(1 + \beta)$, respectively.

Values of 1.26, 1.28₃, and 1.30 have been used for the square root of the ratio of polymer and monomer densities; $(\rho_P/\rho_M)^{1/2}$, at 35, 50 and 60°C , respectively.

RESULTS AND DISCUSSION

Equation (2), which had been already proved to apply for a polymerization temperature of 50°C [9, 10], now is shown to be valid over a broader range of temperature ($35\text{--}60^\circ\text{C}$). Figures 1-3 show the perfectly straight lines which are obtained when dU/dt is plotted

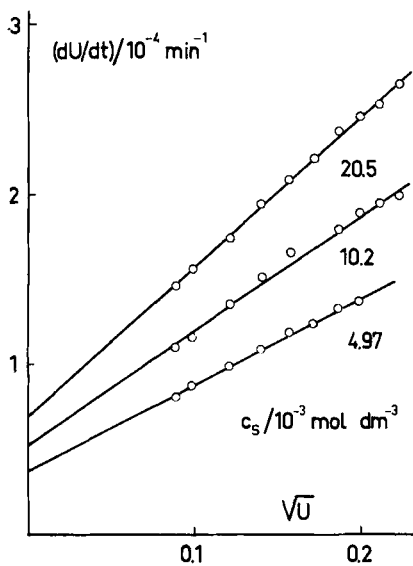


FIG. 2. Plot of dU/dt vs. $U^{1/2}$ [according to Eq. (2)] for the AIBN-initiated bulk polymerization of vinyl chloride at 35°C .

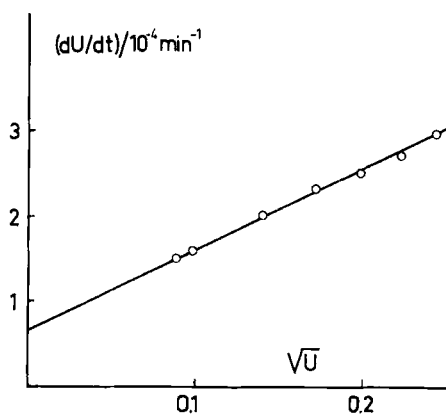


FIG. 3. Plot of dU/dt vs. $U^{1/2}$ [according to Eq. (2)] for the bulk polymerization of vinyl chloride at 60°C initiated by 0.012 mole/dm^3 ACHN.

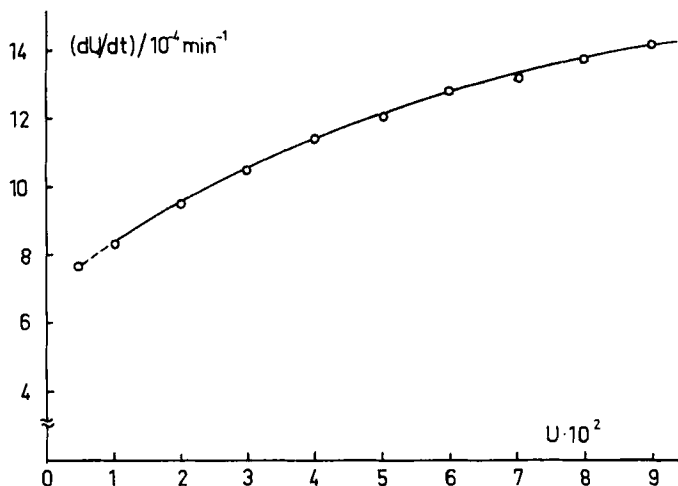


FIG. 4. Plot of dU/dt vs. U [according to Eq. (1)] for the run with the highest AIBN-concentration shown in Fig. 1. $c_S = 2.05 \times 10^{-2}$ mole/dm³.

against $U^{1/2}$. In Fig. 4, for comparison, a plot of dU/dt versus U , corresponding to the predictions of the simple Talamini scheme [Eq. (1)], is shown for one of these runs. No straight line can be drawn in this case, the points showing a significant and systematic deviation from linearity, especially in the lower conversion range.

Thus the Talamini scheme in its basic form is incompatible with these experimental findings. However, there exists a more complicated version [15], which contains additional parameters and which would lead to a rate equation of the form

$$R_p = k_p c_p M_0 R_i^{1/2} \left[(f_1 v_1 / k_{t1})^{1/2} + (f_2 v_2 / k_{t2})^{1/2} (c_M / c_{M0}) \right] \quad (5)$$

where R_p is the overall rate of polymerization; R_i is the overall rate of initiation; v_1, v_2 denote the volume fraction of the phase poor in polymer (1) and rich in polymer (2), respectively; f_1, f_2 denote the fraction of radicals produced by decay of initiator going into phase 1 and 2, respectively; k_p is the rate constant of chain propagation in

either phase (1 and 2); k_{t1} , k_{t2} denote the rate constant of chain termination in phases 1 and 2, respectively; c_{M0} is the "overall" monomer concentration; c_M is the monomer concentration in phase 2. Usually f_1 is assumed to equal v_1 (and $f_2 = v_2$). As v_2 under the conditions of the bulk polymerization of vinyl chloride will be proportional to conversion as long as there is enough monomer left to ensure equilibrium swelling of the polymer particles, this will lead to a relationship between rate and conversion of the form of Eq. (1). Purely formally, if we put $f_2 \approx 1$ [in analogy to the assumptions inherent in our derivation of Eq. (2)], independent of conversion for conversions exceeding 1%, an equation of the type of Eq. (2) could be obtained, too. The difference between our concept and that of Talamini, then, would be mainly reduced to the divergent interpretation of the conversion-independent term of Eq. (2).

The proportionality between κ and $\sqrt{c_S}$ required by Eq. (3) may be checked from a plot of these quantities against each other (Fig. 5).

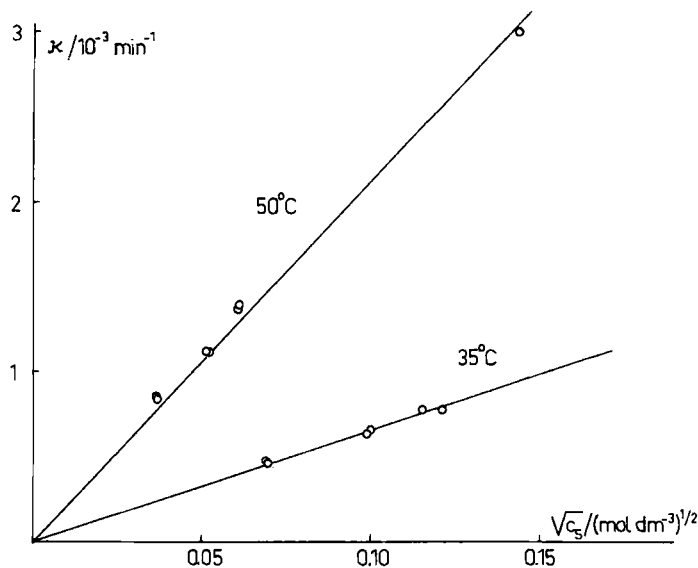


FIG. 5. Plot of κ vs. $c_S^{1/2}$ for the AIBN-initiated bulk polymerization of vinyl chloride at 35 and 50°C.

TABLE 1. Kinetic Data and Swelling Data for Two Different Poly(vinyl Chloride) Samples A and B^a

Temp (°C)	$\kappa/c_s^{1/2}$ [(dm ³ /mole) ^{1/2} / sec]	Sample A ([\eta] = 116 cm ³ /g)		Sample B ([\eta] = 68 cm ³ /g)	
		β	K (dm ³ /mole- sec) ^{1/2}	β	K (dm ³ /mole- sec) ^{1/2}
35	1.08×10^{-4b}	0.39	0.57	0.51	0.45
50	3.58×10^{-4b}	0.42	0.57	0.57	0.44
60	1.44×10^{-4c}	0.44	0.52	0.61	0.40

^aK = $k_p (f/k_t)^{1/2}$ has been calculated according to Eq. (3).

^bInitiator AIBN.

^cInitiator ACHN.

The slopes of these plots (corresponding to $\kappa/c_s^{1/2}$) and the results of the swelling measurements are summarized in Table 1. Table 1 also contains the characteristic ratios $k_p (f/k_t)^{1/2} = K$ which have been calculated tentatively from these quantities by means of Eq. (3). As the two samples differ in their degree of swelling, there is a 20-25% difference in the K values depending on whether the swelling data of sample A or sample B have been used. The temperature dependence of these K values in either case is nearly negligible and hardly significant. Now, however, sample A according to its limiting viscosity number corresponds to a bulk polymer prepared at ca. 45°C, while on the same grounds a polymerization temperature of ca. 65°C may be assumed for sample B. Apparently, we have to deal with a certain dependence of the degree of swelling on molecular weight or, due to the intimate relation between molecular weight and temperature of polymerization in the polymerization of vinyl chloride, on the temperature of polymerization. Strictly speaking, the swelling data of sample A will therefore be appropriate for the kinetic analysis of 45°C experiments only, while those of sample B should be used exclusively for experiments carried out at 65°C. A correct analysis of the data obtained for a certain temperature of polymerization, as a consequence, should be based on the swelling behavior of a polymer produced at exactly that temperature. Unfortunately, no

TABLE 2. K Values Based on Swelling Data at Temperature t for Hypothetical Poly(vinyl Chloride) Samples C Prepared at the Same Temperature

t ($^{\circ}\text{C}$)	β	$K [(\text{dm}^3/\text{mole}\cdot\text{sec})^{1/2}]^a$
35	0.30	0.72
50	0.47	0.52
60	0.57	0.42

^a $K (= k_p \sqrt{f/k_t})$ calculated from Eq. (3).

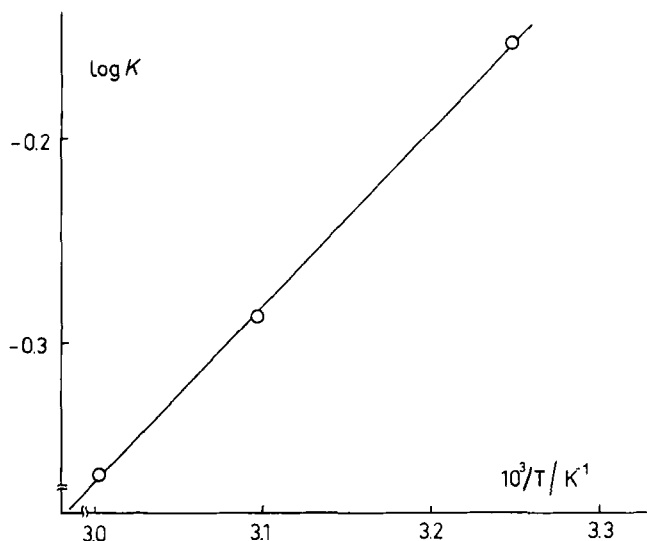


FIG. 6. Arrhenius plot of the quantity $K = k_p (f/k_t)^{1/2}$

such polymers prepared at 35, 50, and 60 $^{\circ}\text{C}$ were available. In order to overcome this lack, therefore, a linear variation of β with polymerization temperature, when measured at that temperature, has been assumed as a reasonable approximation. The swelling behavior of these hypothetical samples (C) is summarized in Table 2. Use of these data for β leads to K values exhibiting a marked decrease with increasing temperature (last column of Table 2).

On assuming f to be independent of temperature, this behavior corresponds to a difference in apparent energies of activations, $E_p - (E_t/2)$, of ca. -4.5 kcal/mole (Fig. 6). For a normal value of the energy of activation of chain propagation, ($E_p \approx 7$ kcal/mole) this would mean that the (apparent) energy of the termination step ought to be of the order of 23 kcal/mole.

The polymer-rich phase, when considered separately, in view of its high polymer content may be taken as equivalent to a homogeneous polymerization system at high conversion.

Together with the high values of K , compared to the homogeneous polymerization of vinyl chloride, where K is 0.077 ($\text{dm}^3/\text{mole-sec}$)^{1/2} at 50°C [16], therefore, such high values of E_t as well as the negative values of $E_p - (E_t/2)$ are consistent with the concept of a marked gel (Trommsdorff) effect to be operative in such a polymer-rich reaction medium as it is constituted by the monomer-swollen particles in the bulk polymerization of vinyl chloride [9]. For example, an overall energy of activation (directly corresponding to $E_p - E_t/2$)

of the order calculated here (-4.5 kcal/mole) has been reported for the homogeneous photosensitized bulk polymerization of methyl methacrylate at 22.5°C at approximately 40-50% conversion [17].

This may serve as further convincing proof for the polymerization of vinyl chloride actually taking place predominantly in the swollen polymer particles, hereby adding to the arguments for the correctness of the reaction scheme outlined previously in [9].

ACKNOWLEDGMENT

We gratefully acknowledge the generous gift of vinyl chloride monomer from Halvic Kunststoffwerke GmbH, Hallein, Austria and we are grateful for support given to us by Max Buchner-Forschungstiftung, Frankfurt.

REFERENCES

- [1] W. I. Bengough and R. G. W. Norrish, Proc. Roy. Soc. (London), **A200**, 301 (1950).
- [2] A. Schindler and J. W. Breitenbach, Ric. Sci. (Suppl.), **25A**, 34 (1955).
- [3] G. Talamini, J. Polym. Sci. A-2, **4**, 535 (1966).
- [4] A. Crosato-Arnaldi, P. Gasparini, and G. Talamini, Makromol. Chem., **117**, 140 (1968).

- [5] J. Ugelstad, H. Lervik, B. Gardinovacki, and E. Sund, Pure Appl. Chem., **25**, 121 (1971).
- [6] J. Ugelstad, H. Fløgstad, T. Hertzberg, and E. Sund, Makromol. Chem., **164**, 171 (1973).
- [7] A. H. Abdel-Alim and A. E. Hamielec, J. Appl. Polym. Sci., **16**, 783 (1972).
- [8] J. D. Cotman, Jr., M. F. Gonzalez, and G. C. Claver, J. Polym. Sci. A-1, **5**, 1137 (1967).
- [9] O. F. Olaj, Angew. Makromol. Chem., **47**, 1 (1975).
- [10] O. F. Olaj, J. W. Breitenbach, K. J. Parth, and N. Philippovich, unpublished results.
- [11] O. F. Olaj, J. W. Breitenbach, H. Reif, and K. J. Parth, Angew. Chem., **83**, 370 (1971); Angew. Chem. Int. Ed., **83**, 351 (1971).
- [12] C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, The Kinetics of Vinyl Polymerization by Radical Mechanisms, Butterworths, London, 1958, p. 220.
- [13] J. W. Breitenbach and A. Schindler, Monatsh. Chem., **83**, 724 (1952).
- [14] O. F. Olaj, Makromol. Chem., **114**, 1 (1968).
- [15] A. Crosato-Arnaldi, G. Talamini, and G. Vidotto, Makromol. Chem., **111**, 123 (1968).
- [16] G. Vidotto, A. Crosato-Arnaldi, and G. Talamini, Makromol. Chem., **114**, 217 (1968).
- [17] P. Hayden and H. Melville, J. Polym. Sci., **43**, 201 (1960).