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DETERMINATION OF KINETIC PARAMETERS FROM GPC-DATA

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ABSTRACT

The molecular weight distribution and its first moments of selected polymers were experimentally determined through GPC-investigations with additional molecular weight detection. In on-line operation discontinuously functioning Ubbelohde-viscometer was used for the determination of degree of polymerization in dependence on elution volume.

The relation between the experimentally determined values and relative kinetic parameters were derived for some polymers prepared by radical mechanism. The relative constants which determines the branching structure in polymer can be now calculated.

From the investigated polymers the effect of chemical nature of monomer units for the branching formation was determined.

INTRODUCTION

When the molecular weight distribution of a polymer is determined by the conditions of synthesis (1), it

must be possible to use a measured distribution of the degree of polymerization to draw conclusions concerning elementary reactions having occurred in the system. These correlations can be used for solving kinetic problems with respect to the reaction of polymer formation provided that the accuracy of the method of determination is very high.

Due to the considerable progress in the methodical development of high-resolving gel permeation chromatography (GPC) with detection of molecular weight, the research workers concerned with high polymers today dispose of a method of analysis meeting all demands with respect to detection sensitivity, precision and reproducibility which are necessary for obtaining exact data on the frequency distribution of molecular weight.

Since separation by GPC, in consequence of the effective separation mechanism, proceeds according to the hydrodynamic volume rather than the molecular weight, a molecular weight detector has to be used additionally in the evaluation of the elution curve with respect to kinetic values, particularly in the investigation of reactions leading to branch formation (2). This combination of detectors results in the fact that the problem of calibration, which is of exceptional importance in the classical evaluation of GPC, becomes unimportant, furthermore, the elution chromatogram can be corrected by the axial dispersion function without any assumptions being made (3). Thus, GPC is reduced to its original application, i.e. the separation of macromolecules according to their size. The error resulting from axial dispersion which is generally inherent in this method can be exactly taken into consideration experimentally without mathematical assumptions.

Similar considerations apply to GPC investigations using combined detection units for determining simultaneously the concentration and the structure of the

eluate. This opens the field of the determination of heterogeneity for the research worker concerned with copolymer analysis. Apart from the well-known and widely used procedures for determining the chemical composition of copolymers in dependence on the elution volume by combining two or more concentration detectors, one structure detector can be used to obtain information on the step probability p_{ab} in the chain (17). This, however, requires that the dependence of the property of a structural unit located in the center of a selected chain segment on its nearest neighbours be known. From the measured p_{ab} the ratios of rate constants $r_a = k_{aa}/k_{ab}$ and $r_b = k_{bb}/k_{ba}$ can be calculated, respectively, the mean length of sequences (a or b) and the distributions of sequences or sequence length. This field of work is still in its initial stage; research work using ethylene-vinyl acetate-copolymers shows however (30), that this is in principle a promising way, although there are still many partial problems which remain to be solved for each of the system to be investigated.

In this contribution a new field of interesting application of the modern high-resolving GPC has been represented. It has been shown that how one can determine independently without assumption of the structural formation of the polymer the number- and the weight average molecular weight from the chromatogram. It is possible about the average values \bar{M}_n and \bar{M}_w to describe a relation between the kinetic of the polymer formation reaction to the microstructure in the given case the branching of the polymers.

EXPERIMENTAL

The continuous determination of molecular weight in the eluate directly at the end of the separating columns

is at present carried out using viscosity and light scattering detectors (low angle laser light scattering-detector). Viscosity measurements can be carried out continuously (4) and discontinuously (5 to 13) in on-line operation with sufficient accuracy. The latter method is not subjected to all points of the basic requirements pointed out by Ouano (14), which must be met by a molecular weight detector. However, if the measurement procedure is optimized using the experimental set-up described in the literature (e.g. 10,11,12), reproducible results are obtained which are confirmed by comparison with absolutely measured mean values \bar{M}_n and \bar{M}_w . The advantage of the discontinuous measurement is the apparatus set-up. As the measuring and the pumping system is not directly connected with each other, the operation of the viscometer is undisturbed and without being affected by the smallest inhomogeneities in the flow rate of the eluent.

All \bar{M}_n and \bar{M}_w values which constitute the basis of the following calculations were determined using an Ubbelohde-viscometer, modified according to the conception of Scheinert (11), as a molecular weight detector. This variant of apparatus is able to prevent deterioration of time measurement by tailings of the solvent from the syphon.

Tetrahydrofuran (THF) was used as solvent. Standard deviation for its hold-up in the viscometer was 8/1000 sec, this meets the accuracy demands which in principle are made for such viscosity measurements.

Elution curves were evaluated in the usual way described in the literature (e.g. 5,10,11,12). The concentration profile was corrected for the axial dispersion according to the procedure by Servotte et al (15,16). For polymers having a narrow molecular weight distribution ($1,5 < \bar{M}_w/\bar{M}_n < 2$) the correction procedures according to Berger (3) should be preferred.

The molecular weight to be assigned to the elution volumes were calculated from the universal calibration

equation (1) determined experimentally for polystyrene standards in the range of molecular weights from 6×10^2 to 2×10^6 g/mol.

$$\lg \left[\left[\eta \right]_M \right]_{25^\circ\text{C}}^{\text{THF}} = -0.15045 v_e + 14.889 \quad (1)$$

(5 Styragel columns with the exclusion limit 10^{-4} , 10^{-5} , 10^{-6} , 10^{-7} and 10^{-8} m; the flow rate of eluent was $0.75 \text{ cm}^3/\text{min}$)

Since the calibration relationship is linear ($d(v_e)/d(\lg M) = \text{constant}$), the calculation of the mean values \bar{M}_n and \bar{M}_w is considerably simplified (17). This is a favourable fact for calculating the relative kinetic constants since the method proposed does not relate the overall distribution but only the first moments of the frequency distribution of the degree of polymerization to the kinetic equations.

Relationships Between the Relative Reaction Constants and the Values Obtainable from the Chromatographic Data

The correlation between the instantaneous degree of polymerization P and the elementary reactions is known for polymers produced by a radical mechanism. Thus, the problem may be solved using the equations by Bamford et al (18). For the present case, the relationship between the time dependence of the degree of polymerization of the value $r - d(P_r)/dt$ and the growing chain $-d(P_r^*)/dt$ is first formulated. The differential equations obtained in this way are transferred to the time dependence of the 0-th, 1-st and 2-nd moments of the frequency distribution by multiplying by r^n and summation over all r 's, with the equations (2) and (3) being introduced.

$$Q_n = \sum r^n P_r \quad (2) \quad Y_n = \sum r^n P_r^* \quad (3)$$

Using the boundary conditions which can be estimated for

the present system, and assuming the steady-state principle to be valid, the differential equation $-d(Q_n)/dM$ or $d(Q_n)/dR$ obtained can be solved analytically in some cases - other cases require numerical integration.

The measured mean degrees of polymerization are defined by equations (4) and (5).

$$\bar{P}_n = \frac{Q_1(M)}{Q_0(M)} \quad \text{or} \quad \frac{Q_1(R)}{Q_0(R)} \quad (4) \quad \bar{P}_w = \frac{Q_2(M)}{Q_1(M)} \quad \text{or} \quad \frac{Q_2(R)}{Q_1(R)} \quad (5)$$

Table 1 contains equations for calculating $Q_0(M)$, $Q_1(M)$ and $Q_2(M)$ for some sequences of elementary reactions occurring in the polymerization of vinyl monomers; these reactions determine the instantaneous molecular weight of the formed polymer. Inserting the measured \bar{M}_n and \bar{M}_w and the selected equations for $Q_{0,1,2}(M)$ from Table 1 in equation (4) and (5) the desired relative reaction constant can be calculated.

The equations for $Q_0(R)$, $Q_1(R)$ and $Q_2(R)$ (Table 2) were also derived under the assumption that $dM/dt=0$, as they are of interest in the emulsion polymerization. In emulsion polymerization, the equations of bulk polymerization can be used for description of the resulting distribution of the degree of polymerization on condition that chain transfer caused by a chain regulator added (or by monomer transfer) is sufficiently large, such that all reactions leading to chain termination can be neglected (20).

RESULTS AND DISCUSSION

The proposed concept for calculating relative kinetic constants related to the propagation constant k_p , such as k_{fm}/k_p (monomer transfer), k_{fr}/k_p (regulator transfer), k_{fp}/k_p (polymer transfer), k'_p/k_p (chain double-bond polymerization) and k_p^*/k_p (terminal double-bond

polymerization) was tested and checked using products of the emulsion polymerization of vinyl acetate, styrene and butadiene with different conversions x . For the emulsion polymerization in the region of constant overall rate of polymerization, the polymerization time t can be set equal to x , i.e. $x=0$ corresponds to $t=0$ and $x=x_c$ (x_c =conversion at which the separate monomer phase disappears) correspond to $t=t_c$, the values between the extremes can be obtained from the time-conversion curves. This substitution is necessary in order to give the possibility of calculating the concentration of regulator R at point x and the polymerization time t at the site of reaction, respectively (cf. the boundary conditions listed in line 4 and 5 of Table 1 and in Table 2).

Examples for evaluating the measured elution curves with respect to the frequency distribution of the molecular weight and hence the mean values \bar{M}_n and \bar{M}_w have been presented in earlier works (21,22). For calculating the above-mentioned relative constants, the equations from Table 1 and 2 have been used, unless references indicating other sources have been given.

Emulsion Polymerization of Vinyl Acetate

The polymerization of vinyl acetate has been extensively studied from the view-point of the development of the mean molecular weights with the conversion. Hence, comparison of the calculated numerical values with those published in the literature (23) for k_{fm}/k_p , k_{fp}/k_p and k_p^*/k_p is easily possible. Evaluation was carried out using polyvinyl acetates obtained by the emulsion method at 70°C in dependence on x .

Fig. 1 shows the result of the measurements - the mean molecular weights \bar{M}_n and \bar{M}_w determined from the chromatograms. The solid curves were calculated using differential equations applying to this system (Table 1 line 6). The

TABLE 1a

Relationships between $Q_0(M)$ and the relative reaction constants ($M=M(t)$; $dM/dt = -k_p M Y_0$; $R_I =$ initial rate; $Q_1(M) = M_0 - M$; $x = (M_0 - M)/M_0$)

reactions determining the degree of polymerization	kinetic parameters to be calculated	$Q_0(M)$
propagation, monomer transfer, termination by disproportionation	$C_{fm} = k_{fm}/k_p$	$C_{fm}(M_0 - M) + (k_{td} R_I)^{1/2} \ln \frac{M_0}{M}$
propagation, monomer transfer	$C_{fm} = k_{fm}/k_p$	$C_{fm}(M_0 - M)$
propagation, regulator transfer $R = \text{const.}$	$C_{fr} = k_{fr}/k_p$	$C_{fr} R \ln \frac{M_0}{M}$
propagation, regulator transfer $R = R_0(1-x)^{C_{fr}}$	$C_{fr} = k_{fr}/k_p$	$R_0 - R_0 \left[\frac{M}{M_0} \right]^{C_{fr}}$
propagation, regulator transfer $R = R_0(1-x)^{C_{fr}}$, chain double-bond polymerization	$C_{fr} = k_{fr}/k_p$ $K = k'_p/k_p$	$R_0 - R_0 \left[\frac{M}{M_0} \right]^{C_{fr}} + KM_0 \left[1 + \ln \frac{M}{M_0} - \frac{M}{M_0} \right]$
propagation, monomer transfer, polymer transfer, terminal double-bond polymerization	$C_{fm} = k_{fm}/k_p$ $C_{fp} = k_{fp}/k_p$ $K^* = k_p^*/k_p$	$\frac{C_{fm} \left[M_0 \left[\frac{M}{M_0} \right]^{K^*} - M \right]}{1 - K^*}$
		$C_{fm} M \ln \frac{M_0}{M}$
only propagation, monomer transfer, polymer transfer or terminal double-bond polymerization	$C_{fp} = k_{fp}/k_p$ $K^* = k_p^*/k_p$	solved in (1,19)

TABLE 1b

Relationships between $Q_2(M)$ and the relative reaction constants (same conditions as in Table 1a)

reactions determining the degree of polymerization	$Q_2(M)$
propagation, monomer transfer, termination by disproportionation	$\frac{2(M_0 - M)}{C_{fm}} \left[1 - \frac{(k_{td} R_I)^{1/2}}{k_{fm} (M_0 - M)} \ln \frac{1 + \frac{M_0 k_{fm}}{(k_{td} R_I)^{1/2}}}{1 + \frac{M k_{fm}}{(k_{td} R_I)^{1/2}}} \right]$
propagation, monomer transfer	$\frac{2(M_0 - M)}{C_{fm}}$
propagation, regulator transfer $R = \text{const.}$	$\frac{M_0^2 - M^2}{C_{fr} R}$
propagation, regulator transfer $R = R_0(1-x)^{C_{fr}}$	$\frac{2 M_0^2}{C_{fr} R_0 (2 - C_{fr})} \left[1 - \left[\frac{M}{M_0} \right]^{2 - C_{fr}} \right] \quad C_{fr} \neq 2$
	$\frac{M_0^2}{R_0} \ln \frac{M_0}{M} \quad C_{fr} = 2$
propagation, regulator transfer $R = R_0(1-x)^{C_{fr}}$, chain double-bond polymerization	$\frac{dQ_2}{dM} = - \frac{2M^{1 - C_{fr}} M_0^{C_{fr}} (1 + K \frac{Q_2}{M})^2}{C_{fr} R_0}$ numerical integration; no particular solution has been found for this Ricatti type differential equation

(continued)

Continuation of TABLE 1b

propagation, monomer transfer, polymer transfer, terminal double- bond polymerization	$\frac{dQ_2}{dM} = - \frac{2 \left[1 + K^* \frac{(M_0 - M)}{M} \right] \left[M + C_{fp} Q_2 + K^* (M_0 - M) \right]}{C_{fm} M + C_{fp} (M_0 - M)}$
	numerical integration

only propagation, monomer transfer, polymer transfer or terminal double- bond polymerization	solved in (1,19)
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elementary reactions which mainly determine the degree of polymerization have to be estimated individually for each system from the course of the frequency distribution of the molecular weight with the conversion.

In this special case, the differential equations can be solved by numerical integration, hence the relative constants can be determined only by approximation calculus. The calculated mean molecular weights can be fitted to the measured molecular weights through the conversion by inserting relative constants obtainable from the \bar{M}_n and \bar{M}_w values in the phase of constant overall rate of polymerization ($dM/dt=0$) according to (20) as starting values for solving the system of differential equations and then varying these constants (24). This procedure is not so very time-consuming. When the measured values agree with the analytical values, the relative constants of reactions monomer transfer, polymer transfer and terminal double-bond polymerization are also fixed.

The differential equations used in this case were derived with the simplifying assumption that the rate of chain termination is negligibly small as compared with the rate of

TABLE 2a

Relationships between $Q_0(R)$ and the relative reaction constants ($M=\text{const.}; dR/dt = -k_{fr}RY_0; R=R_0(1-t)^{C_{fr}}$; $Q_1(R) = \frac{M}{C_{fr}} \ln \frac{R_0}{R}$)

reactions determining the degree of polymerization	kinetic parameters to be calculated	$Q_0(R)$
propagation, regulator transfer	$C_{fr} = k_{fr}/k_p$	$R_0 - R$
propagation, regulator transfer, chain double-bond polymerization	$C_{fr} = k_{fr}/k_p$ $K = k'_p/k_p$	$R_0 - R - \frac{KM}{C_{fr}^2} \left[\ln \frac{R_0}{R} \right]^2$

TABLE 2b

Relationships between $Q_2(R)$ and the relative reaction constants (same conditions as in Table 2a)

reactions determining the degree of polymerization	$Q_2(R)$
propagation, regulator transfer	$\frac{2M^2}{C_{fr}^2} \left[\frac{1}{R} - \frac{1}{R_0} \right]$
propagation, regulator transfer, chain double-bond polymerization	$\frac{1}{K \left[\frac{1}{M} + \frac{2K}{C_{fr}^2} \left(\frac{1}{R_0} - \frac{1}{R} \right) \right]} - \frac{M}{K}$

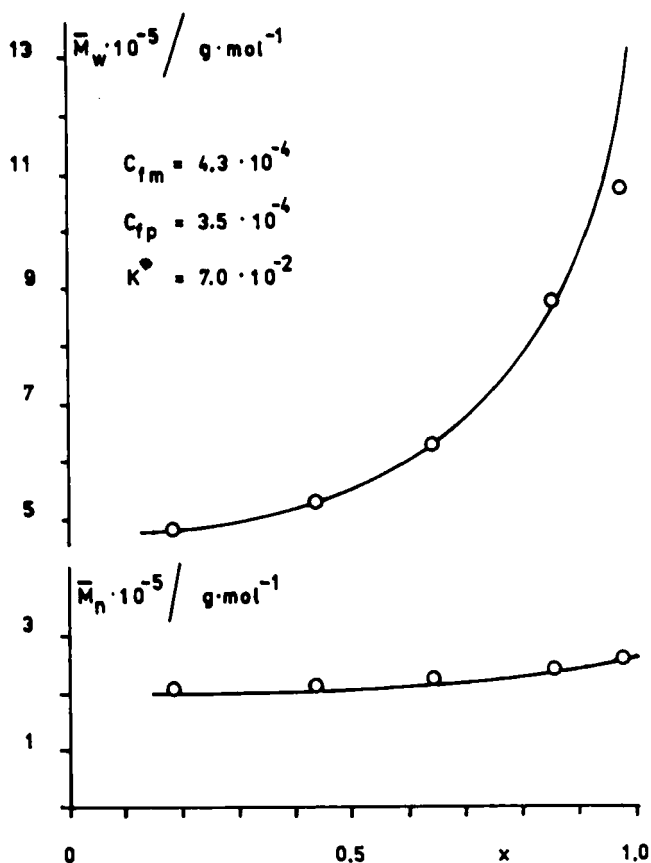


Fig. 1 Development of the molecular weight with the conversion x in the emulsion polymerization of vinyl acetate

○ measured values

— calculated course (equ. from Table 1 line 6)

$x_c = 0.15$; C_{fm} , C_{fp} and K^* cf. legend

transfer to the monomer. The influence of chain termination on the calculation of these relative constants is described in (28).

Regulated Emulsion Polymerization of Styrene

This example is intended to demonstrate how the apparent relative transfer constant to a chain regulator k_{fr}/k_p in a simple polymerization system can be estimated. Dicyclohexylxanthogendisulfide was used as a regulator, the polymerization was carried out at 60°C. The regulator-monomer ratio in the initial solution was 0.0167.

In the phase of constant overall rate of polymerization ($dm/dt=0$), the reactions propagation and regulator transfer are responsible for the instantaneous degree of polymerization, i.e. the equations of Table 2 line 1 provide a sufficient description of this system. Assuming that in the latex particle the same composition of regulator to monomer is encountered as in the initial mixture, and basing the calculation on the measured \bar{M}_n and \bar{M}_w values (Fig. 2), the relative constant k_{fr}/k_p is 0.08. The concentration of monomer in the latex particle can be calculated according to (20) (density of monomer = 907.4 g/l; density of polymer = 1020 g/l; $t_c = 0.55$ and $m_o = 104$ g/mol). If the assumption does not apply - the following example will demonstrate that this indeed may be the case - the value for k_{fr}/k_p will also change. However, the equations for calculating these constants have the property that the order of magnitude of the value k_{fr}/k_p does not change even upon major variations in the regulator concentration at the site of reaction. For example, if the concentration of the regulator at the site of reaction is diminished by one-half, k_{fr}/k_p is found to be 0.16. The constant k_{fr}/k_p determined in this way is of the order of magnitude to be expected for dialkylxanthogendisulfides (with longer alkyl groups). It is smaller by a factor of 10 than the value obtained in

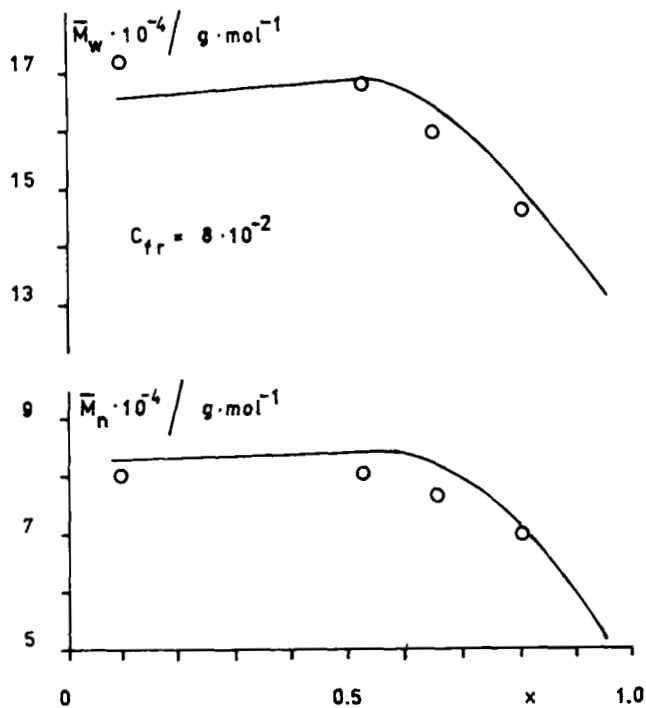


Fig. 2 Development of the molecular weight with the conversion x in the regulated emulsion polymerization of styrene

○ measured values

— calculated course (equ. from Table 1 line 4 and Table 2 line 1)

Regulator: Dicyclohexylxanthogendisulfide

$R/M_{\text{init. mixt.}}$: 0.0167; R_0 : 0.066 mol

Polymerization temp.: 60°C

$x_c = 0.55$; C_{fr} (cf. legend)

butadiene polymerization with a comparable regulator. This is due to the propagation constant k_p in styrene polymerization, which is higher by the same order of magnitude.

This problem does not occur in the regulated solution or suspension polymerization of styrene. To calculate the relative transfer constant k_{fr}/k_p in this case, the equations from Table 1 line 4 must be used. In contrast to the emulsion polymerization, the true ratio of constants is obtained rather than an apparent parameter which also includes the ratio regulator:monomer concentration at the site of reaction.

The phase of constant overall rate of polymerization having been finished, the latex particles polymerize according to the kinetic laws of bulk polymerization, and $R=R(t)$ and $M=M(t)$ apply. Under these conditions - for conversions greater than t_c - \bar{M}_n and \bar{M}_w are related to the quotients of the sums of $Q_{0,1,2}(R)$ plus $Q_{0,1,2}(M)$, where the first term up to t_c and the second for M from $t_c=M_c$ to M have to be calculated. $Q_{0,1,2}(M)$ can be calculated by the equations from Table 1 line 4 with M_0 being replaced by M_c (integration frequencies from M_c to M), and R_0 being replaced by R at the point t_c . Fig. 2 shows the course of \bar{M}_n and \bar{M}_w over the conversion, predicted analytically using the determined constant, including the measured values. For the quotient \bar{M}_w/\bar{M}_n , a value of 2 is measured and calculated up to the regions of greater conversions. The small increase of this value if $x > 0.7$ and the absolute decrease of the mean molecular weights are due to the decreasing monomer concentration. These results are identical with the values discussed in (26).

Regulated Emulsion Polymerization of Butadiene

The emulsion polymerization of dienes results in complicated polymer structures, since apart from the transfer to the regulator, it is mainly the reaction of the double-

bond remaining in the monomer unit which determines the time dependence of the degree of polymerization. When the relative reaction constant k'_p/k_p (chain double-bond polymerization) are known, however, precalculation of the molecular structure before the gel point is possible (22) - with all other constants entering into the relationships being assumed to be known.

The polymerization was carried out at 55°C using the regulator dodecylxanthogendisulfide (DDXDS). Three experimental series with different concentration ratios of regulator:monomer in the initial mixture were evaluated, in order to confirm the result of the calculation of k'_p/k_p .

Obviously, the reactions propagation, regulator transfer and chain double-bond polymerization are responsible for the instantaneous degree of polymerization; transfer reactions to the polymer lead to stable allyl radicals which do not readily undergo further reaction. Hence, in the range of constant overall rate of polymerization ($dM/dt=0$), the equations of Table 2 line 2 should apply to the relationship between \bar{M}_n or \bar{M}_w and the kinetic constants.

The mean molecular weights at polymerization time t which are to be inserted into the quotients of these relationships (according to equation (4) and (5)) for calculating k'_p/k_p were determined from the experimentally measured chromatograms and are plotted in Fig. 3. The solid curves in the Figure were calculated using the optimal values obtained for k'_p/k_p and R_0/M in the latex particles in this way, k_{fr}/k_p was known from other measurements (27). The numerical values are contained in the legend of Fig. 3. Again, the monomer concentration can be calculated according to (20) (density of monomer = 625 g/l; density of polymer = 920 g/l; $t_c = 0.5$ and $m_0 = 54$ g/mol).

The information obtained simultaneously about the R_0/M ratio at the site of reaction is interesting and is discussed in (22). The constant k'_p/k_p , in the determined order of magnitude of 2×10^{-3} , explains why microgel containing products are produced in the unregulated emulsion polymeri-

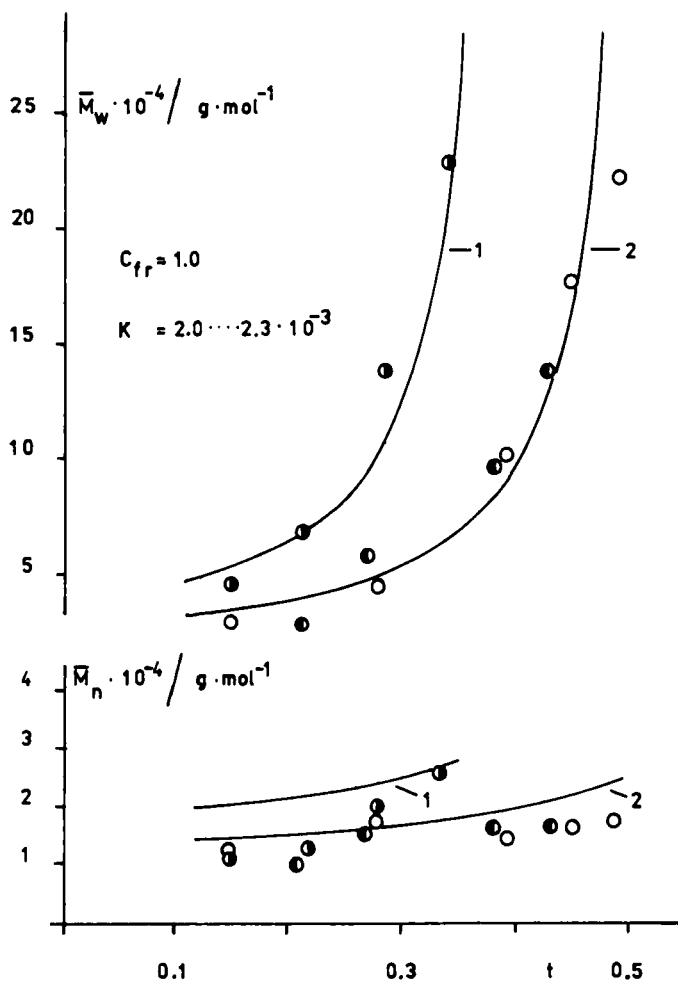


Fig. 3 Development of the molecular weight with the polymerization time t in the regulated emulsion polymerization of butadiene

measured values: $R/M_{\text{init. mixt.}}$ ● $4 \cdot 10^{-3}$; ○ $8 \cdot 10^{-3}$;
 ● $12 \cdot 10^{-3}$

calculated course: curve 1 $R_0/M = 0.003$

curve 2 $R_0/M = 0.0041 \dots 0.0043$

(equ. from Table 2 line 2)

Regulator: DDXDS; Polymerization temp.: 55°C

zation of butadiene already after short polymerization times.

In conversions greater than x_c (in case that soluble products are still formed) the equations of Table 1 line 5 may be treated as described in section -regulated emulsion polymerization of styrene - if it is desired to include these measured values (\bar{M}_n and \bar{M}_w) into the calculation of the constants.

Further polymerizations which are interesting from an industrial point of view can be evaluated according to this procedure. For example, the value of the relative transfer constant to the monomer in the suspension polymerization of vinyl chloride at 50°C is obtained to be 1.4×10^{-3} (28) which is in good agreement with known literature data. The calculations were carried out on the basis of a kinetic formalism which leads to the equations in Table 1 line 2. According to this procedure, the quotient \bar{M}_w/\bar{M}_n can be expected to have a value of 2 even at high conversions. Deviations of up to $\bar{M}_w/\bar{M}_n = 2.68$ (29) found experimentally in batches with high conversions suggest secondary reactions occurring in regions of high conversion. A report on the estimation with respect to the order of magnitude of the feasible reactions is given in (20).

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