KINETIC MODELLING OF ANIONIC POLYMERIZATION INVOLVING A DYNAMIC EQUILIBRIUM BETWEEN TWO GROWTH CENTRES WITH DIFFERENT GROWTH RATES

Jaromír JAKEŠ
Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic, 162 06 Prague 6, The Czech Republic

Received April 6, 1993
Accepted July 14, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

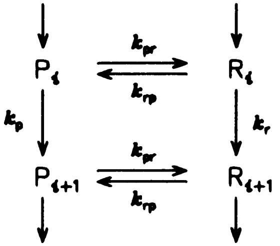
Kinetic modelling of the molecular weight distribution (MWD) of a polymer obtained by an anionic polymerization with two types of growth centres in a dynamic equilibrium, having different growth rates and lifetimes comparable to the polymerization time, was made for low monomer conversions. On the basis of distribution of the growth centres according to the total time spent in the fast growth state, it was shown that MWD of the resulting polymer are mostly bimodal at the beginning of the polymerization and change to unimodal MWD at sufficiently high polymerization degrees depending on the equilibrization rate. When all centres are in the fast state in the beginning, MWD are essentially unimodal throughout. A hint of trimodality is observed in some cases, in an extent hardly detectable in real chromatograms. Hence, a polymodal MWD can be explained only when more than two growth centres with different growth rates are assumed.

In anionic polymerization of acrylates in non-polar solvents, polymodal molecular weight distributions (MWD) are observed at the beginning of the polymerization, which become unimodal as the polymerization proceeds[1]. As a possible reason for this, the presence of several growth centres with different growth rates is considered. For polymodality to disappear at later stages, a dynamic equilibrium between different centres with a lifetime short enough is necessary. A study of methyl 2-lithioisobutyrate in tetrahydrofuran by NMR and Raman spectroscopy[2] showed for this model of the growth centre in acrylic polymerizations the presence of several aggregated forms in dynamic equilibrium. Bimodal distributions[3 – 6] in anionic polymerizations in non-polar solvents or a hint of bimodality[7], ascribed to a multiplicity of growth centres, may be found in the literature. Kinetic calculations of the first and second moments of the number distribution of degree of polymerization (DDP) for a dynamic equilibrium between two growth centres were performed by Szwarc and Hermans[8] for the case when one centre is inactive, by Coleman and Fox[9] for the case when the monomer conversion is negligible, and by Figini[10] for the general case. All these studies assume initial equilibrium concentrations of growth centres. In a study of an exchange among *k* centres, Böhm[11] used a continuous MWD approximation valid for large degrees of polymerization (DP) and sought an approximate solution in the form of a superposition of several Gaussian functions with widths and populations of the components calculated from the moments of DDP.

In this paper the exact DDP of a polymer obtained by a polymerization with negligible monomer conversion, involving two exchanging growth centres with different growth rates, is presented in the form of a closed-form function spread with the Poisson distribution. The real polymerization with a considerable conversion is not expected to differ qualitatively from the case considered; nevertheless, the first and second moments of the number DDP are shown for both cases for comparison. It turns out that ref.[11] missed the fact that the components of different individual centres decay with the conversion at different rates and that the wings of the component of the average rate are cut-off at early polymerization stage.

KINETIC CONSIDERATIONS

We consider the polymerization scheme



where P_i and R_i are the slow and fast growth centres with growth and equilibrization rates independent of DP. In a polymerization with constant monomer concentration [M] during time t, the total time τ spent by a centre in the fast state determines the DP attained: the fraction of growth centres having spent time τ in the fast state produces a Poisson DDP with number-average DP of $k_p t[M] + (k_r - k_p)\tau[M]$. When the monomer concentration is time-dependent, the value $t[M]$ should be replaced by the time integral of the monomer concentration and the value $\tau[M]$ by the same integral taken over time intervals spent in the fast state. Note that we assign zero index instead of unity[8 - 10] to the starting species, which causes our first moments (number-average DP) to be less by one. For the sake of simplicity we consider unit monomer concentration; the non-unit concentration case is easily obtained by replacing the values k_p and k_r by the values $k_p[M]$ and $k_r[M]$, respectively, in all the following formulae. For the unit monomer concentration we obtain

$$\partial p(\tau,t)/\partial t \;=\; k_{rp}r(\tau,t) \;-\; k_{pr}p(\tau,t) \tag{1a}$$

$$\partial r(\tau,t)/\partial t \;=\; k_{pr}p(\tau,t) \;-\; k_{rp}r(\tau,t) \;-\; \partial r(\tau,t)/\partial\tau\,, \tag{1b}$$

where $p(\tau,t)$ and $r(\tau,t)$ are the distributions according to total time τ spent within the time interval $(0,t)$ in the fast state by the growth centres which are in time t in the slow and fast states, respectively. The value τ runs from 0 to t. For the time-dependent [M] the last term in Eq. (*1b*) should be multiplied by [M] and τ runs from 0 to $\int_0^t [\mathrm{M}](x)\mathrm{d}x$. The total distribution of centres according to time τ spent in the fast state during polymerization time t equals $p(\tau,t) + r(\tau,t)$.

The solution of Eqs (*1*) with proper initial and marginal conditions when all centres of unit concentration are initially in the slow state ($p(\tau,0) = \delta(\tau)$, $r(\tau,0) = 0$) is

$$p(\tau,t) \;=\; \{\delta(\tau) \;+\; \sqrt{k_{pr}k_{rp}(t-\tau)/\tau}\;\, I_1\,(2\sqrt{k_{pr}k_{rp}(t-\tau)\,\tau}\,)\}$$

$$\exp(-k_{pr}(t-\tau)-k_{rp}\tau) \tag{2a}$$

$$r(\tau,t) \;=\; k_{pr}\,I_0\,(2\sqrt{k_{pr}k_{rp}(t-\tau)\,\tau}\,)\;\exp(-k_{pr}(t-\tau)-k_{rp}\tau)\,, \tag{2b}$$

where $I_0(z)$ and $I_1(z)$ are modified Bessel functions[12]. This may be easily verified using relations $\mathrm{d}I_0(z)/\mathrm{d}z = I_1(z)$ and $\mathrm{d}I_1(z)/\mathrm{d}z = I_0(z) - I_1(z)/z$. When all the centres are initially in the fast state ($p(\tau,0) = 0$, $r(\tau,0) = \delta(\tau)$), the solution is

$$p(\tau,t) \;=\; k_{rp}\,I_0\,(2\sqrt{k_{pr}k_{rp}(t-\tau)\,\tau}\,)\;\exp(-k_{pr}(t-\tau)-k_{rp}\tau) \tag{3a}$$

$$r(\tau,t) \;=\; \{\delta(t-\tau) \;+\; \sqrt{k_{pr}k_{rp}\tau/(t-\tau)}\;\, I_1\,(2\sqrt{k_{pr}k_{rp}(t-\tau)\tau}\,)\}$$

$$\exp(-k_{pr}(t-\tau)-k_{rp}\tau)\,. \tag{3b}$$

The solution for the case when both centres are initially present is obtained as an appropriate linear combination of Eqs (*2*) and (*3*).

No closed form of solution of Eqs (*1*) is known even for the simplest (exponential) decay of [M], i.e., when both centres are in equilibrium in the beginning. To estimate the effect of monomer consumption on DDP, its central second moment is now calculated for this case, which is an analogy to the calculation made by Figini[10]. The above polymerization scheme yields the following equations

$$\mathrm{d}p_i/\mathrm{d}t = k_\mathrm{p} \exp(-k_\mathrm{m}t)\,(p_{i-1} - p_i) - k_\mathrm{pr}p_i + k_\mathrm{rp}r_i \tag{4a}$$

$$\mathrm{d}r_i/\mathrm{d}t = k_\mathrm{r} \exp(-k_\mathrm{m}t)\,(r_{i-1} - r_i) - k_\mathrm{rp}r_i + k_\mathrm{pr}p_i\,, \tag{4b}$$

where k_p and k_r are the (bimolecular) growth rate constants of the slow and fast centres, respectively, multiplied by the initial concentration $[\mathrm{M}]_0$ of the monomer, k_pr and k_rp are the equilibrization rate constants,

$$k_\mathrm{m} = \frac{k_\mathrm{rp}k_\mathrm{p} + k_\mathrm{pr}k_\mathrm{r}}{k_\mathrm{pr} + k_\mathrm{rp}}\,\frac{[\mathrm{I}]}{[\mathrm{M}]_0}$$

with [I] being the total concentration of growth centres, p_i and r_i are the concentrations relative to [I] of the slow and fast centres, respectively, of DP equal to i. For $i = 0$ the terms p_{-1} and r_{-1} are absent; for $t = 0$, $p_0 = k_\mathrm{rp}/(k_\mathrm{pr} + k_\mathrm{rp})$, $r_0 = k_\mathrm{pr}/(k_\mathrm{pr} + k_\mathrm{rp})$, and all other p_i, r_i are zero. Summing Eqs (*4*) over i from 0 to ∞, we see that $\Sigma p_i = k_\mathrm{rp}/(k_\mathrm{pr} + k_\mathrm{rp})$ and $\Sigma r_i = k_\mathrm{pr}/(k_\mathrm{pr} + k_\mathrm{rp})$; multiplying Eqs (*4*) by i and summing gives

$$\Sigma i\mathrm{d}p_i/\mathrm{d}t = k_\mathrm{p} \exp(-k_\mathrm{m}t)\Sigma p_i + k_\mathrm{rp}\Sigma ir_i - k_\mathrm{pr}\Sigma ip_i \tag{5a}$$

$$\Sigma i\mathrm{d}r_i/\mathrm{d}t = k_\mathrm{r} \exp(-k_\mathrm{m}t)\Sigma r_i + k_\mathrm{pr}\Sigma ip_i - k_\mathrm{rp}\Sigma ir_i \tag{5b}$$

and the addition of Eqs (*5*) and integration yields

$$\Sigma i(p_i + r_i) = \frac{k_\mathrm{rp}k_\mathrm{p} + k_\mathrm{pr}k_\mathrm{r}}{k_\mathrm{pr} + k_\mathrm{rp}}\,\frac{1 - \exp(-k_\mathrm{m}t)}{k_\mathrm{m}}\,. \tag{6}$$

Note that the value of this expression for $t = \infty$ would be attained at $t = 1/k_\mathrm{m}$ if [M] did not decrease ($k_\mathrm{m} = 0$). Introducing Eq. (*6*) into Eqs (*5*) and subsequent integration yields

$$\Sigma i p_i \;=\; A k_{\mathrm{rp}}/(k_{\mathrm{pr}} + k_{\mathrm{rp}}) \;-\; B \qquad (7a)$$

$$\Sigma i r_i \;=\; A k_{\mathrm{pr}}/(k_{\mathrm{pr}} + k_{\mathrm{rp}}) \;+\; B\,, \qquad (7b)$$

where A is the right-hand side of Eq. (*6*) and

$$B \;=\; k_{\mathrm{pr}} k_{\mathrm{rp}} \, \frac{k_{\mathrm{r}} - k_{\mathrm{p}}}{(k_{\mathrm{pr}} + k_{\mathrm{rp}})^2} \, \frac{\exp(-k_{\mathrm{m}} t) \;-\; \exp(-(k_{\mathrm{pr}} + k_{\mathrm{rp}}) t)}{k_{\mathrm{pr}} + k_{\mathrm{rp}} \;-\; k_{\mathrm{m}}} \;.$$

Now, multiplying Eqs (*4*) by $i(i-1)$, summing over i, and adding up yields $\Sigma i(i-1)\mathrm{d}(p_i + r_i)/\mathrm{d}t = 2\exp(-k_{\mathrm{m}} t)(k_{\mathrm{p}} \Sigma i p_i + k_{\mathrm{r}} \Sigma i r_i)$ and integration using Eqs (*7*) gives

$$\Sigma i(i-1)\,(p_i + r_i) \;=\; A^2 \;+\; C\,, \qquad (8)$$

where

$$C \;=\; 2\, k_{\mathrm{pr}}\, k_{\mathrm{rp}} \left(\frac{k_{\mathrm{r}} - k_{\mathrm{p}}}{k_{\mathrm{pr}} + k_{\mathrm{rp}}} \right)^2 \frac{\dfrac{1 - \exp(-2 k_{\mathrm{m}} t)}{2 k_{\mathrm{m}}} \;-\; \dfrac{1 - \exp(-(k_{\mathrm{pr}} + k_{\mathrm{rp}} + k_{\mathrm{m}}) t)}{k_{\mathrm{pr}} + k_{\mathrm{rp}} + k_{\mathrm{m}}}}{k_{\mathrm{pr}} + k_{\mathrm{rp}} - k_{\mathrm{m}}} \;.$$

Using Eqs (*8*) and (*6*) yields the final result for the central second moment of number DDP

$$\Sigma i^2 (p_i + r_i) \;-\; (\Sigma i (p_i + r_i))^2 \;=\; C \;+\; A\,. \qquad (9)$$

Considering the fact that the Poisson distribution with number-average DP equal to p has the central second moment equal to p, the term C may be assigned to spreading caused by different growth rates, whereas the term A may be assigned to spreading caused by the Poisson distribution. Introducing the time integral of [M] (with $[\mathrm{M}]_0 = 1$), $t^* = (1 - \exp(-k_{\mathrm{m}} t))/k_{\mathrm{m}}$, $t = -\ln(1 - k_{\mathrm{m}} t^*)/k_{\mathrm{m}}$, we obtain

$$A \;=\; \frac{k_{\mathrm{rp}} k_{\mathrm{p}} \;+\; k_{\mathrm{pr}} k_{\mathrm{r}}}{k_{\mathrm{pr}} \;+\; k_{\mathrm{rp}}} \; t^* \qquad (10a)$$

$$C = 2\,k_{pr}k_{rp}\left(\frac{k_r - k_p}{k_{pr} + k_{rp}}\right)^2 \frac{t^* - k_m t^{*2}/2 - \dfrac{1 - (1 - k_m t^*)^{1 + (k_{pr} + k_{rp})/k_m}}{k_{pr} + k_{rp} + k_m}}{k_{pr} + k_{rp} - k_m} \,. \qquad (10b)$$

A similar procedure yields the result for the case of constant monomer concentration. When all centres are in the slow state in the beginning, we get

$$\Sigma i(p_i + r_i) = t(k_{rp}k_p + k_{pr}k_r)/(k_{pr} + k_{rp}) -$$

$$- (1 - \exp(-u))k_{pr}(k_r - k_p)/(k_{pr} + k_{rp})^2 \qquad (11a)$$

$$\Sigma i(i-1)\,(p_i + r_i) - (\Sigma i(p_i + r_i))^2 = (k_r - k_p)^2\,k_{pr}\{k_{pr}(1 - 2u\exp(-u) - \exp(-2u)) +$$

$$+ k_{rp}((u+2)\exp(-u) + u - 2)\}/(k_{pr} + k_{rp})^4\,, \qquad (11b)$$

where $u = (k_{pr} + k_{rp})t$; these expressions correspond to the above values A and C, respectively. The respective expressions for the case when all centres start in the fast state are obtained by interchanging the roles of p and r:

$$A = t(k_{rp}k_p + k_{pr}k_r)/(k_{pr} + k_{rp}) + (1 - \exp(-u))\,k_{rp}(k_r - k_p)/(k_{pr} + k_{rp})^2 \qquad (12a)$$

$$C = (k_r - k_p)^2\,k_{rp}\{k_{rp}(1 - 2u\exp(-u) - \exp(-2u)) +$$

$$+ k_{pr}((u+2)\exp(-u) + u - 2)\}/(k_{pr} + k_{rp})^4\,. \qquad (12b)$$

Considering the relation between τ and the number-average DP reached by the respective growth centres after polymerization time t we obtain for the first moment of the total distribution $p(\tau,t) + r(\tau,t)$ when all centres start in the slow state:

$$M_1 = (\exp(-u) + u - 1)k_{pr}/(k_{pr} + k_{rp})^2 \qquad (13)$$

and when all centres start in the fast state:

$$M_1 = t - (\exp(-u) + u - 1)k_{rp}/(k_{pr} + k_{rp})^2 . \qquad (14)$$

The central second moments are obtained from the respective C values by removing the factor $(k_r - k_p)^2$. For any starting mixture of growth centres the first moments may be obtained as weighted averages of those for slow and fast starting states. For the central second moments the weighted averages should be increased by $\alpha(1 - \alpha)(M_1 - M_1')^2$, where $\alpha : (1 - \alpha)$ is the starting ratio of the centres and M_1 and M_1' are their respective first moments. For the starting equilibrium ratio of centres, the first moment is simply $tk_{pr}/(k_{pr} + k_{rp})$, whereas the central second moment is

$$2\,(\exp(-u) + u - 1)k_{pr}k_{rp}/(k_{pr} + k_{rp})^4 \qquad (15)$$

which, after reintroducing the factor $(k_r - k_p)^2$, agrees with the $k_m \to 0$ limit of the C value from Eq. (*8*) and with the expression $\overline{n^2} - \bar{n}^2 - [\mathrm{M}]\bar{k}t$ calculated from Eqs (3.18) and (3.16) of ref.[9].

RESULTS AND DISCUSSION

The $p(\tau,t) + r(\tau,t)$ distributions are shown in Fig. 1 for three values of the equilibrium fraction of the fast centres k_{pr}/k_e ($k_e = k_{pr} + k_{rp}$) equal to 0.1, 0.2, and 0.5 and for five values of $k_e t$ equal to 0.5, 2, 8, 32, and 128, when abscissa runs from 0 to t. Lines *1* correspond to the case when all the centres are initially in the slow state, whereas lines *2* show the initial state with the fast centres. The case when both centres are initially present is represented by an appropriate superposition of both distributions. Ordinates are normalized so that the same area represents the same value of integral distribution. Rectangles at margins represent δ-functions. The distributions for $k_{pr}/k_e = 0.8$ and 0.9 are the mirror images of those for $k_{pr}/k_e = 0.2$ and 0.1, respectively, with lines *1* and *2* interchanged. At the same time, the distributions in Fig. 1 represent the number DDP in the limiting case of a very high DP when the abscissa runs from $k_p t$ to $k_r t$. At lower DP, the marginal δ-functions should be replaced by appropriate Poisson distributions and the central distribution spread with the Poisson distribution, the last step being usually of a negligible effect since the Poisson distribution is very narrow. The Poisson distributions at the margins decay with $\exp(-k_{pr}t)$ and $\exp(-k_{rp}t)$ and a broad, at the beginning shallow distribution develops instead, in which, later on, a maximum appears at DP equal to $t(k_{rp}k_p + k_{pr}k_r)/(k_{pr} + k_{rp})$ corresponding to the weighted average of growth rates. However, a perceptible trimodality can be observed only when equilibrium fractions of both growth centres are approximately equal and $k_e t$ is between about 2 and 8;

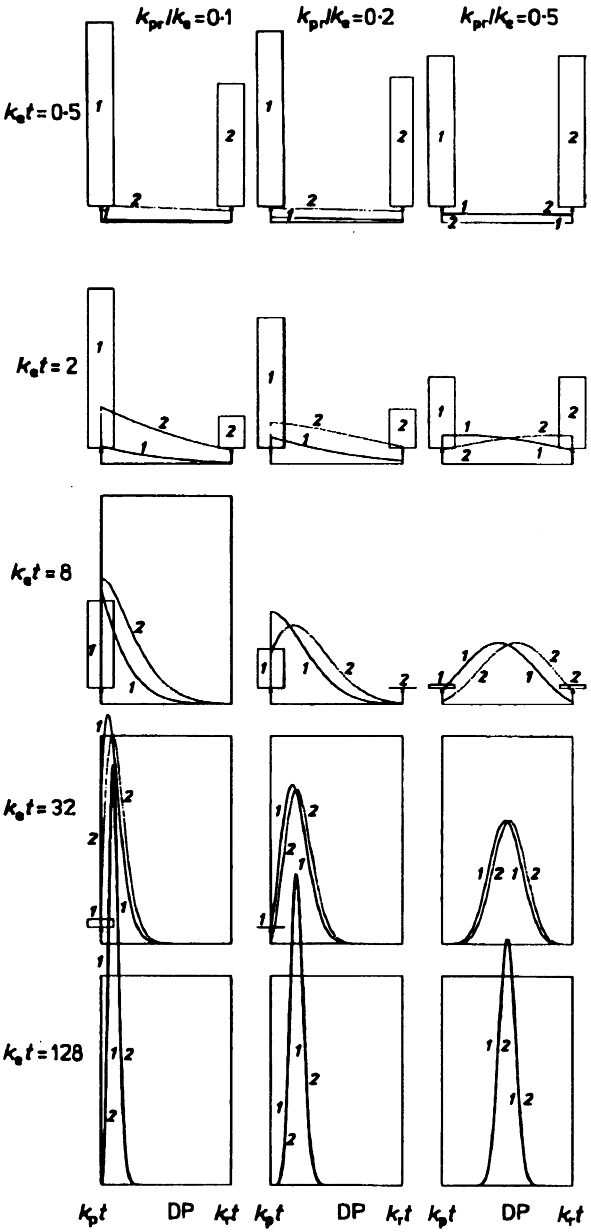


FIG. 1

Number DDP in the large-DP approximation resulting from polymerizations with two exchanging centres of different growth rates: *1* all centres start in the slow state; *2* all centres start in the fast state. The rectangles at margins represent δ-functions even then it may be hardly detected by GPC (at low k_r/k_p values due to longitudinal spreading of chromatograms, at high k_r/k_p, see below). In other cases, one of the marginal Poisson distributions disappears before the central maximum appears. Considering the leading terms for large t in braces in Eqs (*11b*) and (*12b*) ($k_{rp}u$ and $k_{pr}u$, respectively), we see that at large times the central distribution width increases with $t^{1/2}$ and with the growth rate, whereas in logarithmic DP scale or relative to the distribution range it decreases with $t^{-1/2}$; in both cases it decreases with the reciprocal square root of the equilibrization rate. The ratio of the A and C contributions to the central second moment at large t is approximately equal to $(k_{rp}k_p + k_{pr}k_r)k_e^2/(2k_{pr}k_{rp}(k_r - k_p)^2)$, which shows that the contribution of the Poisson distribution is small compared to the different growth rate contribution when the difference of the growth rates is large compared to the equilibrization rate and not too small compared to the growth rate values.

The GPC chromatograms usually show MWD (and hence also DDP) in approximately logarithmic MW scales and in the weight fractions. At large values of ratio k_r/k_p, such a representation differs basically from that shown in Fig. 1. The weight DDP in logarithmic DP scales, spread with a Gaussian function to simulate longitudinal spreading of chromatograms and neglecting the Poisson distribution spreading, are therefore shown for $k_r/k_p = 10$ and 100 in Figs 2 and 3, respectively. The shape and width of spreading used is best seen in Fig. 3, $k_{pr}/k_e = 0.01$, $k_e t = 0.25$, the leftmost peak. Vertical scales of curves *2* are multiplied by k_{pr}/k_{rp}, so that the sum of both curves *1* and *2* represents the case when both growth centres are initially in equilibrium; all vertical scales are divided by t to give comparable heights throughout the time run. At the beginning, the central distribution shows a pronounced maximum at DP close to $k_r t$, which subsequently shifts to DP corresponding to the weighted average of the growth rates. During this shift the distribution acquires a pronounced asymmetry with a tail towards lower DP and this asymmetry is again lost when the DP corresponding to the average growth rate is reached. The shift appears only after the Poisson distribution with DP equal to $k_r t$ essentially disappears; hence MWD are bimodal at the beginning and change to unimodal after the Poisson distribution with the DP equal to $k_p t$ disappears. When no slow centres are initially present, the distribution is essentially unimodal throughout, although an unusual peak shape is sometimes observed. In this case, only a growth rate decrease may be observed, which may be also caused by a dependence of the growth rate constant on DP when only one type of centres occurs. These two possibilities can be distinguished by changing experimental monomer concentration provided that activities of all reaction components are unchanged: in the former case the growth rate decrease depends just on the polymerization time, whereas in the latter on the polymerization degree, which is the product of the polymerization time and the monomer concentration. The asymmetric lines *2* in Fig. 3 strongly resemble MWD obtained in polymerizations autoterminated before monomer expiration[13,14]. However, in this case the low-DP tail persists until polymerization autoterminates

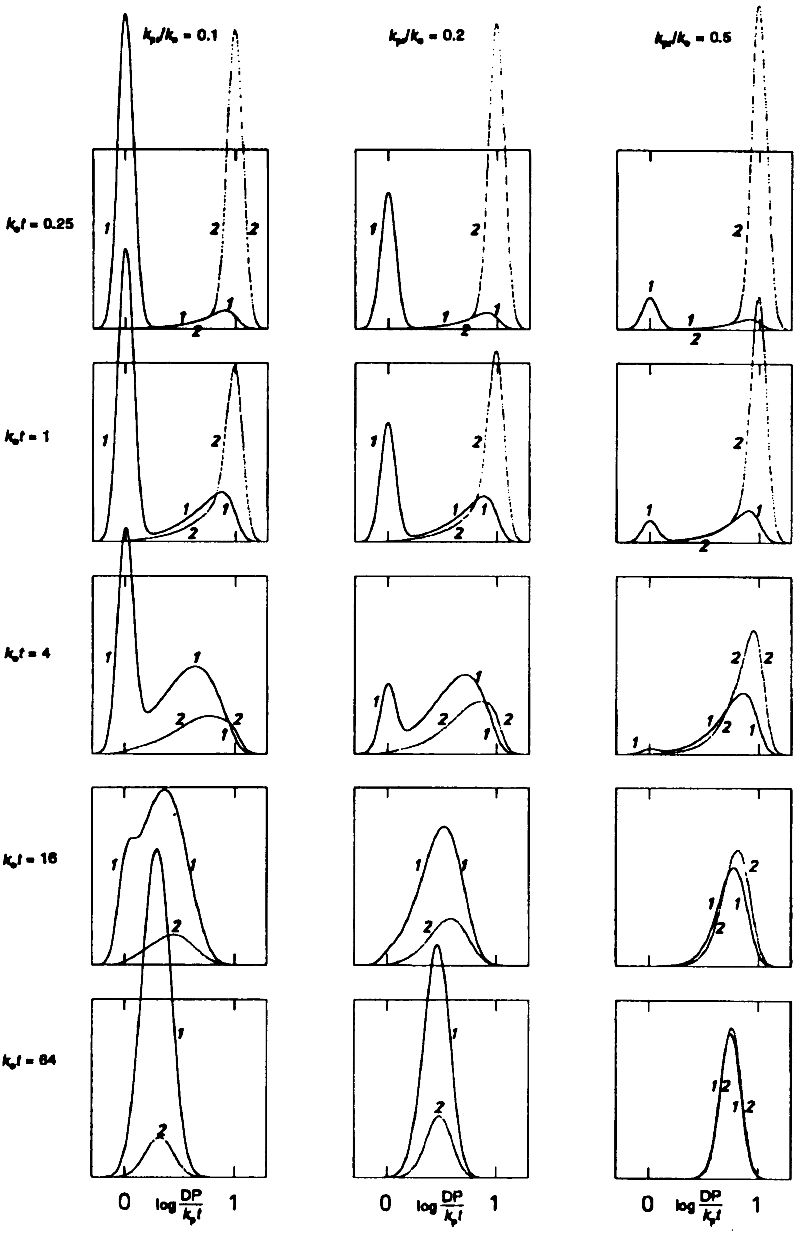


FIG. 2

Weight DDP (in logarithmic DP scales) in the large-DP approximation resulting from polymerizations with two exchanging centres of different growth rates spread with a Gaussian function for growth rate ratio equal to 10: *1* all centres start in the slow state; *2* all centres start in the fast state

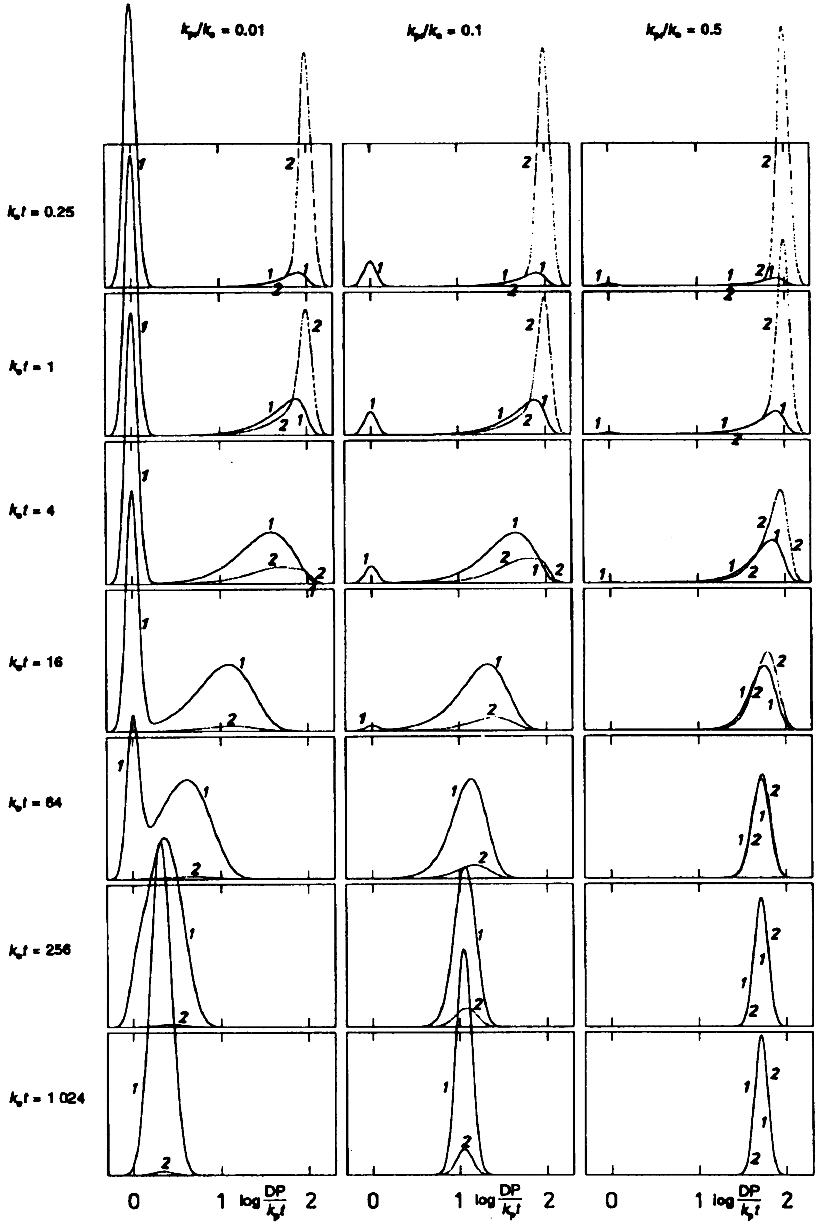


FIG. 3

Weight DDP (in logarithmic DP scales) in the large-DP approximation resulting from polymerizations with two exchanging centres of different growth rates spread with a Gaussian function for growth rate ratio equal to 100: *1* all centres start in the slow state; *2* all centres start in the fast state despite its proportion may decrease relatively to the proportion of the growing main peak. In our case, the tail is eventually absorbed by the main peak. When the equilibrium is pronouncedly shifted towards slow centres, just before disappearing, the Poisson distribution with DP equal to $k_p t$ becomes a side band or a shoulder on the central distribution peak. Thus, to explain the polymodality observed in ref.[1], more than two growth centres with different growth rates should be assumed. The peak asymmetry found at higher conversions[1] is in line with the results of this study.

In a real polymerization with a decrease in the monomer concentration, the monomer may expire before the bimodality can disappear when the monomer consumption is fast compared to the equilibrization rate. In the opposite case, the bimodality disappears at a sufficiently long reaction time. When the decrease is exponential (i.e., both centres are in equilibrium in the beginning), the comparison of the leading term of Eq. (*15*) for long times, $2t(k_r - k_p)^2 k_{pr}k_{rp}/k_e^3$, with that of Eq. (*10b*) (neglecting k_m against k_e), $2(t^* - k_m t^{*2}/2)(k_r - k_p)^2 k_{pr}k_{rp}/k_e^3$, shows that a correcting factor of $1 - k_m t^*/2$ should be applied when comparing second moments at $t^* = t$. This means that the second moment increase slows down during the polymerization, almost stopping when effective time t^* approaches the limiting $1/k_m$ value. After the monomer expires ($t^* = 1/k_m$), the second moments reduce to one half (corresponding to an about 30% decrease in the distribution widths) of their values in the approximation where the monomer consumption is neglected and at reaction time $t = 1/k_m$, i.e. when both number-average DP (expressions A) are equal. This is caused by the monomer consumption, which slows down the polymerization rate and hence relatively speeds up the equilibrization rate, which causes narrowing of the distribution.

This study was supported by the Institute grant No. 1. I am much indebted to Dr P. Vlček for introducing me to the problems of anionic polymerizations and for a stimulating discussion.

REFERENCES

1. Vlček P.: J. Polym. Sci., Polym. Chem. Ed. *28*, 2917 (1990).
2. Kříž J., Dybal J., Vlček P., Janata M.: Makromol. Chem., submitted.
3. Davidjan A., Nikolaew N., Sgonnik V., Krasikow V., Belenkii B., Erussalimsky B.: Makromol. Chem. *182*, 917 (1981).
4. Warzelhan V., Höcker H., Schulz G. V.: Makromol. Chem. *181*, 149 (1980).
5. Davidjan A., Nikolaew N., Sgonnik V., Belenkii B., Nesterow V., Krasikow V., Erussalimsky B.: Makromol. Chem. *179*, 2155 (1978).
6. Davidjan A., Nikolaew N., Sgonnik V., Belenkii B., Nesterow V., Erussalimsky B.: Makromol. Chem. *177*, 2469 (1976).
7. Vlček P., Trekoval J.: Makromol. Chem. *176*, 2595 (1975).
8. Szwarc M., Hermans J. J.: J. Polym. Sci., B *2*, 815 (1964).
9. Coleman B. D., Fox T. G.: J. Am. Chem. Soc. *85*, 1241 (1963).
10. Figini R. V.: Makromol. Chem. *71*, 193 (1964).
11. Böhm L. L.: Z. Phys. Chem. (Frankfurt am Main) *88*, 297 (1974).

12. Abramowitz M., Stegun I. A.: *Handbook of Mathematical Functions*, p. 374. Dover, New York 1965.
13. Vlček P., Otoupalová J., Kříž J.: Makromol. Chem. *194*, 841 (1993).
14. Vlček P., Jakeš J., Otoupalová J.: Collect. Czech. Chem. Commun., in press.

Translated by the author.