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Molecular Weight Distribution in the Production of Homopolymers

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The principal mathematical methods for the simulation of the molecular weight distributions (MWD) in homopolymers obtained by radical polymerisation are examined. An attempt is made at a survey and a systematic arrangement of mathematical models in terms of kinetic mechanisms, type of reaction apparatus, and the mathematical procedure used.
The bibliography includes 45 references.

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I. INTRODUCTION

In studies on polymerisation processes and the properties of polymers much attention is devoted to the investigation of the distribution of polymer and radical chains with respect to molecular weight. Information about the characteristics of the molecular weight distribution (MWD) is necessary for many theoretical and practical problems in polymer chemistry. Nowadays there is an appreciable need to employ MWD in the technology of polymers. The modern principles of the strategy for the simulation of large chemical engineering plants, whereby the process can be optimised from a particular point of view, are of interest also for the technology of polymeric materials. This strategy can be applied to the analytical planning of new large-scale polymerisation processes, their optimisation, and the intensification of the existing processes, but an obligatory condition is always the knowledge of MWD. The initial information required for the solution of problems of this class in relation to polymerisation processes includes, apart from the traditional (for chemistry) mathematical description of the technological process and the set of optimisation criteria, a library of mathematical MWD models. The solution of optimisation problems in the field of industrial polymerisation without the calculation of MWD is impossible, since any optimisation of the polymerisation process must assist the solution of the main problem of polymer chemistry—the synthesis of polymeric materials with specified properties, i.e. ultimately materials having the required set of MWD characteristics.

In the study of a polymerisation process technologists have at their disposal a set of models of various types of reaction apparatus in which polymerisation takes place. In selecting the optimisation factor, the specific features of processes of this kind (the set of requirements which the process must meet is described by several factors and it is important that all such factors be optimised simultaneously) are reflected in the application of multifactor optimisation methods. As regards the use of mathematical MWD models, there is no such clarity. This review is an attempt at a survey and systematic account of mathematical MWD models with respect to the specific mechanism, type of reaction apparatus, and the mathematical procedures employed. The proposed ordered arrangement of the multiplicity of methods for the calculation of distribution functions is designed for a broad class of studies on polymerisation processes with the aim of a rational control of these processes. A systematic arrangement of MWD models is considered in relation to homopolymers obtained in radical polymerisation, although the proposed approach can be used also for branched polymers by extending the set of mathematical methods, for example, by including the method of the theory of graphs developed in topology and introduced for the first time in studies on the chemical kinetics of multistage branched enzymatic catalytic reactions[1-3]. However, the aim of the present review was restricted to the consideration of the MWD in the formation of linear homopolymers by a free radical mechanism.

Table 1. Kinetic scheme for radical polymerisation.

Designation	Reaction mechanism	Reaction rate equation
Initiation		
decompn. of initiator	$I \xrightarrow{k_i} 2R_c$	
start of reaction	$R_c + M \rightarrow R_1$	$w_i = f(I)$
Chain propagation	$R_r + M \xrightarrow{k_p} R_{r+1}$	$w_p = k_p M R_r$
Chain transfer:		
via the monomer	$R_r + M \xrightarrow{k_f} P_r + M^{\cdot}$	$w_f = k_f M R_r$
via the solvent	$R_r + S \xrightarrow{k_{fs}} P_r + S^{\cdot}$	$w_{fs} = k_{fs} S R_r$
Chain termination:		
by recombination	$R_r + R_s \xrightarrow{k_{t_1}} P_{r+s}$	$w_{t_1} = k_{t_1} R_s R_r$
by disproportionation	$R_r + R_s \xrightarrow{k_{t_2}} P_r + P_s$	$w_{t_2} = k_{t_2} R_s R_r$
via the monomer	$R_r + M \xrightarrow{k_{t_3}} P_{r+1}$	$w_{t_3} = k_{t_3} M R_r$
spontaneous	$R_r \xrightarrow{k_{t_4}} P_r$	$w_{t_4} = k_{t_4} R_r$

The generally accepted kinetic mechanism of a free-radical polymerisation process, which includes elementary chain initiation, chain transfer, and chain termination reactions, is presented in Table 1, where the following notation is used: R_C is the primary radical formed on decomposition of the initiator I, R_r and P_r are respectively

the polymer radical and an inactive polymer molecule consisting of r monomer units, M is the monomer molecule, S the solvent molecule, M$^{\cdot}$ and S$^{\cdot}$ are the corresponding low-molecular-weight radicals, w_i and w_p are the rates of chain initiation and propagation, w_f and w_{fs} the rates of chain transfer via the monomer and the solvent, w_{t_1}, w_{t_2}, w_{t_3}, and w_{t_4} the rates of chain termination via recombination, disproportionation, via the monomer, and via a spontaneous mechanism respectively, and k_p, k_f, and k_t the rate constants for the corresponding reactions. In the equations presented for the rates of the elementary reactions and throughout the review, M, R_r, S, and P_r denote the concentrations of the corresponding substances.

Apart from the kinetic mechanism of the polymerisation process and the rates of the elementary reactions determined by it, the characteristics of the MWD of the polymer formed are influenced by the mass-exchange conditions during the reaction, which depend mainly on the type of reaction apparatus used. In the present review we shall consider the following extreme idealisations: continuous operation ideal displacement reactor, periodic-operation mixing reactor, and ideal continuous-operation mixing reactor. The hydrodynamic conditions for reactors of the intermediate type permit their description with the aid of combined models, including as their elements the above idealised reactor types. Evidently in systems of the first type (ideal displacement reactor, periodic-operation mixing reactor) the concentration of the reactants and the characteristics of the MWD are non-stationary (with respect to time for the mixing reactor and with respect to length for the ideal displacement reactor) are satisfactorily described by differential equations in terms of the usual derivatives. In reaction systems of the second type (continuous operation ideal mixing reactor or a cascade of such reactors) the concentration of the reactants and all the MWD characteristics remain constant in time and are described by algebraic equations.

There exist different mathematical approaches whereby analytical MWD models can be obtained. The choice of the method of calculation of the distribution with respect to molecular weights is determined by the kinetic mechanism and, to a greater extent, by the simplifying assumptions adopted concerning the polymerisation kinetics. Frequently the abandonment of one hypothesis entails the necessity to employ a new mathematical procedure. The methods for the calculation of the MWD considered in the present review have a kinetic bias in the simulation of the molecular weight distributions of polymers, which is based on the physical chemistry of the process. The statistical approach to the calculation of the MWD, based on the estimation of the probability of the summation of polymer chains of the given size without an explicit allowance for the process kinetics, described in a number of monographs[4-6], is not considered in this review. The statistical approach is known to be phenomenological in character overall. With the aid of the statistical distribution, it is possible to characterise rapidly the polymerisation mechanism in broad outline and to predict the approximate MWD parameters of the polymer obtained under specified conditions. Furthermore, in the calculation of the MWD at the end of an industrial technological process, organised with the aid of reactors of different types, it is necessary to know the law governing the evolution of this distribution in time in addition to the adoption of a statistical distribution as a set of exponential functions of the same type. On the other hand, in the kinetic approach account is taken not only of the kinetic mechanism of the polymerisation process but also of the way in which the reaction is carried out (the type of reaction apparatus). The physics and chemistry of the process are reflected in the final distribution, which establishes a relation between the MWD and the parameters of the polymerisation process and this makes it possible to regulate the MWD.

II. CLASSICAL METHOD FOR THE CALCULATION OF THE MOLECULAR WEIGHT DISTRIBUTION

The analytical method for the calculation of the MWD in polymers, which can now be properly referred to as classical since it was used in early studies on the calculation of the MWD, [6-9,11] consists of a direct solution of a system of an infinite number of material balance equations for all the components of the polymerisation system.

We shall explain the essential features of this method in relation to the calculation of the MWD in a reaction of the periodic type quoted by Bamford et al.[6]; a radical polymerisation reaction takes place in the reactor via the kinetic mechanism illustrated in Fig. 1, where $k_{t_3} = 0$ and $k_{t_4} = 0$, i.e. chain termination takes place only via recombination and disproportionation. The equations for the rates of change of the concentrations of the active and inactive polymer radicals and the monomer assume the following form in this instance:

$$\frac{dR_1}{dt} = w_i - k_p M R_1 + (k_{fs}S + k_f M)\sum_{i=2}^{\infty} R_i - (k_{fs}S + k_f M)R_1 - (k_{t_1} + k_{t_2})R_1 \sum_{i=2}^{\infty} R_i, \quad (1)$$

$$\frac{dR_r}{dt} = k_p M R_{r-1} - k_p M R_r - (k_{fs}S + k_f M)R_r - (k_{t_1} + k_{t_2})R_r \sum_{i=2}^{\infty} R_i, \quad (2)$$

$$\frac{dM}{dt} = w_i + k_p M \sum_{i=2}^{\infty} R_i + k_f M \sum_{i=2}^{\infty} R_i, \quad (3)$$

$$\frac{dP_r}{dt} = (k_{fs}S + k_f M)R_r + \frac{1}{2}k_{t_1}\sum_{k=1}^{r-1} R_k R_{r-k} + k_{t_2}R_r \sum_{i=2}^{\infty} R_i, \quad (4)$$

$$r = 2, 3, \ldots \infty.$$

Calculation of the MWD from an infinite system of differential equations (1)–(4) without the adoption of any additional simplifications is unduly difficult. The mathematical method for the calculation of the MWD under consideration postulates the use of the following assumptions, normally adopted in the kinetics of radical polymerisation.

Firstly, it is assumed that at low degrees of conversion the rate of formation of radicals becomes at some instant equal to the rate of their disappearance. This assumption makes it possible to set dR_r/dt and dR_1/dt equal to zero which simplifies further mathematical treatment. There exists a criterion of the applicability of the hypothesis of "quasi-stationarity" or the "Bodenstein–Semenov hypothesis": the residence time in the reaction zone τ is incomparably longer than the time required for the polymer radical to attain stationary conditions (τ_{st}). The time τ_{st} agrees fairly accurately with the average lifetime of the polymer radicals[10].

However, in many cases the validity of this hypothesis is doubtful. In the first place caution must be exercised in applying it when one is considering adiabatic polymerisation conditions. It follows from general considerations that, depending on the activation energy for the decomposition of the initiator and the destruction of the radicals, in an adiabatic process an increase of temperature in the system should have different effects on the rates of formation and destruction of macroradicals.

An increase of the temperature of the reaction medium should then have a much greater influence on the rate of decomposition of the initiator because of the much higher activation energy for the initiation reaction. Therefore, over a fairly long reaction temperature range, a case may arise where the application of the hypothesis of quasi-stationary concentrations becomes incorrect. It has been established[13] theoretically that there is an appreciable difference between the quasi-stationary and non-stationary adiabatic polymerisation conditions (Fig. 1). Evidently the application of the Bodenstein–Semenov hypothesis is unjustified also in the case of an extremely low initiator concentration, since the attainment of stationary conditions is then limited by the initiator concentration. However, in the vast majority of cases of isothermal free-radical polymerisation reactions the MWD obtained using the hypotheses of quasi-stationary concentrations and without it agree satisfactorily[8].

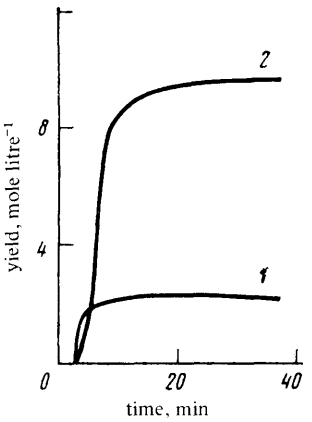


Figure 1. Time variation of the yield of the polymer[13]: 1) with the quasi-stationary hypothesis; 2) without the quasi-stationary hypothesis.

Secondly, the rate constants for the elementary reactions are assumed to be independent of the radical chain length and the degree of conversion of the reaction mixture, which makes it possible to characterise with the aid of a single constant all the steps of elementary reactions of one type. Evidently this assumption greatly simplifies the calculations. However, it has been shown[14] that the hypothesis that the polymerisation reaction rate constants are independent of the length of the macromolecule is in general not justified theoretically and must be proved for each specific case.

Thirdly, it is assumed that, for fairly long chains, the monomer is mainly consumed in the formation of the polymer chain, which makes it possible, by neglecting the consumption of the monomer in initiation and chain transfer, to write instead of Eqn. (3)

$$-\frac{dM}{dt} \cong k_p M \sum_i R_i, \qquad (3')$$

where ΣR_i is the concentration of "living" macromolecules.

Summation of Eqns. (1) and (2), where $r = 2-\infty$, using the hypothesis of quasi-stationary concentrations and the invariance of the rate constants for the elementary reactions, yields the overall concentration of radicals:

$$R = \sum_i R_i = [w_i (k_{t_1} + k_{t_2})]^{1/2}. \qquad (5)$$

On substituting this value of R in Eqns. (1) and (2), we obtain expressions for R_1 and R_r. Integration of the last two equations using the expressions obtained for R_1 and R_r yields the concentration of polymer molecules P_r consisting of r units. Having calculated P_r for various chain lengths r, we obtain the required molecular weight distribution curve. In the general case it is impossible to obtain an analytical expression for P_r by the above procedure. However, in many special cases (in the absence of individual elementary reactions and for constant concentrations of the monomer and other components) it is possible to solve Eqns. (1)–(4) for P_r, i.e. to obtain in an explicit form the equation of the MWD curve.

If the radical polymerisation reaction is carried out in a continuous-operation reaction, the stationary state is described by a system of algebraic equations, each of which represents the material balance with respect to the rth radical, where $r = 1, 2, \ldots$. We shall now explain how the MWD is calculated for a reaction apparatus of this type, following the work of Thiele[9], who considered a kinetic mechanism of radical polymerisation with chain termination via recombination. The material balance equations for the radicals R_1, R_2, R_3, etc. assume the following form in this instance:

$$2k_i f I + k_f M \sum_i R_i = \theta^{-1} R_1 + k_p M R_1 + k_{t_1} R_1 \sum_i R_i, \qquad (1')$$

$$k_p M R_1 = \theta^{-1} R_2 + k_p M R_2 + k_{t_1} R_2 \sum_i R_i + k_f R_2 M, \qquad (2')$$

$$k_p M R_2 = \theta^{-1} R_3 + k_p M R_3 + k_{t_1} R_3 \sum_i R_i + k_f R_3 M, \qquad (2'')$$

where θ is the average residence time of the polymerising system in the reactor $2k_i f I$ the rate of the initiation reaction, and f the efficiency of the initiation. Summation of Eqns. (1'), (2'), ... yields the expression

$$2k_i f I = \theta^{-1} R + k_{t_1} R^2. \qquad (5')$$

We may note that here we are using in essence the assumption that the rate constants for the elementary reactions are independent of chain length. Successive representations of R_r in terms of R_{r-1} yield

$$R_r = \frac{(k_p M)^{r-1} (2k_i f I + k_f M R)}{[\theta^{-1} + (k_p + k_f) M + k_{t_1} R]^r}. \qquad (6)$$

The substitution of the expression for the overall concentrations of macroradicals R from Eqn. (5') in the above formula yields the distribution of active radicals along the chain length. Taking into account Eqn. (6), we obtain the required distribution of polymer chains P_r from the material balance equation for the polymer:

$$\theta^{-1} P_r = \frac{k_{t_1}}{2} \sum_{k=1}^{r-1} R_k R_{r-k} + k_f R_r M. \qquad (7)$$

A considerable mathematical simplification is achieved compared with a periodic-operation reactor, since there is no need to integrate differential equations, which is frequently impossible in terms of quadratures and in the simpler version complex mathematical transformations are needed. This extends the range of models for which it is possible to find an analytical expression of the MWD.

Furthermore, the very expressions for the MWD simplify compared with a periodic-operation reactor as a result of the constancy of the concentrations of all the components of the polymerising system.

If it is assumed that the chain lifetime is short compared with the residence time in the reactor, then evidently the probability that the active radical leaves the reactor before it undergoes chemical reaction and loses its activity is small. This finding is reflected in the initial system of algebraic equations by the relatively low value of the $\theta^{-1}R_r$ terms. The system of algebraic equations for active radicals in a continuous-operation reactor is then identical to the quasi-stationary condition for a periodic-operation reactor and the distributions of radicals with respect to length should be similar for reactors of both types.

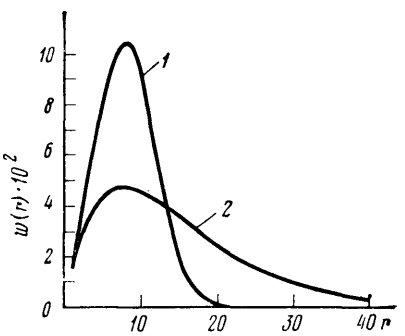


Figure 2. The influence of the type of reactor on the MWD when the lifetime of the active radicals is comparable to the residence time in the reactor[7]: 1) periodic-operation reactor; 2) continuous-operation reactor.

In relation to polystyrene, the lifetime of the growing chain of which is measured in seconds[10,15] while the residence time in the reactor amounts to hours, it has been confirmed[7] that the distribution with respect to the residence time of the species does not affect the MWD of polystyrene. When the residence time of the species in the reaction zone and the chain lifetime are comparable, one must expect a broader MWD for the polymer obtained in a continuous-operation reactor compared with a periodic-operation reactor. This is confirmed by calculations of the MWD [7] (Fig. 2) and can be accounted for by the influence of segregation and micromixing effects on the rate of reaction[16]. Fig. 2 shows a decrease of the homogeneity of the polymer when the process is carried out in a continuous operation reactor compared with a periodic-operation reactor. Analogous results of the calculation of the MWD in the initiated polymerisation of polystyrene, carried out in reactors of both types on the assumption that chain termination takes place as a result of recombination and that there is no chain transfer reaction, have been obtained by Thiele and Hartman[11].

Compared with the large number of theoretical studies on the calculation of the MWD, there are only a few publications presenting the results of the corresponding experimental investigations. In one of the early studies[12] a satisfactory agreement was obtained between experimental and theoretical molecular weight distributions in polystyrene calculated with the aid of the given method. The theoretical MWD curve for suspension polystyrene, obtained in a periodic operation reactor under ideal mixing conditions, has been compared[17] with experimental data. MWD curves have been calculated[18,19] for polystyrene on the assumption that chain termination takes place solely as a result of recombination and that there is chain transfer via the monomer and the solvent. The influence of the solvent concentration was taken into account in the model by a coefficient obtained experimentally[19] as a correction to the rate constant for chain transfer via the monomer. Among a series of experimental results obtained under the conditions of regulated solvent concentration and solution viscosity, best agreement with calculation is observed for low solution viscosities and low solvent concentrations. These results are illustrated in Fig. 3.

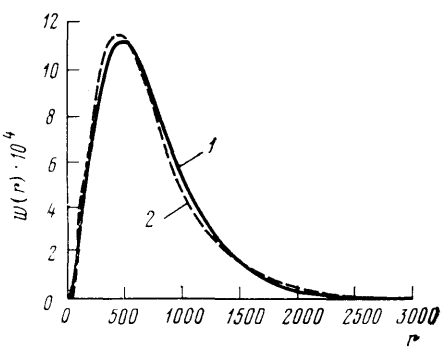


Figure 3. Comparison of the MWD obtained for a low solution viscosity[19]: 1) theoretically; 2) experimentally.

Table 2. Comparison of the calculated and experimental MWD parameters on the basis of the data of Hamielec et al.[19]

MWD parameter	Calculated value	Experimental value
μ_1	48 940	47 460
μ_2	73 920	73 610
μ_2/μ_1	1.51	1.55

The experimental and calculated values of important MWD parameters proved to be very similar under these conditions (Table 2). An experimental characteristic of the MWD (average degree of polymerisation) has been used[17] to determine the elementary reaction constants, which were calculated by minimising the sum of squares of the differences between the measured and calculated average degrees of polymerisation and conversion of styrene.

III. METHOD OF GENERATING FUNCTIONS

The method of generating functions from the theory of random functions has been used in the mathematical simulation of radical polymerisation processes. Liu and Amundson[20] were the first to introduce the above method in the study of processes of this kind. In the investigation of discrete distributions use is frequently made of the generating functions representing them[21]. We shall assume that the probability of a quantity ξ, assuming values of 1, 2, ..., is p_r when $\xi = r$. The term generating function of a random quantity ξ is applied to the function $G(s) = \sum_r s^r p_r$, where $s \leqslant 1$. The generating function satisfies the self-evident relations

$$G(0) = 0; \quad G(1) = 1.$$

With the aid of generating functions, it is possible to obtain a simple solution of many problems associated with the summation of independent random quantities. Their use makes it possible to replace the complex operation involving the setting up of the distribution functions of random quantities, which is necessary when the latter are added together, by a product of the generating functions of the components. Suppose for example, that ξ and η are independent random quantities. The generating function of the sum of the random quantities $\varphi = \xi + \eta$ is then expressed as follows in terms of the generating functions of the components:

$$G_\varphi(s) = G_\xi(s) \cdot G_\eta(s).$$

The wide-scale employment of the method of generating functions in the calculation of the fundamental MWD parameters is to a large extent associated with the most important property of generating functions, arising from their differentiability and from the existence of simple relations between the nth order moments of the distributions of the random quantities and the nth differential of the generating function. It appears natural to apply the method of generating functions to the calculation of MWD, since the polymer chain length is a typical discrete random quantity. Indeed, at each step of the propagation process, the radical has a number of possible choices: it can continue to grow by interacting with a monomer molecule, or it can participate in a chain transfer reactor, or it can react with other radicals, which leads to their mutual destruction. The employment of the method of generating functions gives rise to a number of significant advantages compared with the classical method. In the first place it makes it possible to eliminate the quasi-stationary hypothesis, which is important in the simulation of radical polymerisation processes up to high degrees of conversion in a periodic-operation reactor, when the polymerisation process is carried out under adiabatic conditions, and in a number of other instances.

The calculation of the MWD by the method of generating functions begins with the usual mathematical treatment of the kinetic mechanism of the polymerisation process. We shall show how the calculation is carried out for the polymerisation in a periodic-operation reactor, considered by Liu and Amundson[20], where

$$w_i = k_i M^n; \; k_f = k_{fs} = 0; \; k_{t_1} = k_{t_2} = k_{t_4} = 0,$$

for the kinetic scheme presented in Table 1. Eqns. (1)–(4) are then written in the following form:

$$\frac{dM}{dt} = -k_i M^n - (k_p + k_{t_3}) MR, \tag{8}$$

$$\frac{dR_1}{dt} = k_i M^n - (k_p + k_{t_3}) MR_1, \tag{9}$$

$$\frac{dR_r}{dt} = k_p R_{r-1} M - (k_p + k_{t_3}) MR_r, \tag{10}$$

$$\frac{dP_r}{dt} = k_t M R_{r-1}; \quad r = 2, 3, \ldots \infty. \tag{11}$$

On multiplying Eqns. (9) and (10) by s^r and carrying out the summation from $r = 1$ to ∞, we obtain

$$\frac{dG}{dt} = sk_i M^n + (k_p s - k_p - k_{t_3}) MG(s). \tag{12}$$

The solution of Eqn. (12) subject to the initial conditions $G(s, t)|_{t=0} = 0$ (i.e. at the initial instant there are no active radicals) yields

$$G(s) = \int_0^t sk_i M^n \cdot \exp\left[-(k_p + k_{t_3}) \int_{t_1}^t M\,dt_2\right] \cdot \exp\left[k_p s \int_{t_1}^t M\,dt_2\right] dt_1. \tag{13}$$

Subsequent expansion of $s \cdot \exp\left(k_p s \int_{t_1}^t M\,dt_2\right)$ in Taylor's series in terms of powers of s in the vicinity of $s = 0$, yields

$$s \cdot \exp\left[k_p s \int_{t_1}^t M\,dt_2\right] = s\left[1 + \frac{sk_p \int_{t_1}^t M\,dt_2}{1!} + \frac{s^2\left(k_p \int_{t_1}^t M\,dt_2\right)^2}{2!} + \ldots + \frac{s^{r-1}\left(k_p \int_{t_1}^t M\,dt_2\right)^{r-1}}{(r-1)!} + \ldots\right] = \sum_r \frac{\left(k_p \int_{t_1}^t M\,dt_2\right)^{r-1}}{(r-1)!} s^r.$$

We substitute this expression in Eqn. (13) and then compare the latter with the definition of the generating function $G(s, t) = \sum_r s_r p_r$. Setting the coefficients of identical powers of s equal to one another, we obtain

$$R_r = k_i \int_0^t M^n \exp\left[-(k_p - k_{t_3}) \int_{t_1}^t M\,dt_2\right] \frac{\left(k_p \int_{t_1}^t M\,dt_2\right)^{r-1}}{(r-1)!} dt_1. \tag{14}$$

In order to calculate $M(t)$, we make use of Eqns. (8) and (12) and the initial conditions

$$M|_{t=0} = M_0, \quad G(1)|_{t=0} = 0.$$

We obtain for $n = 1$

$$\frac{dM}{dG(1)} = -\frac{k_t + (k_p + k_{t_3}) G(1)}{k_i - k_{t_3} G(1)}.$$

Hence

$$M = M_0 + \frac{k_p + k_{t_3}}{k_{t_3}} G(1) + \frac{k_i (k_p + 2k_{t_3})}{k_{t_3}^2} \lg \frac{k_i - k_{t_3} G(1)}{k_i}. \tag{15}$$

Eqn. (11) yields

$$P_r = k_{t_3} \int_0^t MR_{r-1}\,dt_1. \tag{16}$$

Substitution of the expression for R_r from Eqn. (14) and of M from Eqn. (15) in Eqn. (11) gives the required distribution $P = f(r)$.

The formulae for the calculation of the MWD by the method of generating functions in the given case for other radical polymerisation mechanisms are not as cumbersome as might have been expected when the Bodenstein–Semenov hypothesis is abandoned. The introduction of generating functions made it possible to replace an infinite system of differential equations (9) and (10) in terms of

ordinary derivatives by a single first-order differential equation (12), also in terms of ordinary derivatives. This considerable advantage of the method led to its wide scale employment in studies of the mathematical simulation of radical polymerisation[20,22-24].

The principal statistical characteristics of the distribution—its moments—frequently permit more clear-cut inferences about the form of the distribution than does the knowledge of the analytical expression for the MWD and their calculation is much easier than the calculation of the MWD itself. The relation between the moments of the distribution and the generating function for $s = 1$ in the following way:

$$\mathcal{M}_1 = \sum_r rP_r = \left.\frac{dG}{ds}\right|_{s=1},$$

$$\mathcal{M}_2 = \sum_r r^2P_r = \mathcal{M}_1 + \left.\frac{d^2G}{ds^2}\right|_{s=1}.$$

The application of the method of generating functions yields compact analytical expressions for the number-average (μ_1) and weight average (μ_2) molecular weights of the polymers. Suppose that

$$G(s) = \sum_n s^nR_n,$$

$$H(s) = \sum_n s^nP_n$$

are the generating functions of the concentration of free radicals and the polymer. Consider a function $F(s) = G(s) + H(s)$. The number-average and weight-average molecular weights can then be expressed as follows in terms of the derivative functions $F(s)$:

$$\mu_1 = \frac{\sum_n nR_n + \sum_n nP_n}{\sum_n R_n + \sum_n P_n} = \frac{d\ln F(1)}{ds},$$

$$\mu_2 = \frac{\sum_n n^2R_n + \sum_n n^2P_n}{\sum_n nR_n + \sum_n nP_n} = 1 + \frac{d^2F(1)}{ds^2} \Big/ \frac{dF(1)}{ds}.$$

Higher-order moments can be calculated by a similar use of the derivative functions $F(s)$. The function $F(s)$ is found as the solution of a system of equations set up for any reactor (individual or in a reactor cascade) using the technique of generating functions.

IV. THE CONTINUOUS VARIABLE METHOD

The application of the method of generating functions to the calculation of the MWD or a finite number of its moments is limited to the region where the assumption of the invariance of the chain propagation and termination rate constants holds regardless of the length of the molecular chain. The principle of the independence of the reactivity of the terminal or any other group of the polymer molecule of its length does not hold in many instances, for example, in polymerisation in highly dilute solutions.

The continuous variable method makes it possible to calculate the MWD without adopting the drastic simplifying assumption that the rate constants for the elementary reactions are independent of the molecular chain length. The principal idea of the method involves the approximate representation of the mathematical problem with an infinite number of discrete variables by a continuous problem. An attempt at such an approximation would be natural for any mathematical system involving an infinite number of discrete variables. These considerations enabled Zeman and Amundson[25-27] and Thiele et al.[28] to treat the concentration of polymer molecules with a length P_r in the calculation of the MWD not as a function of a discrete variable r but as a function of a continuous variable $P(r)$. From the physical standpoint, this is a very satisfactory approximation, since the change in length by unity can be regarded as fairly small for fairly long chains.

The continuous variable method will be demonstrated in relation to the calculation of the MWD in radical polymerisation[25], where the reaction is carried out in a continuous-operation reactor via the following kinetic mechanism (Table 1).

$$k_f = k_{s_1} = 0, \quad k_{t_1} = k_{t_2} = k_{t_4} = 0, \quad w_i = k_iM.$$

We shall abandon the hypothesis that the rate constants for the chain propagation and termination reactions are independent of chain length. In this case the equations for the stationary state are

$$M_0 - M\left[1 + k_t\theta + \theta\sum_r k_{p_r}R_r + \theta\sum_r k_{t_r}R_r\right] = 0, \tag{17}$$

$$-R_1[1 + \theta k_{p_1}M + \theta k_{t_1}M] + \theta k_iM = 0, \tag{18}$$

$$-R + k_t\theta M - \theta M\sum_r k_{t_r}R_r = 0, \tag{19}$$

$$-P_r + k_{t_{r-1}}\theta MR_{r-1} = 0, \tag{20}$$

$$-R_r + \theta M(k_{p_r}R_r - k_{p_{r-1}}R_{r-1}) - \theta Mk_{t_r}R_r = 0,$$

$$r = 2, 3, \ldots \infty. \tag{21}$$

We shall use the fundamental relations of the continuous variable method:

(a) Suppose that the propagation and termination rate constants are known functions of chain length: $k_p = k_p(r)$ and $k_t = k_t(r)$;

(b) A relation between the continuous variable $R(r)$ and a function of the discrete variable R_r is established with the aid of the Euler–Maclaurin formula[29]:

$$R = \sum_r R_r = \int_1^\infty R(r)\,dr + \frac{R(1) + R(\infty)}{2},$$

where $R(1) = R_1$ by definition and $R(\infty) = 0$ from physical considerations; there is a zero probability of the appearance of a concentration of a polymer with an infinite chain length;

(c) The expansion of $R(r - 1)$ in Taylor's series, neglecting terms with orders of smallness higher than the first, yields correspondingly

$$R(r-1) = R(r) - \frac{dR(r)}{dr}.$$

After changing to a continuous variable, the system of Eqns. (17)–(21) becomes

$$M_0 - M\left[1 + k_t\theta + \theta\int_1^\infty k_p(r)R(r)\,dr + \theta\int_1^\infty k_t(r)R(r)\,dr + \frac{\theta}{2}[k_p(1) + k_t(1)]R(1)\right] = 0, \tag{17'}$$

$$R(1) = \frac{k_t\theta M}{1 + \theta[k_p(1) + k_t(1)]M}, \tag{18'}$$

$$R = k_t\theta M - \theta M\int_1^\infty k_t(r)R(r)\,dr - \frac{1}{2}\theta k_{t_1}MR(1), \tag{19'}$$

$$P(r) = \theta k_t (r-1)\, MR(r-1), \tag{20'}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[k_p(r)\,R(r)] + \frac{1+\theta M k_t(r)}{\theta M} R(r) = 0, \quad r \geqslant 2. \tag{21'}$$

Eqn. (21′) can be integrated after obtaining an expression for the distribution of active radicals:

$$R(r) = \frac{k_{p_1}}{k_p(r)} R(1) \exp\left(-\int_1^r \alpha(r)\,\mathrm{d}r\right); \quad r \geqslant 1, \tag{22}$$

where $\alpha(r) = [1 + \theta k_t(r)M]/\theta M k_p(r)$ and $R(1)$ is defined by Eqn. (18′). After substituting Eqn. (22) in Eqn. (20′), we obtain an expression for the distribution of polymer molecules with respect to chain length:

$$P(r) = \theta M R(1)\, k_{p_1} \frac{k_t(r-1)}{k_p(r-1)} \exp\left[-\int_1^{r-1} \alpha(r)\,\mathrm{d}r\right]; \quad r \geqslant 2\,. \tag{23}$$

In order to calculate the distribution by Eqn. (23), it is first necessary to find M. For this, one must substitute $R(1)$ from Eqn. (18′) and $R(r)$ from Eqn. (22) in Eqn. (17′) and the resulting expression must then be solved for M. In the given calculation of the MWD one must postulate that the chain propagation and termination rate constants depend on the chain length instead of the assumption that the reactivity of the radicals is constant, which was abandoned at an earlier stage. A linear relation between the activation energies for elementary chain propagation and termination reactions and chain length was adopted[26]. A relation has been proposed[14] between the chain propagation rate constant and the molecular weight of the polymer molecule.

A simple case, where the chain propagation and termination rate constants are independent of chain length, follows from Eqns. (17′)–(21′). Eqns. (17′)–(21′) can then be written as follows:

$$M_0 - M[1 + k_i\theta + \theta(k_p + k_t)R] = 0, \tag{17''}$$

$$R(1) = \frac{\theta k_i M}{1 + \theta(k_t + k_p)M}, \tag{18''}$$

$$P(r) = \theta k_t M R(1) \exp[-\alpha(r-2)], \tag{19''}$$

$$R = \frac{\theta k_i M}{1 + \theta k_t M}, \tag{20''}$$

$$R(r) = R(1)\exp[-\alpha(r-1)], \quad \alpha = [1 + \theta k_t M]/\theta k_p M. \tag{21''}$$

Hence we find the distribution of the active radicals and polymer molecules:

$$R(r) = R(1)\exp[-\alpha(r-1)], \tag{22''}$$

$$P(r) = \theta k_t R(1)\exp[-\alpha(r-2)]. \tag{23''}$$

The use of the continuous variable method for a periodic-operation reactor will be demonstrated by the following example: suppose that chain termination takes place only via the monomer, i.e. in Table 1 $k_{t_1} = k_{t_2} = k_{t_4} = 0$, there is no chain transfer reaction ($k_f = k_{f_S} = 0$), and the rate constants for the elementary reactions are invariant. The rate equations for the variation of the concentrations of the active polymer radicals assume the following form in the case under consideration:

$$\frac{\mathrm{d}R_r}{\mathrm{d}t} = -k_p M(R_r - R_{r-1}) - k_t M R_r; \quad R_r(0) = 0; \quad r = 2, 3, \ldots \infty. \tag{24}$$

On changing to a continuous variable, this infinite system of differential equations with ordinary derivatives can be transformed into a single equation in terms of partial derivatives:

$$\frac{\partial R(r,t)}{\partial t} = -k_p M \frac{\partial R(r,t)}{\partial r} - k_t M R(r,t); \quad R(r,0) = 0; \quad R(1,t) = R_1(t); \quad r \geqslant 2. \tag{25}$$

Similarly the infinite system of differential equations in terms of ordinary derivatives, which describes the rate of change of the concentrations of inactive molecules,

$$\frac{\mathrm{d}P_r}{\mathrm{d}t} = k_t M R_{r-1}, \quad P_r(0) = 0; \quad r = 2, 3, \ldots \infty \tag{26}$$

is transformed, within the framework of the continuous variable method, into a single partial differential equation:

$$\frac{\partial P(r,t)}{\partial t} = k_t M R(r,t), \quad P(r,0) = 0; \quad r \geqslant 2. \tag{27}$$

Thus, with the aid of the continuous variable method, the infinite system of algebraic material balance equations for a continuous-operation reactor can be reduced to a single differential equation and the infinite system of differential equations describing the non-stationary state of the polymerising system in a periodic-operation reactor is reduced to several partial differential equations.

V. POLYMERISATION AT HIGH CONVERSIONS

The mathematical methods for the calculation of the MWD examined above are applicable mainly to radical polymerisation processes occurring up to low degrees of conversion of the monomer. At high conversions the analytical relations for the rate of polymerisation, obtained by considering the classical kinetic mechanism, lead to appreciable discrepancies with experiment: virtually none of the mechanisms reproduces the experimental dependence of the rate of polymerisation of styrene on the degree of conversion obtained by one of the present authors and his coworkers[37]. The majority of polymerisation processes, particularly industrial processes, are continued up to high degrees of conversion. At high conversions the rate constants for the elementary reactions can no longer be regarded as constant[6,26,38]. An increase of the viscosity of the reaction medium during polymerisation is known to have a major influence on the rate of the chain termination reaction; however, there is no doubt about the influence of this factor also on the rates of other elementary reactions.

The form of the distribution function associated with the changes in these constants varies with the degree of conversion. At high conversions another simplification postulating that the radical concentrations are quasi-stationary, does not hold either. The point is that at high conversion one should expect a considerable increase of the lifetime of polymer radicals and hence also of their concentration, since radicals become relatively immobile in a highly viscous medium and cannot be destroyed as a result of interactions. The adoption of the Bodenstein–Semenov hypothesis would lead to an appreciable error in this instance. The above factors greatly complicate the kinetic calculation of the MWD at high conversions. On the other hand, polymerisation processes continued up to high degrees of conversion of the monomer are in fact of practical interest for the solution of many problems in the industrial application of the process: in the selection of a

technological scheme and type of reactor and in the calculation of the optimum technological conditions.

Isolated studies concerned with quantitative descriptions of radical polymerisation at high conversions have been carried out recently. One of the methods for the theoretical calculation of the MWD in radical polymerisation at high conversions has been proposed by Graessley et al.[39] It is based on the recognition and allowance for an important factor—the dependence of the rate constants for the elementary reactions on the degree of conversion. In order to simplify the problem, the author disregarded the remaining factors. A parameter, defined as the average number of units contained in the growing chain from the instant of its formation in the initiation of radicals up to deactivation on chain transfer or termination, was introduced:

$$\lambda = \frac{w_p}{w_f + w_{fS} + w_{t_1} + w_{t_2} + w_{t_3} + w_{t_4}}.$$

Since the rate constants for the elementary reactions vary with the degree of conversion, the parameter λ reflects these changes: $\lambda = \lambda(C)$, where C is the degree of conversion of the monomer. This exhausts the kinetic approach and the author[39] turns to a purely statistical treatment. In particular, he assumes that the growing molecules obey an exponential distribution law with respect to lengths:

$$f_r(C) = \frac{1}{\lambda} \exp\left(-\frac{r}{\lambda}\right).$$

In polymerisation in a periodic-operation reactor the total number of chains formed for an increment in the degree of conversion ΔC is proportional to $\Delta C/\lambda(C)$. Then the fraction of molecules with a chain length r, present for a degree of conversion C, is

$$F_r(C) = \int_0^C f_r(\xi) \frac{\mathrm{d}\xi}{\lambda(\xi)} \Big/ \int_0^C \frac{\mathrm{d}\xi}{\lambda(\xi)}.$$

Thus the characteristics of the polymerisation are taken into account exclusively by the parameter λ. The proposed method employs to a significant extent fairly drastic simplifications, which to some extent obliterate the characteristic features of polymerisation at high conversions. The influence of disregarded factors is in no way smaller than the variation of the rate constants for the elementary reactions with the degree of conversion, which has been taken into account.

An interesting approach to a quantitative description of polymerisation has been proposed[40]. Assuming that all the characteristics of the thermally initiated polymerisation of styrene in bulk which lead to discrepancies between theory and experiment at high conversions can be accounted for by changes in the rate constants for the elementary reactions, the constants are calculated on a computer by means of the following equations:

$$w(k_i, k_t, k_p) = w^{\mathrm{emp}}(C, T), \quad (28)$$

$$P_N(k_i, k_t, k_p, k_f) = P_N^{\mathrm{emp}}(T), \quad (29)$$

where $w(k_i, k_t, k_p)$ and $P_N(k_i, k_t, k_p, k_f)$, the theoretical expressions for the rate of reaction and the number-average degree of polymerisation as a function of the rate constants for the elementary reactions, are set equal to the simpler equivalent empirical expressions $w^{\mathrm{emp}}(C, T)$ and $P_N^{\mathrm{emp}}(T)$. An expression from the paper of Gleizer et al.[37] was adopted as the empirical equation for the rate of reaction $w(C, T)$:

$$w(C, T) = k_0 \exp[-E/RT] f(C), \quad (30)$$

where C is the degree of conversion and $f(C)$ an empirical function; the following expression is fitted to the experimental relation $P_N(T)$:

$$P_N(T) = a_N \exp[b_N/T]. \quad (31)$$

The rate constants for the elementary reactions obtained from Eqns. (28) and (29) are introduced into the theoretical equations for all the required MWD moments.

The above approach is analogous to the earlier method[41] for the solution of the converse problem involving the determination of the elementary rate constants as a function of temperature and the degree of conversion by minimising the Bayes factor[42]. The mathematical model of the MWD of the polymer obtained in the thermally initiated polymerisation of styrene was based on the kinetic mechanism for radical polymerisation with chain transfer to the monomer and the adduct, chain termination by recombination, and two different initiation mechanisms (with second and third orders with respect to the monomer). Equations for the rates of variation of the concentration of the active and inactive radicals and the monomer were set up in the traditional manner for the case under consideration. With the aid of the method of generating functions, the infinite system of ordinary differential equations in terms of the rate of variation of the concentration of polymer radicals (active and inactive) was converted into two ordinary differential equations in terms of generating functions of the concentrations of free radicals $[G(s)]$ and the polymer $[H(s)]$. Analytical expressions for the number-average and weight-average molecular weights can be obtained from these equations as a function of the rate constants for the elementary reactions. Empirical formulae relating the latter to the degree of conversion have been proposed. In the determination of the unknown coefficients in these formulae the authors[41] used one of the identification algorithms[42], which was executed using the experimental points representing the changes in the degree of conversion and in the number-average and weight-average molecular weights with time under isothermal conditions.

The essential feature of the method is that one has to find m unknown parameters θ_n ($n = 1, 2, \ldots, m$) from n observed values of Y_{iu} ($i = 1, 2, \ldots, k$; $u = 1, 2, \ldots, n$) (i.e. from n measured degrees of conversion and number-average and viscosity-average molecular weights) of the function $f_i(X^g_{iu}, \theta_n)$, the form of which is known:

$$Y_{iu} = f_i(X^g_{iu}, \theta_n) + \varepsilon_{iu},$$

where X^g_{iu} (with $i = 1, 2, \ldots, k$; $u = 1, 2, \ldots, n$; $g = 1, 2, \ldots, r$) represents r variables corresponding to n observations for each ith constituent vector-function and ϵ_{iu} is the error of the observation.

The relations obtained for the rate constants, which take into account all the characteristics of the polymerisation at high conversions, enabled the authors[41] to carry out a theoretical computer calculation of the MWD of polystyrene obtained in thermally initiated polymerisation. Fig. 4 reveals a fairly satisfactory agreement between the theoretical and experimental MWD curves. Table 3 shows that the fundamental experimental and calculated MWD parameters also proved to be fairly close. The mathematical model for the MWD of a polymer obtained by radical polymerisation (continued up to virtually complete

conversion of the monomer), proposed in the study under consideration, is of undoubted interest for the planning and optimisation of industrial polymerisation processes.

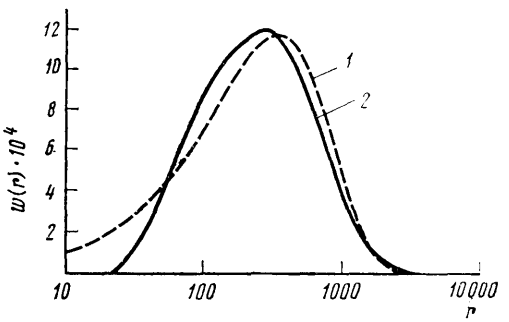


Figure 4. Comparison of the MWD obtained for a high degree of conversion of the monomer under isothermal conditions[41]: 1) calculated; 2) experimental.

Table 3. Comparison of the calculated and experimental MWD parameters at high conversion (X_{calc} = 95.1%, X_{exp} = 95.9%) on the basis of the data of Hui and Hamielec[41].

MWD parameter	Calculated value	Experimental value
M_n	35 000	35 500
M_w	70 600	71 200

VI. CALCULATION OF THE MOLECULAR WEIGHT DISTRIBUTION IN THE PRODUCTION OF HOMOPOLYMERS IN A CASCADE OF REACTORS

The study of the MWD at the output end of a cascade of polymerisation reactors merits particular attention, because a reactor cascade constitutes the most suitable technical means for carrying out polymerisation which permits a stepwise alteration of the temperature and concentration of the reactants, i.e. a stepwise alteration of the polymerisation conditions from the reactor to reactor.

For a cascade of Λ ideal mixing flow reactors, in which the polymerisation reaction takes place in accordance with the mechanism presented in Table 1 with $k_f = 0$ and $k_{t_2} = k_{t_4} = 0$, a system of algebraic equations defining the function $F(s) = G(s) + H(s)$ is set up by the generating function method:

$$M(n) = \frac{M(n-1) - \theta_n k_i(T_n) I_n}{1 + \theta_n \{[k_p(T_n) + k_f(T_n)] G(1, n) - k_f(T_n) R_1(n)\}}$$

$$R_1(n) = \frac{R_1(n-1) + \theta_n \{k_i(T_n) I_n + k_f(T_n) M(n) G(1, n)\} s}{1 + \theta_n \{M(n) [k_p(T_n) + k_f(T_n)] + k_i(T_n) G(1, n)\}}$$

$$G(s, n) = \frac{G(s, n-1) + \theta_n \{k_i(T_n) I_n + k_f(T_n) M(n) G(1, n)\} s}{1 + \theta_n \{M(n) [k_p(T_n)(1-s) + k_f(T_n)] + k_{t_1}(T_n) G(1, n)\}}$$

$$H(s, n) = H(s, n-1) + \theta_n \left\{\frac{k_{t_1}(T_n)}{2} G(s, t)^2 + k_f(T_n) M_n [G(s, n) - sR_1(n)]\right\}.$$

$$n = 1, 2, \ldots N.$$

The elimination of computational difficulties, associated with the calculation of the moments of the MWD function, with the aid of the derivative functions $F(s)$ (see Section III) makes it possible to formulate and solve the problem of the optimisation of ideal mixing polymerisation flow reactors taking into account the quality of the polymer obtained. Ray and coworkers[22,23] made the first attempt at the optimum design of the polymerisation process in a cascade of chemical reactors in order to obtain the required MWD parameters for the polymer. In this case the problem reduces to the determination of the optimum polymerisation conditions by an appropriate choice of the initiator concentration, temperature, and the residence time of the polymerising mass in the reaction system. A linear function of the standard of deviations of the principal MWD parameters and of the degree of conversion from the required values of the latter is adopted as a criterion which determines whether or not optimum conditions have been obtained:

$$f = (\mu_1 - \bar{\mu})^2 + \lambda_1 \left(\frac{\mu_2}{\mu_1} - \bar{S}\right)^2 + \lambda_2 (1 - C)^2,$$

where λ_1 and λ_2 are the weighting factors taking into account the relative importance of the polydispersity and the degree of conversion of the finished product and $\bar{\mu}$ and $\bar{S}$ are the required molecular weight and polydispersity coefficient respectively. The optimum conditions for the polymerisation process were calculated on a computer in relation to the polymerisation of styrene in one flow reactor or in a cascade of two reactors. The calculations were performed for different versions of the requirements imposed on the width of the MWD (for the minimum width of the MWD, $\bar{S} = 1$; for a wider distribution, $\bar{S} = 3$), the weighting factors of the components of the above criterion being varied by altering the ratio λ_1/λ_2. The calculations yielded the optimum values of the technological parameters ensuring the maximum degree of conversion and the minimum polydispersity of the polymer.

The continuous variable method has found extensive applications in calculations of the MWD in radical polymerisation processes in a cascade of reactors of different types. The MWD for polystyrene has been calculated[8] taking into account chain transfer to the monomer and chain termination by recombination in continuous-operation reactors. The authors[8] compared two methods for the theoretical calculation of the MWD and observed that the MWD curve calculated by the continuous variable method virtually coincides with the distribution curve calculated by the classical method. For the same initial conditions and the same average residence time, a comparison was made in the same study of the MWD for one-, two-, and three-cascade polymerisation processes. In the calculation of the MWD for the polymer in a reactor cascade the advantage of the continuous variable method over the classical method is particularly manifest; for a cascade of three isothermal reactors, the classical method is already unsuitable even when computers are used, whereas with the aid of the continuous variable method the computational difficulties can be fully overcome.

Calculations on the cascade method of industrial polymerisation with intermediate injection of the initiator can also be performed by the continuous variable method. The influence of various reaction conditions on the MWD of polystyrene has been calculated in relation to the initiated polymerisation of styrene[30]. The calculations showed that, by altering the process conditions (reaction temperature, residence time of the polymerising mass in the reactors, initial monomer concentration, and the

intermediate supply of the initiator, monomer, and solvent), it is possible to affect the MWD appreciably. Hence we believe that a natural step to take would involve optimum planning of the polymerisation process in order to obtain a finished product with specified properties, subject to the condition that the relation between the physicomechanical properties of the polymer and the MWD [31-36] is expressed in a mathematical form. Although exact correlations between the MWD and the physicomechanical properties of polymers have not as yet been established, there now exist many empirical and qualitative relations which can be used in the optimisation and planning of the industrial technological process under conditions where these properties depend on the MWD.

A combination of theoretical equations for the MWD parameters with empirical equations has been used[43-45] to describe the rate of an industrial polymerisation process in order to optimise the thermally ionised polymerisation of styrene in a continuous-operation apparatus consisting of N series-connected isothermal ideal mixing reactors and a reactor of the column type. The stationary state of thermally initiated block polymerisation of styrene was described, taking into account the non-ideality of the flow of the polymerising mass in the column, by a system of algebraic and differential equations. The mathematical description of the process is based on the representation of the rate of polymerisation by the product of two functions, one of which characterises the dependence of the rate on temperature and the other its dependence on the degree of conversion:

$$w(T, C) = w_0(T) f(C).$$

The term expressing the temperature dependence is described by the Arrhenius law

$$w_0(T) = k_0 \exp(-E/RT),$$

and $f(C)$ is specified by an empirical curve constructed on the basis of experimental data and showing how the rate of polymerisation decreases relative to the initial rate of polymerisation $w_0(T)$ at the same temperature as the degree of conversion increases.

Relations obtained on the basis of the definition of the number-average and weight-average molecular weights as the ratios of the corresponding moments of the MWD function have been proposed for the calculation of the principal characteristics of the MWD (see Section III). The presence of an empirical element in the proposed[43-45] mathematical model of the thermally initiated block polymerisation of styrene in a cascade of industrial reactors of different types deprives this approach of the generality characteristic of a purely theoretical calculation; however, the approach permitted a simple and effective solution of the specific problem of the optimum connection of reactors and of the search for the optimum operating conditions of an industrial polymerisation apparatus. Fig. 5 presents a diagram illustrating the technological conditions calculated using digital computers on the basis of algorithms and models developed by Gleizer and coworkers[37,43-45]. The region with the smallest polydispersity is located in the upper right-hand corner of the diagram. The optimum technological parameters selected from this region (the degree of conversion in the first reactor C_1, the temperature in the first reactor T_1, and the temperature in the second reactor T_2) ensure the minimum residence time of the polymerisation mass in the reactor cascade (τ) and the minimum polydispersity of the final polymer (μ_f) for fixed requirements to be met by the final degree of conversion of the finished product (C_f) and its viscosity-average molecular weight (M_f).

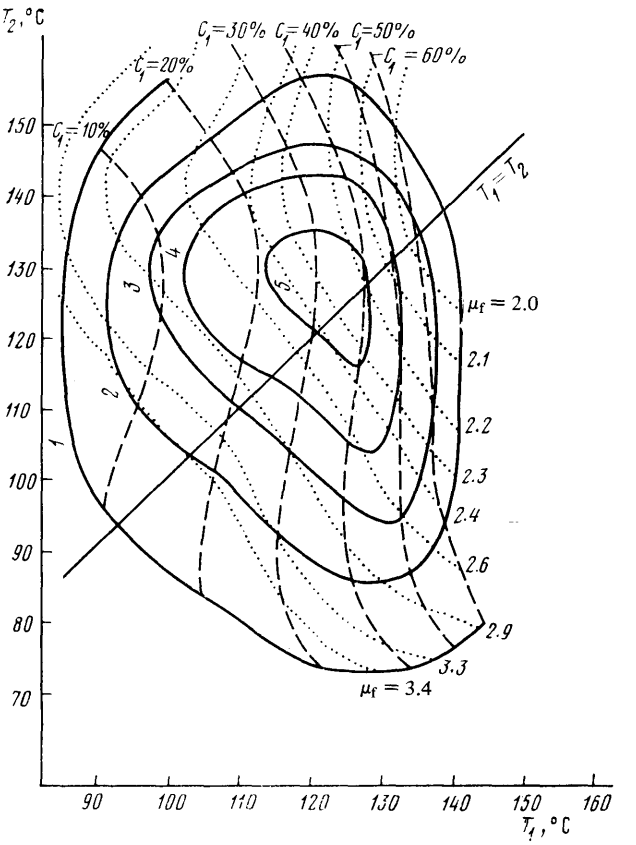


Figure 5. Diagram of technological conditions for the polymerisation of styrene in a cascade of reactors[45] (M_f = 350 000; C_f = 98%): overall residence time of the polymerising mass in the system $\Sigma\tau$ (hours): 1) 15; 2) 10; 3) 8; 4) 7; 5) 6.

Hitherto calculations have been made on polymerisation reactions which can occur both in an individual reactor and in a technological apparatus consisting of series-connected reactors. The type of reactors and the sequence in which the polymerising mass passes through them were assumed to be specified. However, in the development of a technological polymerisation process one of the problems is in fact the selection of the optimum polymerisation system. Evidently the type of reactors and the method of their connection have a significant influence on the degree of reaction of the initial monomer and the composition of the polymer produced. The study where an advance was made towards the next level of the investigation of polymerisation reactors on the basis of their kinetic models—the creation of a polymerisation system of reactors on the basis of a criterion whose optimisation ensures the best functioning of the system—is therefore of interest[24]. This problem must be solved using apparatus for the

polymerisation reaction comprising only one reactor. It is known that, for all reactions (including polymerisation reactions) whose order is positive, a higher degree of conversion of the initial product is attained in a periodic-operation reactor than in an ideal mixing flow reactor with the same reaction volume. The absence of the mixing of the reaction mixture with a fresh stream of the initial monomer in the periodic-operation reactor, of the kind that takes place in a flow reactor, makes the average rate of reaction in the latter always lower than in a periodic-operation reactor. However, in ideal mixing flow reactors processes at higher monomer concentrations take place more effectively. On the other hand, a narrower MWD is frequently obtained in a periodic-operation reactor than in a flow reactor (for example, when the lifetime of the active radical is comparable to the residence time in the reactor[7]).

Industrial polymerisation processes take place up to high conversions and it is desirable to investigate a narrow MWD. Taking into account the nature of the flow of the reaction mixture through the reactors, it is therefore important to arrange them in the following sequence: one or several continuous-operation reactors in the form of fore-polymerisers followed by a displacement reactor (or a periodic-operation reactor) which ensures a high degree of conversion of the monomer. However, even for a system consisting of only two reactors, one of which is of the flow type and the other is of the periodic-operation type, it is not easy to solve the problem of the redistribution of the stream between the reactors, the additional injection of reactants at intermediate stages, and the recycling of part of the stream. Examination of these features from the standpoint of their influence on the degree of conversion and the MWD requires calculations on numerous versions using mathematical models of polymerisation reactors. The addition to a single flow reactor of a further series-connected device, which leads to a higher degree of conversion of the initial monomer, increases sharply the number of versions for which calculations must be made in order to select the optimum conditions. The problem arises of the development of computer algorithms which permit calculations, on the basis of mathematical models of polymerisation reactors, for different versions of the schemes for their connection and a choice of one of them in terms of a criterion.

The scalar function

$$\mathcal{K} = \alpha_1 M + \alpha_2 (\sigma - \bar{\sigma})^2 + \alpha_3 (\Delta - \bar{\Delta})^2,$$

where M is the monomer concentration at the outlet from the polymerisation system, $\bar{\sigma}$ and $\bar{\Delta}$ are the specified degree of dispersion and the mathematical expectation of the MWD function, and α_i (where $i = 1, 2, 3$) are weighting factors, has been proposed as a criterion[24]. The minimisation of the function $\mathcal{K}(M, \sigma, \Delta)$ ensures the attainment of the maximum degree of conversion of the monomer and the minimum deviation of the zeroth, first, and second moments of the MWD from their specified values at the outlet from the system.

We shall now analyse the procedure for the selection of the optimum system of reactors from the multiplicity of permissible systems on the basis of the criterion proposed[24]. For a more detailed analysis of the existing versions and the elucidation of ways of applying the proposed methods, we shall consider initially a technological scheme comprising two series-connected reactors: an ideal mixing flow reactor (FR) and a periodic-operation reactor (POR). We shall consider all possible ways of connecting the FR and the POR for a fixed overall reaction volume of the system. They give rise to a multiplicity of structures of the reaction system and the optimum structure is in this case selected as follows. In the first place, for each stream mixing point, material balance equations with respect to the initiator and the monomer and the equations for the calculation of the MWD moments at the stream merging points from the moments in each of the streams being mixed are set up.

In order to calculate the moments, one sets up with the aid of the generating function method a kinetic model of the initiated radical polymerisation taking into account the chain propagation reaction and chain termination by recombination. The kinetic equations supplemented by stream material balance equations form a universal mathematical model describing various structures of the reaction system. With the recirculation coefficients varied from 0 to 1 (which thus leads to a selection of various structural versions of the reaction system), this model permits computer calculations of all possible structural versions for different requirements to be met by the resulting polymer (by fixing a set of weighting factors for the optimum conditions criterion).

On the basis of these calculations, the structural features of the given reaction system are established. In the first place, it was found that the recirculation of a large proportion of the stream is undesirable, since it leads to an appreciable increase of the target function. The recirculation of very small proportions of the streams in the organisation of the reaction system must be ruled out in view of their insignificant influence on the process, which is expressed by the virtually unchanged values of all the components of the target function. The recirculation of the stream both from the outlet of the FR and from the outlet of the POR to the inlet of the FR is undesirable, since it leads to an increase of the target function owing to the increase of the monomer concentration at the outlet from the system due to the decrease of the overall residence time of the polymerising mass in both reactors. The deviation of the variance and of the mathematical expectation of the MWD function from the specified values then decreases only slightly owing to the mixing of the molecules, emerging from the outlet during the process, with the incoming molecules (the former thus acquire some, albeit small, capacity for growth).

An optimum structural version has been proposed for the polymerisation system under consideration: series-connection of the FR and POR, which are bypassed by a fraction of the streams (0.336 and 0.704 respectively) and in which the ratio of the POR and FR volumes is 0.294. The influence of the changes in the rate constants for the elementary reactions on the polymerisation process has been analysed for the optimum system obtained. A study was also made of the influence of the temperature conditions on the given polymerisation process in this system. For this purpose, the POR was subdivided into two temperature zones. The consequent increase of the target function is associated with the improvement of the MWD parameters.

The methods for the investigation of processes involved in the production of homopolymers, which were considered here on the basis of a mathematical description of the MWD, give rise to considerable possibilities for the analytical development (with the aid of computers) of new polymerisation processes, the theory of calculations on chemical reactors and of the mathematical simulation of the MWD being related to the technological apparatus for the polymerisation processes.

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