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The Macrokinetics and Rheokinetics of the Hardening of Oligomers

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The review deals with the investigation and phenomenological description of the macrokinetics of the hardening of reactive oligomers and the change in their rheological properties observed in the course of this process. Attention has been concentrated on the establishment of a relation between the macrokinetics and rheokinetics of the hardening process. The influence of deformation on the hardening kinetics is examined and the role of non-isothermal effects induced by various factors as well as the formulation of the hydrodynamic problems concerning the flow of liquids with variable rheological properties are discussed. The bibliography includes 143 references.

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I. INTRODUCTION

The hardening of reactive oligomers (RO), i.e. the transition from the comparatively non-viscous liquid to a solid infusible material, is one of the principal technological processes associated with the chemistry of macromolecular compounds and is widely used in various branches of modern industry, including aerospace engineering, machine engineering, power engineering, etc. This process occurs in the manufacture of reinforced plastics of all types, plays an important role in the deposition of protective and insulating coatings, and recently has found application in the preparation of constructional components. The wide variety of the structures of RO and the possibility of their comparatively simple combination with various fillers and reinforcing elements are responsible not only for the extremely broad spectrum of the properties of the final products and articles made from them but also for different versions of the kinetics of the reactions occurring during the hardening of RO as well as the topology of the structures produced. Many problems associated with the chemistry of RO have been considered not only in hundreds of original communications but also in reviews.[1]

At the same time there exists an important aspect of the general problem of the investigation of the RO hardening processes which has so far been comparatively little reflected in the scientific literature, although there can be no doubt about its fundamental and technological importance. This concerns the general features of the time variation of the rheological properties of RO during the hardening process, so that there arises a single macro- and rheo-kinetic problem which involves the establishment of a correspondence between the macrokinetics of the hardening process and the change in the rheological properties of the RO as a consequence of this process. The terms "kinetorheology" or "rheokinetics", first proposed in 1976 [2] and then used in Soviet literature,[3] aptly reflect the range of processes which should be considered in studies on the kinetics of the variation of rheological properties; however, it is essential to establish a relation between the rheokinetics and macrokinetics of a chemical process.[4] Certain aspects of this problem, considered in the literature up to 1980, were dealt with in a previous review.[5] This review is devoted to a more detailed discussion of the problems associated with the macrokinetics and the rheokinetics of the hardening of oligomers; mainly the literature data of the last five years are considered.

The study of the rheokinetics of the hardening reactions of RO is of dual interest. On the one hand, measurement of the rheological properties of the reaction mass in the course of the process constitutes a way of following the latter. On the other hand, the intrinsic characteristics of the rheological properties are of direct technological interest: in the field of the conservation of the fluid state—for the assessment of the possibility and ways of filling the mould or the impregnation of the reinforcing structure; after the formation of an involatile product—for the direct assessment of the mechanical (operational) properties.

It is noteworthy that many methodological procedures and experimental methods used to investigate the rheokinetics of the hardening of RO are related to or are analogous to the procedures and methods employed in the technology of processes such as the "monomeric" or "cast" moulding, where the final product is a linear polymer below the melting point and not a cross-linked polymer.[6-9] This enhances the generality of the rheokinetic problem and at the same time poses a new question concerning the role of deformation in chemical processes leading to the formation of the final product. Furthermore, the role of the non-isothermal conditions in hardening processes,[10-12] which is due to the significant exothermicity of the chemical reactions, leading to hardening, as well as the dissipative heat evolution during the flow of highly viscous liquids and the heating from an external source, must be emphasised. The non-isothermal nature of the process itself leads to a series of new phenomena which are of general importance for its kinetics and mechanics.[10,11]

II. CHANGES IN THE RELAXATION STATES DURING HARDENING

The rheokinetic transformations during the hardening of RO are associated not only with a change in the molecular structure of RO (with increase in the chain length and/or the degree of branching) but also (and possibly primarily) with relaxational transitions occurring even under isothermal conditions at the moulding temperature T_m as a consequence of the shift of the glass point T_g of the polymer formed. This fundamental approach was formulated more than ten

years ago and has been developed in numerous investigations.[13-20] Its essential feature is illustrated in Fig. 1, which presents the relaxation processes as a function of T_m in a schematic form. Several main situations are possible. Firstly, the temperature T_m may be higher than the glass point of the final product $T_{g,\infty}$ which is thus in a highly elastic state. During the hardening process, the initial liquid loses its fluidity at some instant as a consequence of the formation of a gel (there is a transition from the fluid to the highly elastic state) and the reaction is completed in the gel. Secondly, T_m may be lower than $T_{g,\infty}$ and a gel is then formed initially (i.e. there is a transition from the fluid state to the highly elastic state) and this is followed by the conversion of the gel into a glass as a consequence of the further progress of the reaction involving the formation of cross-links. Thirdly, at still lower values of T_m, the reaction mass can vitrify before the formation of the gel, which results in the cessation of the structure formation process at an extremely early stage. Fourthly and finally, T_m may be below the glass point of the starting material $T_{g,0}$ and the hardening reaction does not then occur at all.

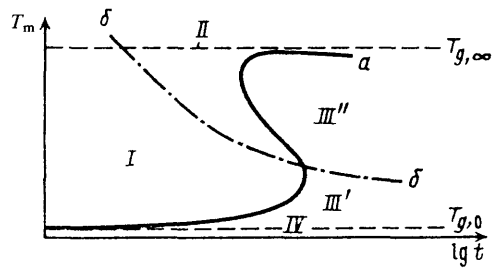


Figure 1. The relaxation states and transitions in the oligomer hardening processes.[18]

The possible situations are clearly seen from the temperature–time diagram (Fig. 1), which has been subdivided into a number of regions by the vitrification lines of the starting material ($T_{g,0}$) and the final product ($T_{g,\infty}$), the line of the gel formed (line *aa*), and the gelation line—the line corresponding to the transition from the fluid to the highly elastic state (line *bb*). Correspondingly I represents the region of the fluid (liquid) state, II the region of the highly elastic state, III′ the vitreous liquid, III″ the vitrified elastomer, and IV the region corresponding to the existence of the vitreous reactive starting material which does not, however, react. The pathway followed by the isothermal reaction is represented by the horizontal line, which intersects lines *aa* and *bb*; at the instant corresponding to this intersection, relaxation transitions take place, which are observed, for example, by the attainment of maxima in the tangent of the mechanical loss angle tan δ.[13]

A rheological method for monitoring the process can be chosen accordingly on the basis of the position of the T_m = const. line (the "reaction pathway"). In region I this is viscometry but, as line *bb* is approached, the viscosity increases without limit and the material loses its fluidity. In all the remaining regions the state of the reaction mass can be inferred from the modulus of elasticity and the tangent of the mechanical loss angle. We may note further that I is the region where the material is "live", i.e. is in a state where it is possible to impart to it the required form; in region II the chemical reaction may continue; in regions III–IV the reaction is significantly arrested possibly long before the attainment of the state of equilibrium. This implies in addition that the properties of the resulting product may depend to a very great extent on the reaction pathway (i.e. on the character of the time variation of the temperature) and that they can be altered by raising the temperature relative to T_m.[21-23]

The diagram presented in Fig. 1 is fairly universal and its configuration is therefore important for various systems capable of hardening and it is also important to establish the exact form of the transitions line. The last problem is evidently associated, primarily, with the description of the macrokinetics of the hardening process and, secondly, with the specification of the character of the dependence of the transition temperatures on the composition (and structure) of the oligomeric products. The first of these problems is of general importance for the problem considered here and the next Section of the review is devoted to it. The second problem was dealt with in a fairly general form by Enns and Gillham[18] and therefore merits further analysis and solution in relation to the principal classes of hardening systems.

III. THE MACROKINETICS OF THE HARDENING PROCESS

1. General Characteristics

A description of the kinetics of the hardening of reactive oligomers is one of the central problems in this field, whose solution makes it possible, firstly, to draw inferences about the chemistry of the process, secondly, to introduce a quantitative parameter in order to compare various materials, and, thirdly, to justify the predictions of the course, productivity, and efficiency of real technological processes. Here there is a possibility of two significantly different approaches: the kinetic and macrokinetic approaches. In the first case the changes in the concentrations of particular reactive groups are inferred by direct physical or spectroscopic methods. This procedure is quite evident and yields clear results, but is by no means always effective from the standpoint of the assessment of the extent and degree of hardening and also the characterisation of the products obtained. This is associated with the fact that the hardening process consists of a set of very many reactions, occurring both simultaneously and consecutively and that the same reactions (reactions of the same chemical type) can lead to the formation of materials with completely different properties, since the topology of the products of isotypical reactions may be fundamentally different.[1,24-26] This method for the estimation of the extent of the hardening reaction is therefore undoubtedly of independent importance, but by no means always leads to an exhaustive solution of the problem.

The macrokinetic method, based on the observation of the time variation of a particular integral parameter reflecting the entire set of the chemical reactions occurring in the hardening of the oligomer, is more widely used and is apparently more effective in practice. Here it is possible to indicate in principle three main methodological approaches. In the first, the concentration of the reactive groups is measured by a chemical or physicochemical method and its time variation is described by a suitable equation regardless of which reactions are undergone by these groups and without specifying in detail the individual stages of the chemical process. In the second method, which may be

called "calorimetric", one measures the time variation of the total heat of reaction and the question which particular possible reaction makes a given contribution to the observed heat change is not discussed. Thus, if the total heat of the hardening reaction is Q and an amount of heat $q(t)$ has been evolved at time t, then the quantity $\beta_c = q(t)/Q$ is adopted as the "calorimetric" degree of conversion β_c.

Such an estimate is very widely used in practice but it has an unambiguous physical significance only when Q does indeed correspond to the overall transformation. This can occur (naturally for a sufficiently long observation) when the final product remains in the highly elastic state. On the other hand, when the reaction mass vitrifies before the completion of the hardening process, then the quantity Q corresponding to the attainment of line *bb* in Fig. 1 is found to depend on the temperature T_m and the quantity β_c, calculated as the ratio $q(t)/Q(T)$, does not characterise the degree of reaction, because different degrees of reaction correspond to the same value of the ratio at different temperatures.[27,28]

The third common method for the estimation of the degree of reaction is based on the measurement of a particular physical characteristic of the substance which depends on the degree of reaction, for example, the viscosity, the modulus of elasticity, hardness, etc. Thus, if the modulus of elasticity of the starting material is G_0, that of the final product (in the highly elastic state) is G_∞, and that of the reaction mass at a certain instant is $G(t)$, then the quantity $\beta_r = [G(t) - G_0]/(G_\infty - G_0)$ may be adopted as the "rheological" extent of reaction β_r. An additional consideration supporting the introduction of this measure of the degree of hardening may be the familiar concept according to which the modulus of elasticity of oligomers capable of being hardened is related to the density of the network of cross-links.[23-25]

It is noteworthy that in the general case one cannot expect β_c and β_r to be identical or to agree with other possible characteristics of the macrokinetics of the hardening process, because these quantities may reflect different reactions of the test substance.

It has been shown that the instant of the attainment of the gel point in no way affects the values of β_c, β_r, as well as other measures of the extent of the hardening reaction employed in the literature. However, this instant (the reaction time corresponding to it will be designated by t^*) is always of independent interest for the physical chemistry and technology of reaction oligomers; t^* also constitutes a macrokinetic measure of the extent of the hardening process and its temperature variation is an important characteristic of the reaction. The value of t^* must therefore be estimated by other procedures, for example, from the instant of the attainment of the maximum in $\tan\delta$ [13,15] or from the instant when the viscosity η reaches a certain arbitrary high level,[29] or when one can assume that $\eta \to \infty$.

The appearance of a residual equilibrium (relaxation) modulus of elasticity or modulus of high elasticity may serve as reliable evidence for the attainment of the gel point, i.e. for the formation of a continuous three-dimensional network.[30] Naturally, it is fairly difficult to determine experimentally whether a non-zero component of the modulus has appeared. The instant when the modulus of elasticity reaches a certain not very high but easily measurable value, for example 10^3 Pa, may be adopted as an experimentally unambiguous (but more arbitrary) criterion of the attainment of t^*.

It is of interest to note that the time t^* determined in this way is correlated[30] (at least in certain cases) with another arbitrary but also unambiguously determined time, namely that when $\tan\delta = 1$ is attained. The latter estimate may be particularly valuable in practice, because it has been established for nine different thermoreactive resins[31] that the times t^* determined by the standardised ASTM method (the resin to be hardened is slowly stirred by hand with a wooden rod and t^* is assumed to correspond to the instant when the rod breaks owing to the high viscosity of the mass) and as the point at which the true (G') and imaginary (G'') components of the modulus of elasticity become equal (i.e. $\tan\delta = 1$) are similar for systems in which t^* varies over a very wide range—from 1 to 1000 min. Bearing in mind the arbitrary nature of the estimate of t^* from the strength of the wooden rod, it becomes evident that the method based on the measurement of the modulus of elasticity is naturally preferable (if one disregards the fact that it requires an expensive measuring technique). The choice of frequency is important for the measurement of the modulus of elasticity, because t^* depends on the frequency. Indeed an increase of the frequency by an order of magnitude corresponds to a shift of the point t^*, at which $G' = G''$, approximately by 1 min along the time axis, which corresponds to a frequency dependence of the relaxation transition point. A frequency of 1.6 Hz ($\omega = 10$ rad s^{-1}), which is approximately equal to the rate of shear used in tests by the ASTM method, is therefore recommended as "standard".[31]

The method of estimating t^* as the time when $\tan\delta = 1$ is very clear and unambiguous; however, generally speaking, it should not be correlated with other methods. Thus in a study of the hardening of unsaturated polyester resins it was found[27] that the point at which $\tan\delta = 1$ coincides with the gel point found by the ASTM method only at low hardening temperatures; with increase of temperature, $\tan\delta = 1$ is reached earlier than the maximum in the loss modulus G'' characterising the instant of the transition.

It is thus evident that, just as one cannot expect a complete correspondence between β_c and β_r, the values of t^* estimated by different methods may not agree owing to the arbitrary nature of the methods employed; only the estimate of t^* from the time when $\eta \to \infty$ is absolute, but the very determination of the attainment of the situation (which can be achieved only asymptotically) also involves greater or smaller errors.

As regards the method used to describe the $\beta(t)$ relation, the essential feature of the macrokinetic approach used to solve this problem is expressed by the equation[4,10]

$$\dot{\beta} = K_0 f(\beta) e^{-U/RT} , \qquad (1)$$

where K_0 is a normalising multiplier, U the activation energy for the hardening process, and $f(\beta)$ a macrokinetic function. The reason for its introduction is that it includes only one variable parameter, namely the degree of reaction β, i.e. in this approach one deliberately ignores the different, possibly very complex, variants of the hardening reaction as a multi-stage process or as a reaction proceeding via several parallel pathways, etc., all this being approximately generalised by the single factor β.

Generally speaking, this approach does not guarantee success and one cannot claim *a priori* that it is applicable in all possible situations. However, the experience gained in describing the hardening processes involving a very large number of oligomers demonstrated the fruitfulness of this approach and the possibility, when the form of the function $f(\beta)$ has been selected appropriately, of describing with its aid all situations encountered in reality. Thus the problem reduces to an appropriate selection of the type of macrokinetic function $f(\beta)$.

Apparently the most general approach to the choice of the function $f(\beta)$ has been proposed by Kamal and Sourour[32,33] and Progelhof and Throne,[34] who formulated a macrokinetic hardening equation [Eqn.(1)] in the isothermal case as follows:

$$\dot{\beta} = (k_1 + k_2\beta^m)(1-\beta)^n \qquad (2)$$

where k_1, k_2, m, and n are empirical constants and k_1 and k_2 can vary with temperature in different ways, while m and n are independent of temperature.

In contrast to many early investigations,[35-38] where an nth order equation was proposed for the description of the macrokinetics, i.e. it was assumed that $f(\beta) = (1-\beta)^n$, Eqn.(2) takes into account explicitly the autoacceleration or autocatalytic effect, expressed by the first multiplier on the right-hand side of Eqn.(2), which is important for hardening reactions.

An undoubted advantage of Eqn.(2) is its general character, while its disadvantage is its extreme generality, since four "adjustable" constants are as a rule too many to achieve an unambiguous macrokinetic characteristic of the hardening process. In most cases it is therefore sufficient to employ simpler relations which are special cases of Eqn.(2).

Thus the macrokinetics of the formation of polyamide-6 are described by an equation of the autocatalytic type but in a much simpler form, which is obtained from Eqn.(2) when $m = n = 1$ on the assumption that the reaction rate constant obeys the Arrhenius relation as a function of temperature:[9,39-42]

$$\dot{\beta} = K_0 e^{-U/RT}(1-\beta)(1+C\beta)\ , \qquad (3)$$

where there are only two "adjustable" parameters, K_0 and C, which vary as a function of the conditions of the synthesis, i.e. the concentrations of the catalyst and the activator, the nature of the active centres, etc., while U is the activation energy for the polymerisation process.

The macrokinetics of the formation of polyamide-12 from dodecalactam are described by a first-order equation without an autocatalytic term, i.e. in this case $C = 0$;[8,9,41] however, this is of course an exceptionally simple and atypical case.

There is no doubt that Eqn.(2) represents the most general case, but in practice it is nevertheless desirable to have fairly simple values of the constants m and n.

2. The Macrokinetics of Structure Formation in the Principal Types of RO

We shall now consider the principal results of the application of the macrokinetic method to the description of the hardening of the RO described in the literature. The most important and most frequently investigated case, to which the greatest number of communications have been devoted, is the hardening of epoxide resins. It has been shown that Eqn.(2), where β has been most often determined from the results of calorimetric measurements, is entirely suitable for this case with the constants $m = n = 1$.[32,33,43,44] This conclusion terminates a fairly prolonged controversy concerning the character of the macrokinetic equation for the description of the hardening of epoxide resins, because earlier various publications proposed equations for $f(\beta)$ of zero,[45] first,[46] and fractional[47] orders in the degree of reaction. The conclusion that the hardening reactions of epoxide resins proceed with autoacceleration, reached by Kamal,[33] can also be found in Rozenberg's paper[48] (on the basis of data obtained calorimetrically, i.e. β_c), and was later confirmed also by the rheological method,[49] i.e. on the basis of β_r. In the last study β was determined for the hardening of the diglycidyl ether of bisphenol-A with dicyanogendiamine and it was established that the constant k_2 in Eqn.(2), characterising the autoaccelerating effect of the reaction, is fairly high, but the autoacceleration effect degenerates with increase in the concentration of the hardening agent.

The question of the temperature variation of the rate or duration of the structure formation reaction is important (in both practical and theoretical respects). Here one must emphasise that the effective activation energy U can be determined by various methods, which generally speaking can yield different results depending on the choice of conditions in comparing the values of the given parameter under non-isothermal conditions. Thus U found from the gelation time, i.e. from the gel point t^*, may not agree with the value determined from the temperature variation of the maximum rate of change of β or from the time coresponding to the attainment of a specific level of the values of β, etc. Whether or not the values of U found by different methods agree depends on the form of the macrokinetic equation for $\dot{\beta}$ and on the presence or absence of an influence by temperature on the constants which it includes.

The discrepancy between the values of U found from different characteristic points has been demonstrated very clearly in a study[50] where it was found that $U = 55$ kJ mol^{-1} when it is calculated from the point corresponding to the onset of gel formation, $U = 66$ kJ mol^{-1} when found from the most rapid increase of the modulus of elasticity (the rigidity of the material), $U = 83$ kJ mol^{-1} when found from the instant corresponding to the completion of the rapid increase of the modulus, and, finally, $U = 103$ kJ mol^{-1} when found from the time of attainment of the final value of the modulus. The observed monotonic increase of U as one moves from the beginning to the end of the reaction is fairly striking, because it apparently shows that the two constants which determine the macrokinetics of the structure formation process nevertheless vary with temperature in different ways, so that a single value of U does not exist. In this respect an unusual simple exception is provided by the situation described by Malkin et al.,[49] who found that the autoacceleration constant is independent of temperature and the effective activation energy (70 kJ mol^{-1}), determined from $\dot{\beta}$ (or from the rate constant $K = K_0 e^{-U/RT}$) proved to be identical with the values calculated from the temperature variation of $1/t^*$ and from calorimetric data published previously.[46]

However, one should note that in Eyerer's study[51] the activation energy calculated from spectroscopic data for different stages of the reaction with bisphenol-A and dicyanogendiamine was also found to be the same in all cases but its value was 84 kJ mol^{-1}. The significantly smaller value $U = 51$ kJ mol^{-1}, obtained[19] for the reaction of a mixture of diglycidyl ethers with 2,4-tolylene-1,1'-bis-3,3-dimethylurea contrasts significantly with the high values of U quoted above.

Naturally the specific value of U depends on the detailed composition of the reaction mass, because the rate-limiting reaction may be various. Thus the effective activation energy for an epoxyorganoelemental oligomer, hardened with oligobutoxytitanophosphoroxan, found from the temperature variation of $1/t^*$, varied in the range 47–60 kJ mol^{-1} as a function of the content of the hardening agent.[52]

Somewhat more detailed results of a macrokinetic study of the structure formation process in epoxide resins (without specification or the hardening composition) have been given in a communication[53] based on certain earlier results of calorimetric studies.[54-56] The authors[53] observed, firstly, that the curves obtained by the method of differential

scanning calorimetry show two "humps", which correspond to the existence of two different main reactions and, secondly, that the $\beta(t)$ relation is described in different ranges of β by different macrokinetic equations; a first-order equation, where $U = 56.6$ kJ mol^{-1}, proved to be fairly suitable for $\beta > 0.3$. For low values of β, the rate of reaction is described by an extremely complex equation incorporating two constants which vary with temperature in different ways, so that there is no single activation energy.

Apparently if one follows the "averaging" procedure, then $U \cong 84$ kJ mol^{-1}, which should be adopted[46,57,58] as the most reliable (most frequently quoted in the literature) value of U for the reactions of epoxide resins; however, it has been pointed out[57] that cases are possible where the temperature variation of the rate of reaction (or t^*) is not described by the Arrhenius relation at all and in another communication[58] even lower values of U have been quoted. (Other values of U and different methods for describing the temperature variation of the hardening of epoxide resins were mentioned above.)

In conclusion of the discussion of the macrokinetics of the hardening of epoxide oligomers, we shall note also certain facts associated with this reaction. Firstly, one should approach the estimation of β_c with caution, since account must be taken of the very considerable (almost by a factor of two) variation of the specific heat and thermal diffusivity in the hardening process.[44] Secondly, the extent of reaction at the gel point β^* varies very appreciably as a function of composition (functionality) of the reaction mass, but as a rule deviates significantly from theoretical estimates. Thus $\beta^* = 0.3-0.47$ for tetrafunctional compounds (instead of the theoretical value of 0.58), which is associated in the general case with failure to take into account the role of secondary reactions.[57] Values of β^*, varying to a very large extent as a function of the recipe for the hardening of the composition, have been published.[59] Naturally, one may not expect agreement between the values of β^* and the instant of the appearance of the gel fraction in the reaction system.[52] In the general case this is apparently associated with the heterogeneity of the network formed.[50,60]

In connection with the development of the "oligomer" technology, numerous studies on the formation of polyurethanes have been carried out. The macrokinetics of this process have been frequently described by a power relation,[61,62] where $n = 1.5$, which was dictated primarily by the convenience of the solution of hydrodynamic problems involving the use of this equation,[62-64] although the authors who proposed it[61] noted themselves that it yields an insufficiently accurate approximation to the real picture of the phenomenon. The kinetics of the formation of polyurethanes have been described[65] by a second-order equation on the basis of the results of measurements by differential scanning calorimetry (DSC). A more complex two-term equation, reflecting both the forward second-order reaction and the reverse first-order reaction, has also been proposed.[66]

In reality the reaction under discussion is fairly complex and a second-order equation, which seemingly should be sufficiently effective at least when a bifunctional hardening agent is employed, is inapplicable to the entire polymerisation process, although it can describe successfully shorter or longer parts of the process.[67] As in the previous case, the most complete and exact description of the $\beta(t)$ relation for polyurethanes can be achieved when a macrokinetic equation of type (2) is employed. However, a significantly new aspect of this equation has been discovered precisely in relation to polyurethanes, namely it was found[68] that the constant $C < 0$ in Eqn. (3), which is the main special case of Eqn. (2). This means that the hardening reaction does not in principle go to completion: when $\beta = C^{-1}$, the rate of the process falls to zero, i.e. the reaction stops at this value of β and this happens under both isothermal and adiabatic polymerisation conditions.

The third main system to which numerous studies on the macrokinetics of the hardening process have been devoted consists of unsaturated polyester resins. In essence, an equation of type (3) has in fact been formulated precisely for such substances as well as epoxide resins,[32,44,69,70] although a simpler power equation had been used in the very earliest publications.[71] Later studies confirmed the validity of the macrokinetic equation (3).[27,28,72-76]

It is of interest to note the following results of these studies. Firstly, the sum of the exponents $m + n = 2$, which reduces the number of "adjustable" constants. Secondly, m and n are almost independent of temperature (the variation of m and n with temperature has been indicated only by Han and Lem[27]). Thirdly, whereas both k_1 and k_2 depend on temperature very markedly, their ratio, characterising the autoacceleration effect in the hardening process, is almost insensitive to changes in temperature. The effective activation energy calculated by many investigators from k_2 is in the range 76 ± 3 kJ mol^{-1}; Han and Lem also quote a value of U calculated from k_2 which is significantly higher (approximately 103 kJ mol^{-1}) than that found from the temperature variation of k_1. Only Yap and Williams[77] quote an appreciably lower value $U \cong 40$ kJ mol^{-1}, found from the temperature variation of the dynamic modulus of elasticity measured at a fixed frequency.

The values of m and n found by different workers are quoted below:

m	0.25	0.33	0.45	0.49
n	1.75	1.67	1.55	1.51
References	[32]	[69]	[70]	[27]

It is of particular interest to note that the critical gel point β^*, defined as the instant when $\eta \to \infty$, depends to a large extent on temperature.[27,28] Apparently this is associated with the influence of temperature on the degree of heterogeneity of the polymer structure formed.

There have been few studies devoted to the macrokinetics of the hardening of systems other than the three enumerated above. These are primarily studies concerning the hardening of the methylphenylsiloxane oligomer[78,79] and other low-molecular-weight organosilicon rubbers.[80] Although limited regions of variation of β can be described by nth order equations (in particular those where $n = 2$),[78] nevertheless extended ranges of values of β necessitate the employment of a macrokinetic equation of type (2) or (3). Incidentally, in certain cases, similarly to what has been observed for polyurethanes, there is a possibility of a situation where $C < 0$.[80]

It is also possible to find other examples of studies on the kinetics of structure formation in various products (not necessarily hardening): in certain instances this can be cyclisation,[81] the copolymerisation of organsiloxane oligomers,[82] various intrachain transformations,[15,83,84] etc. However, the experimental data quoted in these and other reports have not been subjected to a realistic quantitative macrokinetic analysis, in view of which their consideration is somewhat outside the framework of the present review.

Problems associated with the non-isothermal nature of volumetric data occupy an important place in the consideration of the macrokinetics of hardening processes.[10-12]

There is a possibility of three sources of non-isothermal conditions: heat exchange with the ambient medium, the exothermicity of the reaction, and the dissipation of the work due to external friction. When non-isothermal macrokinetics are considered, the cause of the local change in temperature is insignificant, but the external source of heat usually plays a smaller role than the internal sources. The factor associated with dissipative heat evolutions will be considered below in the section devoted to the rheology of the RO. Here we shall concentrate attention on the exothermic effects, particularly since in many cases of practical importance hardening can occur under virtually adiabatic conditions and the temperature rise due to the exothermic nature of the reaction can exceed 100 °C.[85]

It is therefore extremely important to have at one's disposal a method for calculations on hardening under non-isothermal conditions. It is based on the integration of Eqn.(1) taking into account the familiar $T(t)$ relation or the relation specified by the course of the process itself; such a relation is simply formulated in an adiabatic regime:[10,11]

$$T(t) = T_0 + \frac{Q}{c\rho}\beta \quad ,$$

where Q is the total heat of reaction, c the specific heat, ρ the density, and T_0 the initial temperature. In the general case the factor $c\rho$ can depend on T, which requires an independent consideration. When this expression is substituted in Eqn.(1), we obtain an equation containing only one unknown function $\beta(t)$, which can be found by numerical methods. Naturally, the function $T(t)$ is then also found without difficulty. In essence, a completely analogous approach is applicable when the temperature variation of $\dot{\beta}$ is described by a non-exponential equation, for example the familiar Williams–Lundell–Ferry equation.[86] Such a generalised approach is applicable also in the calculation of the variation of viscosity under non-isothermal conditions.[59,87]

The calculation of $\beta(t)$ and $T(t)$ not in an adiabatic regime but under conditions involving partial removal of the heat of reaction to the ambient medium is more complex but quite feasible at the present level of development of computer techniques.[8]

The change in the temperature of the system in the hardening of RO plays such an important role that on this basis it is possible to propose a method for the monitoring and regulation of the technological process by measuring the temperature at separate points in the material being hardened.[88]

Various aspects of the problem of non-isothermal polymerisation (and hardening) have been considered in detail in reviews.[10–12] Here we should like to mention only one phenomenon associated with non-isothermal conditions—the frontal propagation of the reaction as a consequence of the exothermic nature of the process occurring during its "ignition" in a certain local region,[12,89,90] which is one of the most effective methods of carrying out the hardening process. This phenomenon is of general importance and may arise in reactions of different types—radical polymerisation,[91] polymerisation in suspension,[92] etc. It has been shown recently[93,94] that frontal polymerisation can also occur in a combined process, namely when the heat evolution due to the crystallisation of the product formed is superimposed on the exothermic effect of the polymerisation reaction. Although it is still obscure whether such a "running wave" can arise in the hardening process, there is no doubt about its possibility for the related "chemical moulding" process in the activated ionic polymerisation of lactams.

In concluding this section we may note that the macrokinetics of the hardening process in both isothermal and non-isothermal cases can be deduced fairly simply if the reaction takes place in the kinetic region. On passing to the diffusion-controlled region, the situation becomes fundamentally more complex until even the adiabatic temperature rise, characterising the extent of reaction, begins to depend on the rate of stirring characterised by the Reynolds number.[95] Nevertheless, from the standpoint of the mathematical modelling of the RO hardening process as a whole, which is central to the aim of the present review, the situation is simplified by the fact that, so long as the reaction takes place in the supply channels where the flow (and mixing) take place, the viscosity of the medium is low, the material is homogeneous, and one can assume that the initial stages of the hardening process take place in the kinetic region. After the mould in which the RO hardening process proper is completed has been filled, there is no flow at all, the reaction takes place in a non-deformable material, and its macrokinetics therefore reflect the situation which, although possibly in fact complex, is similar for comparable conditions, i.e. for various recipes and different geometrical dimensions of the article.

IV. THE RHEOLOGY (RHEOKINETICS) OF THE HARDENING PROCESS

Two rheological methods are most widely used to follow the kinetics of structure formation in oligomers: from the change in viscosity η and from the change in the modulus of elasticity G, the latter being susceptible to measurement also in the dynamic regime of periodic oscillations.[4,5] The general character of the variation of η and G with time t is illustrated in Fig. 2, the scheme referring to the case where $t > t^*$ and the system undergoing hardening is in a highly elastic (or gel-like) state, so that the hardening reaction can go to completion. It is striking that the modulus of elasticity begins to increase before the time t^* has been reached. This phenomenon is observed when the initial oligomers have a chain sufficiently long to manifest its flexibility or when the formation of cross links is accompanied by an increase in chain length (by a continued increase) when the reactive end groups interact. In such cases the appearance of the condition $G \neq 0$ is due to the formation of physical entanglements, contributing to the network structure, which is formed as a whole as a consequence of the existence of nodes of not only chemical but also physical nature.[96] It is likewise of interest to note that the attainment of t^* is not as a rule reflected in the character of the increase of the modulus, whereas viscosity rises very sharply as this point is approached: at $t \to t^*$ the material loses its fluidity ($\eta \to \infty$).

The character of the variation of the modulus of elasticity during the hardening process, largely discussed in the previous Section, where the quantity β_r, calculated from the relative change in the modulus of elasticity during the hardening process, was proposed as one of the possible parameters for the estimation of the extent of reaction. This in essence exhausts the problem of the macrokinetic description of the hardening process in terms of the change in the modulus of elasticity, particularly if we consider in addition that the measurement of the modulus G belongs to the same series of physical methods for monitoring the RO hardening process as the methods for following the hardening kinetics: by a dielectric procedure from the change in the dielectric constant and in the tangent of the dielectric loss angle (fairly numerous communications have

been published on this topic; among them, mention may be made of those of Badalov et al.[97] and Siemon et al.[98]), from the change in the electrical conductivity of the composition,[99] from the spin–spin relaxation time measured by the pulsed NMR method,[100] from the change in the refractive index,[101] etc.

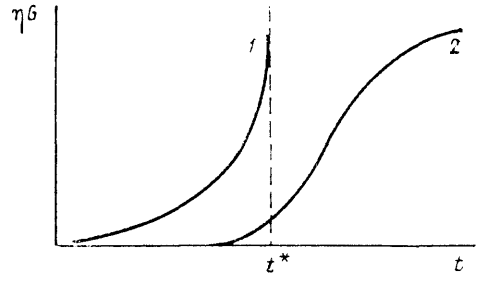


Figure 2. Character of the variation of the viscosity (curve *1*) and the modulus of elasticity (curve *2*) with time in the oligomer hardening process.

However, viscometric measurements in the region where $t < t^*$ are of independent importance. Firstly, in this region all the methods based on the measurement of the density of the network of cross links are unsuitable (because at this stage of the hardening process there is as yet no network); secondly, the measurement of the $\eta(t)$ relation is central for the technological monitoring of the "liveness" and quality of the RO and compositions based on them; thirdly, the quantitative estimate of the $\eta(\beta)$ relation constitutes the basis for the solution of all the hydrodynamic problems associated with flow in the casting channels, with the filling of the mould, etc.; fourthly, and finally, measured viscosities can be compared directly with the molecular characteristics of the test substance, particularly when one is considering not structure formation but an increase in chain length in the interaction of the end groups or in polymer-analogue transformations within the chain.

At the present time equations of two types for the description of the $\eta(t)$ relation in the hardening of RO are being discussed. In equations of the first type it is assumed explicitly that, when $t \to t^*$, the viscosity increases without limit. In equations of the second type a sharp, usually exponential, increase of viscosity is also postulated, but the equation itself formally does not have a singularity.

Among the equations of the first type, power expressions which follow from scaling ideas are of greatest interest:[102–105]

$$\eta \propto (\beta^* - \beta)^{-s} \quad . \tag{4}$$

Equations of this type are applicable over a very narrow range of β near β^* when $(\beta^* - \beta)/\beta^* \ll 1$; since it can be assumed that $\beta \propto t$ over such a narrow range of values of β, instead of Eqn.(4) one formulates a relation which is analogous in structure:

$$\eta \propto (t^* - t)^{-s} \quad , \tag{5}$$

where s is a constant, which, according to the available measurements[105] for two systems of different chemical types, amounts to 0.78 ± 0.05 and this result agrees with the theoretical estimate obtained by Monte Carlo methods.[105]

As regards the question of the relation between the viscous properties of the hardening RO and its molecular characteristics, this has been studied most systematically and solved for polyurethanes, probably because hitherto this has been virtually the only system to which the "oligomeric" moulding method, requiring serious quantitative calculations, has been applied on an industrial scale.

According to the available data,[62,106,107] the dependence of the viscosity η on the weight-average molecular weight $\bar{M}_w$ is expressed by the formula

$$\eta = A\bar{M}_w^a \exp\left(\frac{E}{RT}\right) \quad , \tag{6}$$

where A, a and E are constants. In this approach it is most important that $\bar{M}_w$ should be unambiguously related to the degree of reaction and one obtains $\bar{M}_w \to \infty$ when $\beta \to \beta^*$ and hence $\eta \to \infty$, i.e., firstly, in Eqn.(6) the existence of the gel point is expressed explicitly and, secondly, it is possible to establish an unambiguous function $\eta(\beta, T)$. The latter has been achieved by Castro and co-workers,[108,109] who showed that the entire set of experimental data for the $\eta(\beta, T)$ relation can be described by the generalised formula[108,109]

$$\frac{\eta(\beta, T)}{\eta_0(T)} = \left(\frac{\beta^*}{\beta^* - \beta}\right)^{A + B\beta} \quad , \tag{7}$$

where η_0 is the initial viscosity of the system. Here the influence of temperature on the viscosity has been expressed by the relation $\eta_0(T)$, provided of course that one disregards the influence of temperature on the hardening kinetics. It is also of interest to note that in all the instances investigated the constants A and B assumed the "universal" values $A = 3.5$ and $B = -2.0$.

The existence of such a generalised relation $\eta(\beta, T)$ is specially remarkable, since the reaction under discussion was not carried out under homogeneous conditions but was accompanied by phase separation;[108,110] nevertheless, it has been possible to find a general law governing the variation of viscosity which is valid during the period from the start of the reaction directly until the attainment of the gel point, i.e. for a change of viscosity within a range corresponding to five decadic orders of magnitude.[106]

It is at present difficult to say whether this approach can be extended to other RO. In a qualitative form the answer should probably be yes, but the search for optimum specific quantitative relations still remains an independent and laborious problem. In this respect one must emphasise that there is a possibility of specific problems for each system. For example, in the hardening of polyesters not only an increase of β^* with increasing temperature accompanied by the corresponding displacement of the $\eta(\beta)$ relation towards higher values of β but also the possibility of a flow of the polymer, albeit with a lower viscosity, under conditions where $\beta > \beta^*$, associated with the formation of a highly heterogeneous suspension, has been observed.[27] In the hardening of epoxide resins at different temperatures it was established[58] that the $\eta(t)$ relations can be superimposed by a vertical shift of the plot by an amount a_η and a horizontal shift by an amount a_t. The effective activation energy for viscous flow can be found from the temperature variation of a_η and the corresponding activation energy for the cross-linking process can be found from the corresponding temperature variation of a_t.

Equations of the second type, proposed for the description of the variation of viscosity in the hardening of RO, do not take into account explicitly the existence of the gel point, which is clearly seen in the most widely used of the

equations:[32,33]

$$\eta=\eta_0 \exp(kt) \quad , \tag{8}$$

where η_0 is the initial temperature-dependent viscosity and k a constant characterising the influence of the rate of the chemical reaction on the increase of viscosity, which depends in its turn on temperature, so that one can write

$$\eta_0=\eta_\infty \exp(E/RT) \quad , \tag{9}$$

$$k=k_\infty \exp(U/RT) \quad . \tag{10}$$

Evidently the influence of temperature on viscosity is manifested to a greater extent via k than via η_0, because in the former case the exponential function occurs twice. It also follows from Eqn.(8) that $\eta \to \infty$ only when $t \to \infty$, so that it would seem that the gel point does not exist. Naturally, this is only a formal conclusion, since evidently it is almost always possible to adopt as t^* the time corresponding to the attainment of a certain constant level of viscosity; however, in the solution of applied problems Eqn.(8) may prove to be more convenient than the formulae examined previously, which are formally more rigorous. The equation with argument β can be formulated analogously:

$$\eta=\eta_0 \exp(k'\beta) \quad , \tag{11}$$

$$k' = k'_\infty \exp(E'/RT) \quad . \tag{12}$$

The use of Eqns.(8)–(12) makes it possible to extend the $\eta(t)$ relation readily to the case of hardening under non-isothermal conditions, which has been analysed in detail in a review,[5] so that this question will not be considered here.

Equations of type (11) have indeed been used successfully to describe real hardening systems. Thus Eqn.(11) describes with satisfactory accuracy[53] the $\eta(\beta)$ relation for the hardening of epoxide resins with viscosity varying over a range of three decadic orders of magnitude; here it was found that $k' = 14.1 \pm 1.2$. On the other hand, the effective activation energy E reflecting the temperature variation of viscosity proved to be 90.8 kJ mol^{-1}, which exceeded appreciably the activation energies found from β_c (these were discussed above). This finding is the evident consequence of the fact that E "incorporates" the activation energy for the chemical reaction and viscous flow and these quantities are not additive.[4,111,112]

In view of the practical importance of formulae of the exponential type, it is of interest to establish correlations between their constants and the characteristics of the compositions based on the RO. This is an extremely promising procedure for the quantitative estimation of the quality of the initial materials to be hardened. Numerous instances referring to this approach have been described.[59] In essence, a method for the estimation of the efficiency of catalysts of the formation of polyurethanes in a chain propagation reaction has been proposed on the basis of an analogous idea but without a mathematical treatment.[113]

The use of rheological methods for the investigation of the macrokinetics of the hardening of RO gives rise to certain questions concerning the role of the rate of deformation, namely (1) does the rate of shear $\dot{\gamma}$, at which measurements are made, influence the character of the $\eta(t)$ relation, i.e. the kinetics of the process; (2) what is the form of the rheological equation, i.e. of the dependence of the effective viscosity on the rate of shear $\eta(\dot{\gamma})$ for different stages in the hardening of RO. Apparently there is no general answer to these questions and the answers can be different depending on the nature of the reaction mass.

As regards the role of the rate of shear $\dot{\gamma}$, it has been found that $\dot{\gamma}$ does not usually influence the rate of increase of viscosity. At any rate special studies of this question, referring to the formation of polyurethanes, have shown[108] that, even under phase separation conditions, neither a change in $\dot{\gamma}$ nor a transition from continuous to periodic (only at the instant of the measurement of viscosity) deformation influence the observed character of the increase of viscosity $\eta(t)$. Apparently this situation corresponds to polymerisation under homogeneous conditions, while on passing to the heterogeneous region one should expect deformation to influence the rate of hardening. Thus it has been demonstrated theoretically[114] that in diffusion-controlled reactions an increase of mechanical stresses entails an increase of the rate of the chemical reaction. However, in practice, at least in one instance which has been investigated,[115] exactly the opposite picture has been observed: under phase separation conditions (where the polymer formed was insoluble in the reaction medium), an increase in the rate of deformation led to a significant retardation of the reaction.

However, one should note that the amount of experimental data concerning this problem is very small and the available information is not unambiguous. Thus the data quoted in certain communications[116,117] about the influence of deformation on the rate of radical polymerisation are hardly reliable, since, in the deformation regimes employed in the relevant investigations, dissipative heat evolutions apparently occurred to an extent sufficient to cause the change in rate described above as a result of the deviation from isothermal polymerisation conditions (for a description of the role of dissipative heating, see below).[118]

On the other hand, in general the kinetic role of deformation in RO polymerisation and hardening processes has been clearly studied inadequately: neither the scale nor the limits of the manifestation of the influence of deformation on these processes are known at present.

The influence of the periodic shear deformation on the rate of hardening of RO belongs to the same series of phenomena. This effect was first described a fairly long time ago[119] and it was emphasised that periodic deformation influences not only the kinetics of the hardening process but also the properties of the final products. Subsequent publications[120–122] confirmed these observations; however, here too the question of the quantitative description and limits of this phenomenon remains on the whole open.

An unusual instance of the influence of deformation on the RO hardening kinetics is the situation where intense deformation leads to significant heat evolution, which increases in its turn the temperature of the reaction mass and hence appreciably accelerates the hardening reaction. Observations of this kind have been described in two communications[123,124] and subsequently a complete quantitative theory was developed. It explained this effect, agreed with experiment, and virtually ruled out the need for the consideration of deformation as a direct kinetic factor and it related the role of deformation solely to the non-isothermal conditions in the hardening process caused by it.[125–128] This effect can accelerate the hardening of RO by a factor of many tens but only by virtue of the internal non-isothermicity of the process.

Yet another question related to this range of problems is that of the character of the $\eta(\dot{\gamma})$ relation for RO. In the initial stages of the hardening process reactive oligomers are as a rule Newtonian liquids[109,129] which show no elasticity, although anomalous cases are possible.[130] On the whole, in terms of their rheological properties, RO do not differ from any other polymeric materials[131] and the questions associated with the specific features of the behaviour of filled compositions based on the RO have already been discussed.[5] In the solution of applied

problems associated with the chemical moulding of articles from RO, the flowing liquid is usually seen to be Newtonian but with a viscosity which depends on time or on the degree of reaction;[62,63,129,132] sometimes the so-called power law is employed[64] (similarly to what is done in almost all cases where theoretical problems associated with the flow of thermoplastics are considered[133]). The most complete rheological equation of state of this kind includes terms taking into account the existence of a flow region with a constant (most Newtonian) viscosity and also the transition to the flow region (at sufficiently high rates of shear) described by a power law,[64] the effect of the anomalously viscous flow being determined by the dimensionless product $\lambda\dot{\gamma}$, where the relaxation time λ itself depends on the degree of reaction. The onset of this effect shifts towards lower rates of shear the higher the value of λ, i.e. the greater the extent of the hardening process. Next, for filled compositions based on RO, it is necessary to take into account the existence of the yield point,[134] which incidentally has to be done also for any other filled polymer melts (this question has been discussed in detail in an earlier review[5] and for this reason there is no need to dwell on it here).

Although in the absolute majority of instances where the rheology of RO is the subject under discussion their viscous properties are considered, in reality the question should be understood in a broader sense and other characteristics of such media should also be considered. In the first place mention should be made of their elasticity which is characterised by the appearance of normal stresses σ_W.[131] In an earlier communication[135] it was already stated that the elasticity of the material varies in the region of structure formation to a much greater extent than its viscosity. Few measurements have been made of the changes in the elasticity of RO in the hardening process,[27,28] but they all demonstrate both the role of the normal stresses and the methodological difficulties associated with the measurements of σ_W and the treatment of the results of the measurements: during the hardening process, the volume of the RO diminishes, which looks like the manifestation of negative σ_W, although in reality it is not associated with such stresses, which appear in the shear flow of viscoelastic liquids and are of intrinsic interest from the standpoint of the rheology of polymers and the rheokinetics of structure formation in RO.

V. THE FLOW OF REACTIVE OLIGOMERS

The development of the technology of chemical "reactive" moulding aroused interest in a new class of hydrodynamic problems—the flow of liquids whose rheological properties vary with time. The closest analogue of these problems is provided by problems of non-isothermal flow, where viscosity varies with temperature. In the case of RO non-isothermal conditions constitute only one of the aspects of a more complex general problem of flow with a variable viscosity and it is not even the most important aspect. In essence one is dealing with classical hydrodynamic problems in a new formulation.

Within the framework of the present review, it would be inappropriate to consider the mathematical aspect of the problem but it is useful to deal with fundamental starting points. The general formulation of problems concerning the flow of liquids with a variable viscosity has been described in a number of communications,[62–64,66,129,132,136–140] in which the underlying ideas were in essence identical. They involve the introduction into the equilibrium equation for the variation of viscosity either with time or with the degree of reaction; in the latter case it is necessary to consider in addition the kinetic equation for the extent of reaction. The non-isothermal process conditions, caused not only by heat exchange with the walls but also by the dissipative heat evolutions and the exothermic heat of the hardening reaction, do not introduce any fundamental complications into the solution of the problem,[132] although the size of necessary calculations increases. In all cases it is naturally necessary to employ a fairly powerful computer technique in order to obtain quantitative results. The choice of the rheological equation of state does not play a significant role either. However, the formulation of dynamic boundary conditions on the walls of the channel is of fundamental importance. The usual adhesion hypothesis is by no means satisfactory in all cases. The point is that for hardening compositions a time is always attained where $\eta \to \infty$, which corresponds to the formation of a stationary layer sticking to the walls of the channel, which grows with time until the entire channel is "grown over" by a mass incapable of flowing, which in principle rules out the possibility of a steady flow. To ensure the possibility of a steady flow, it is therefore necessary to adopt the hypothesis of slip near the wall.[64,134]

A rigorous formulation of problems concerning the flow in channels of liquids with varying rheological properties, in flows both with and without a head pressure, makes it possible to determine all the significant hydrodynamic characteristics—such as the distribution of velocities, degrees of reaction, and temperatures along the cross-section and length of the channel, as well as the length corresponding to complete reaction. The latter concept does not occur in normal hydrodynamics, but in this instance it is significant, because it characterises the length of the channel necessary for the attainment of a specified degree of reaction β even at the most unfavourable point (for hardening RO, it must be evidently smaller than β^*). The concrete results of calculations associated with such problems are extremely non-trivial and are frequently unexpected; they demonstrate the existence of extremely unusual characteristics of the flow, but their consideration constitutes a separate task and here it is useful to limit the description to initial problems in the formulation and not to undertake a hydrodynamic analysis.

However, whereas problems concerning flow in filled channels are fairly clear in their formulation, those associated with flow in an incompletely filled channel or with the flow of a hardening liquid having a free surface at the front of the flow are not quite so self-evident. Clearly, for the technology of chemical moulding, this problem is no less important than that of the steady flow through fully filled channels, which necessitated the analysis of such problems.

From numerous direct observations, it has long been known that in the region of the front of the flow there exists the so-called "fountain" effect,[63,66,141–143], which consists in the spreading of the liquid from the axial zone to the walls and this leads to a significant equalisation of the residence times of various particles of the liquid in the channel and hence to a considerable change of the entire hydrodynamic arrangement compared with a one-dimensional flow. Thus the flow near the front becomes two-dimensional in contrast to the one-dimensional flow in a filled channel. A rigorous formulation of this problem is very complex and virtually all the investigators dealing with it have pointed out that there is no need for such a rigorous approach, because it is sufficient to adopt an approximate empirical model of the flow of liquid from the centre to the wall based on experimental data[66] and the specification of the flow pattern in the front in greater detail does not introduce

fundamental changes into the final picture. Since there is no doubt that the fountain effect exerts a significant influence on the entire situation in the filled channel (or mould), including the distribution of residence times, degrees of reaction, and molecular and rheological characteristics of the test substance, the choice of an adequate model of this phenomenon remains an extremely important problem in the theory of chemical moulding.

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The initiation and development of the modern technology of the production of polymer articles by chemical moulding have generated a whole series of new problems. The chemical problems associated with the requirements which must be met by the properties of the resulting material have been supplemented by physicochemical problems associated with the necessity to ensure specified hardening kinetics and also mechanical problems, since the rheological characteristics of the products and the characteristics of the flow of the moulded compositions have a decisive influence not only on the properties of the final product but sometimes even the very feasibility of the technological process.

Overall, all these factors make it possible to construct a mathematical model of the hardening of RO and compositions based on them, which enables us to achieve the most important aim (on passing to large-scale technology): to control the process in order to ensure the required quality of the material in combination with the optimisation of the techno-economic process parameters. The transition from general characteristics, which in many respects have already been elucidated, to concrete quantitative results, which can be used in practice requires nevertheless very careful laboratory studies for an adequate quantitative description of the rheology of RO and the macrokinetics of the hardening process in relation to specific materials. The industrial realisation of the results of such research ensures the development of a stable and effective technological reaction-moulding process.

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