

Use of the Branching Theory in Approximation of Viscosity of the Thermoset: Phenol–Formaldehyde Resin and Boron Oxide

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ABSTRACT: The kinetics of step polycondensation is described on the basis of the classical branching theory. A simple method is proposed for calculation of the average longest length (L) of the linear chain in a crosslinked molecule under arbitrary functionalities of original monomers. A viscosity of the system is represented as a product of a structure factor by a friction factor. The latter was taken as the Arrhenius exponent. The structure factor was chosen in the form of a power function of L . The method has been used for the approximation of the viscosity of phenol–formaldehyde resin in the course of curing by boron oxide. An activation energy of 11.8 kcal/mol was found by the method of a best matching of the structure factor for the different viscosity kinetic isotherms in the scale of a reduced time of the reaction. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 319–328, 1997

INTRODUCTION

Prediction of a changing of the rheological state of polymer compositions in time under nonisothermal conditions is of value in the technology of polymer molding¹ and obtaining foam materials on the base of thermosets. The cure kinetics is of particular interest while synthesizing the polymer intumescent fire-protective coatings and paints.^{2,3} A general principle determining the effect of such coatings consists of a multiple increase of a volume of a polymer composition due to an intensive foam formation under the action of a flame or heat. A fast solidification of the polymer composition is the main condition of the stabilization of the foam, which is why the synchronization of the curing reaction and the reaction of gas formation is a vital factor determining the effect of

the coatings. We shall consider a number of problems concerning the intumescent coatings in the next article,⁴ while the goal of present article is to discuss a method that allows one to estimate the rheological state of thermosets, which undergo a step polycondensation, through parameters of the curing reaction and the reduced time of the reaction. The system consisting of phenol–formaldehyde resin and boron oxide will be considered as a particular illustration. Note that this system can serve as an example of intumescent coating with a coefficient of the volume increase equal to ≈ 20 –30.

THEORETICAL APPROACH

Curing Kinetics

A stepwise polycondensation $A_f + B_g$ can be described from the viewpoint of the classical branching theory.^{5–7} In the latest decades, efforts were made to explain the formation of branching polymer structures by using the percolation the-

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ory.⁸ Despite the serious arguments⁹ against the classical Flory and Stockmayer theory, there are still no grounds to call in question its simple and often confirmed experimentally^{10,11} criterion of gel formation. Discussing the kinetics of nonlinear polycondensation, we shall be guided by the theses of the classical theory.

According to the branching theory, the formation of a polymer network does not lead to the decelerating of the reaction between the functional groups of a compound A_f with the functionality f and a compound B_g with the functionality g . In the absence of the substitution effect, the degree of conversion of functional groups of any of these compounds is determined by the kinetics of the second-order reaction. For example, for the extent of conversion of the A groups, we have

$$dp/dt = [k_s \exp(-E_s/RT)/V] \times gN_B(1-p)(1-\beta p) \quad (1)$$

where R is the gas constant; T is the temperature; $p = (A - A_t)/A$ is the extent of conversion; A and A_t are, respectively, the initial and remaining numbers of groups in the compound A_f in moles; V , the system volume; N_B , the initial amount of the B_g compound in moles; k_s , the reaction rate constant; E_s , the activation energy; and β , the stoichiometric ratio. The value of β connects the extents $p = p_A$ and p_B of the conversions of the groups of the A_f and B_g compounds as

$$p_B = \beta p_A = \beta p, \quad \beta = fN_A/gN_B$$

where N_A and N_B denote the initial mol amounts of the A_f and B_g compounds in the reaction blend, and f and g are functionalities. The system volume is expressed by the formula

$$V = M_A N_A / d_A + M_B N_B / d_B$$

where M_A , M_B and d_A , d_B are the molecular weights and the densities of the A_f and B_g compounds, respectively. Denoting

$$\bar{k}_s = k_s g N_B / (M_A N_A / d_A + M_B N_B / d_B) \quad (2)$$

one may write the solution of eq. (1) for the case of nonisothermal kinetics as follows:

$$p = [1 - \exp((\beta - 1)\bar{k}_s \tau)] / [1 - \beta \exp((\beta - 1)\bar{k}_s \tau)] \quad (3)$$

where τ is the reduced reaction time:

$$\tau = \int_0^t \exp[-E_s/RT(t)] dt$$

or $\tau = \int_{T_0}^T \exp(-E_s/RT)(dt/dT) dT \quad (4)$

where T_0 is the initial temperature.

The variation of the concentrations of the particles of different composition and polymerization degree is described by a system of differential equations of an infinite order. Since each of these equations is autonomous, an immediate molecular weight distribution is determined unambiguously by the extent of conversion p . An analytical solution of the problem concerning the molecular weight distribution can be obtained¹² only in the case of one-component polycondensation ($A_f + A_f$), although the change of molecular weight distribution with the conversion extent p can be calculated also in a general case by the Monte Carlo method.¹³ Unfortunately, there are no experimental methods of determination of molecular weight distributions of the crosslinked polymers and their calculation is exclusively of a theoretical interest. Only the integral characteristics of distributions, e.g., an average-weight molecular weight, M_w , can be valuable for practical applications.

The expression for M_w can be deduced by different, although equivalent methods. The recursive Miller and Macosko method¹⁴ seems to be the simplest and most efficient one, which for the general case of nonlinear polycondensation under consideration leads to the formula

$$M_w = \frac{M_A^2 g [p_B + p_A (g - 1) p_B^2] + M_B^2 f [p_A + p_B (f - 1) p_A^2] + 2 p_A p_B M_A M_B g f}{(p_B g M_A + p_A f M_B) \times [1 - p_A p_B (f - 1)(g - 1)]}$$

According to the Flory theory, gel formation is determined by the condition $M_w \rightarrow \infty$. This condition is fulfilled if

$$G = 1 - \beta p^2 (f - 1)(g - 1) = 0 \quad (5)$$

At the point of gelation ($G = 0$), the viscosity of the composition should tend to infinity. Thus, the dynamic changes of viscosity give one of the methods of experimental testing of the criterion

expressed by eq. (5). Modern studies¹¹ have shown that it holds true.

Equation (5) gives a simple method of calculation of the reaction rate constant \bar{k}_s on the basis of the determination of the points of gel formation at different temperatures. Combining the condition

$$p_r = [\beta(f - 1)(g - 1)]^{-1/2} \quad (6)$$

and eq. (3), we find an expression for the rate constant through the reduced reaction time τ_r and the conversion extent corresponding to gelation

$$\bar{k}_s = \tau_r^{-1}/(\beta - 1)\ln[(p_r - 1)/(p_r\beta - 1)] \quad (7)$$

The value of τ_r does not depend upon the temperature while physical time t_r preceding the gelation significantly depends upon the temperature and for isothermal conditions is determined by the formula

$$t_r = \tau_r \exp(E_s/RT) \quad (8)$$

Approximation of a Viscosity of Thermosets Under Nonisothermal Conditions

With the above assumptions, the most important parameter for the calculations is the reduced reaction time τ . This determines unambiguously the conversion extent p , which, in turn, according to the branching theory, determines the immediate molecular structure of the material.

The immediate mechanical properties of the composition, e.g., its dynamic viscosity η , are determined by both the structure of the material and temperature, i.e., $\eta = \eta[T, p(\tau)] = \eta(T, \tau)$. Since the properties of a small amount of a polymer should not depend upon the way of the process by which it reached the state with the parameters (T, τ) , in any of the planes $\eta \div \tau$ ($T = \text{const}$) or $\eta \div T$ ($\tau = \text{const}$), the viscosity should be an unequivocal function of one of the variables τ or T . We note that in the systems, where several reactions with different activation energies take place, the immediate molecular composition of the melt would depend upon the way of the process and the attempts of quantitative approximation of the viscosity dependence upon the time for the nonisothermal conditions would probably be futile.

The modern problems of approximation of chemorheological data are considered by Bitsrup

and Macosko.¹¹ The authors proceed from the general principle of representing the viscosity as product of the friction factor ξ by the structure factor F :

$$\eta = \xi F$$

The structure factor F does not depend upon the temperature and is determined by the integral characteristics of the molecular-weight distributions. At a point of gelation, $F \rightarrow \infty$.

The friction factor in the general form¹⁵ can be expressed as follows:

$$\xi = \xi_0 \exp\{B/[f_g + a_1(T - T_g)]\} \quad (9)$$

where a_1 is a factor of liquid expansion; f_g , a free volume at the glass-formation temperature T_g ; B , a free volume in the proximity of a segment necessary for that segment to make a jump; and ξ_0^{-1} , an inherent jump factor. Empirical coefficients are considered as being temperature-independent. The critical temperature T_g is very sensitive to the average molecular weight of a polymer and, therefore, depends on the conversion extent p . Since p , in turn, depends on reduced time τ and, consequently, to a great extent is determined by the form of the function $T(t)$, formula (9) obviously does not allow one to separate explicitly the temperature-dependent and structural components of the viscosity.

One may assume that the functions $T_g(p)$ and $F(p)$ are always monotonously increasing ones; then, the viscosity is an unequivocal function of the system state. Under isothermal conditions with an increase in time, both the friction factor ξ (due to decrease of segment mobility) and the structure factor F (due to enlargement of molecules) increase. In this situation, there arises a question as to whether an unlimited growth of viscosity is due to the transition of the system into the glasslike state or into the gel.

Isothermal solidification was studied in detail by Gillham et al.^{16,17} The authors discovered that there exists the critical temperature $T_g^{(\text{gel})}$ below which the composition transforms directly into glass, omitting the gel-like (rubber-like) state. At temperatures higher than $T_g^{(\text{gel})}$, the system first transforms into a gel and then into a glass. Furthermore, there exists a critical temperature of glass formation T_g^∞ , that if higher, the system does not transform into glass, but transforms into a gel in accordance with the criterion expressed by eq.

(5). At very high temperatures, the reactions of destruction and coke formation begin to occur in the system. These processes at high temperatures proceed much faster than does polycondensation, since they are characterized by higher activation energies E_{de} and E_{co} (e.g., Ref. 17, for the epoxy systems $E_{de} \approx 50\text{--}75$ kcal/mol and $E_{co} \approx 36\text{--}42$ kcal/mol, while $E_s \approx 11\text{--}15$ kcal/mol). Thus, at high temperatures, the system can transform from liquid straight into coke.

A question of attaining of the glasslike or rubberlike (gel-like) state under nonisothermal conditions is very complex and should be solved individually for each thermoset. Unfortunately, the quantitative theory of the glass formation is very weakly developed. The only rational approximation, which holds true only for stoichiometric mixtures ($\beta = 1$), is known. This is the Di Benedetto¹⁸ equation that can be represented for the nonisothermal conditions as follows:

$$T(t) = T_g[p(\tau)] \\ = T_{g_0} + \frac{T_{g_0}(E_x/E_m - F_x/F_m)p(\tau)}{1 - (1 - F_x/F_m)p(\tau)} \quad (10)$$

where E_x/E_m is a ratio of the lattice energies for a crosslinked and uncrosslinked polymer, respectively; F_x/F_m is the corresponding ratio of segmental mobilities; and T_{g_0} is a temperature of glass transition at no reaction. It is obvious that $T_g^\infty = T_g(1)$. It is noteworthy that the extent of conversion p_r at the point of gel formation, in accordance with eq. (5), does not depend upon the form of the $T(t)$ curve, whereas the conversion extent at the moment of glass formation depends on the rate of heating of the system. Equations (3), (4), and (10) form an algebraic system, on the basis of which the values of $T = T_g$ and $p = p_g$ corresponding to eq. (10) can be calculated. With increase in the heating rate, the values of τ_g , with which eq. (10) is fulfilled, are shifted toward higher temperatures. Since the function $T_g(p)$ is monotonous, with increase in the heating rate, a tendency for an increase in the both T_g and p_g should be observed. If $p_g > p_r$, the system first transforms into a gel and then into a glass. If $p_g < p_r$, the system transforms directly into a glass. At high heating rates, eq. (10) should not have a solution, indicating that the system can only be in the liquid or viscoelastic states. The epoxy systems, for instance,¹⁹ do not transform into the glasslike state upon the rates of linear heating surpassing $\approx 8^\circ\text{C}/\text{min}$. It is known that at low

heating rates a “falsification” of the chemical kinetics takes place.¹⁹ It ceases to conform to eq. (1) and is determined by eq. (10). In other words, the conversion extent changes with temperature so that the system always remains on the verge of transition from the liquid (or elastic) state into the glasslike state. In this case, a polymer, remaining a solid, can be crosslinked so deeply that its next melting can occur only as a result of chemical destruction.

For nonstoichiometric mixtures, the Di Benedetto equation does not hold true and it is impossible, at present, to predict their behavior. Upon deviation of β from the unity, the critical temperature T_g seems to have to decrease, since a part of low molecular fractions of the excessive component increases, which, in principle, can limit T_g . Anyway, eq. (5) is the only orientation in the theory of curing the nonstoichiometric mixtures. We shall further assume that the unlimited growth of viscosity ($\eta \rightarrow \infty$) is due to the structure factor ($F \rightarrow \infty$).

If the temperature is greater than $T_g + 50^\circ\text{C}$, then¹⁶ the Arrhenius law can be used for approximating the viscosity, viz.:

$$\eta = \eta_0 \exp(E_\alpha/RT)F \quad (11)$$

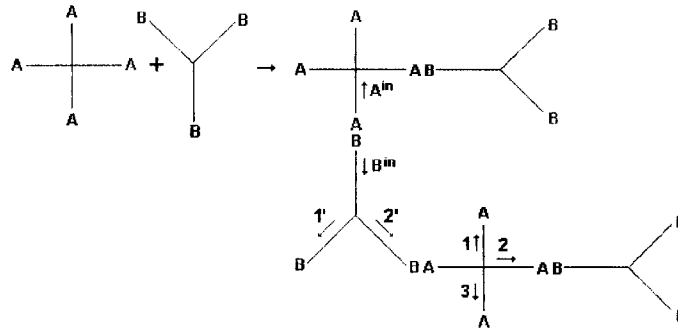
where E_α is the activation energy of the viscous flow and η_0 is an empiric parameter that within a narrow temperature range can be considered to be a constant. Equation (11) expresses a known law of logarithmic “additivity.”^{20,21} Equation (11) is more convenient in comparison with eq. (9) because the former explicitly separates the temperature and structural factors of viscosity. The activation energy $E_\alpha \approx 10$ kcal/mol seems to be suitable for many polymer systems.²⁰ This value will be used below as a reasonable estimation.

There are several ways to give an empirical presentation of F . For example, F can be considered as a function of reduced time τ or as a function of the conversion extent p . Unfortunately, in these cases, any empirical formulas for F will hold true only for mixtures of a definite composition. The coefficients of these formulas cannot be constant upon the change of β . The methods of a representation of F through the integral parameters of the molecular weight distributions have advantages because these provide for the approximation of viscosity with different β . The Lipshitz–Macosko formula²² can serve as an example of

such approximations: $F = M_w^\alpha$, where $\alpha \approx 3.4$. However, the method of expression of F through an average longest length L of the polymer chain improves the correlation in the calculations of viscosity. So, one may expect that the equation

$$\eta = \eta_0 \exp(E_a/RT) L^\alpha \quad (12)$$

where α is an empirical parameter ($\alpha \approx 3.4$), will provide for a good approximation with different β within a wide range of p up to the point of gelation. Since $L = L[p(\tau)]$, eq. (12) is a generalized



Following the method of Miller and Macosko, let us introduce a probability of an event that in the direction B^{in} "looking in" the B_g parent molecule chosen at random there will be disposed along some linear chain more than one B_g molecule (see above scheme):

$$\begin{aligned} P_B^{\text{in}}(L_B^{\text{in}} \geq 1) \\ = 1 - \{1 - p\beta[1 - (1 - p)^{f-1}]\}^{g-1} \end{aligned} \quad (13)$$

where p is a conversion extent of the A groups that is equal to probability of joining the functional groups of the A type to the groups of the B type in one of the directions 1, 2, 3, ..., $f - 1$, and $p\beta[1 - (1 - p)^{f-1}]$ is the probability of the continuation of the chain $-B_g-A_f-B_g-\dots$ in one of the directions $1', 2', \dots, g - 1$.

Let $pP_B^{\text{in}}(L_B^{\text{in}} \geq N)$ be the probability of a continuation of a chain of the length $L_B^{\text{in}} \geq N$ in one of the directions 1, 2, ..., $f - 1$. When replacing p in the round brackets of formula (13), by the latter probability, we obtain the probability of an event that in the direction B^{in} along any chain there will be more than $N + 1$ of B_g molecules, i.e.:

$$P_B^{\text{in}}(L_B^{\text{in}} \geq N + 1) = 1 - \{1 - p\beta[1$$

method of expression of viscosity as a function of a temperature and reduced time.

An Average Longest Linear Chain in a Branching Molecule

Miller et al.^{23,24} deduced the formulas for the calculation of L on the basis of the recursive method following from simple relationships of the probability laws. These formulas^{23,24} were obtained for the case $f = 3, 4$ and $g = 2$. Here, we shall consider a general case when f and g are arbitrary. Let us imagine a situation when the molecules A_f and B_g interact with each other by the scheme

$$- (1 - pP_B^{\text{in}}(L_B^{\text{in}} \geq N))^{f-1}]\}^{g-1} \quad (14)$$

Similar formulas can be obtained for the direction A^{in} :

$$\begin{aligned} P_A^{\text{in}}(L_A^{\text{in}} \geq 1) \\ = 1 - \{1 - p[1 - (1 - \beta p)^{g-1}]\}^{f-1} \end{aligned} \quad (15)$$

$$\begin{aligned} P_A^{\text{in}}(L_A^{\text{in}} \geq N + 1) = 1 - \{1 - p[1 \\ - (1 - \beta pP_A^{\text{in}}(L_A^{\text{in}} \geq N))^{g-1}]\}^{f-1} \end{aligned} \quad (16)$$

Let us neglect the difference in the end groups. Then, we can express the maximum chain lengths in the directions $B^{\text{in}}, A^{\text{in}}$, as was done by Macosko and Valles:

$$\bar{L}_B^{\text{in}} = 2 \sum_{N=1}^{\infty} P_B^{\text{in}}(L_B^{\text{in}} \geq N) \quad (17)$$

$$\bar{L}_A^{\text{in}} = 2 \sum_{N=1}^{\infty} P_A^{\text{in}}(L_A^{\text{in}} \geq N) \quad (18)$$

We shall not make any difference between the types of the connected molecules and we shall express the chain length as a total number of the connected molecules in the chain; that is why the multiplier 2 appears in formulas (17) and (18).

In other words, the length of the chains A_f-B_g is accepted to be equal to 2. In Ref. 23, the chain length is calculated as the number of the molecules of B_g type ($g = 2$) in this chain. That is why the chains $-B_g-A_f-B_g-A_f$ and $-B_g-A_f-B_g$ are considered indiscernible. With such an approach, it is natural that the end groups are not taken into account.

A total number of the molecules in the chain of the maximum length, passing through molecules B_g and A_f , is expressed as

$$L_B = \bar{L}_B^{\text{in}} + \beta p \bar{L}_A^{\text{in}} + 1 \quad (19)$$

$$L_A = \bar{L}_A^{\text{in}} + p \bar{L}_B^{\text{in}} + 1 \quad (20)$$

It is noteworthy that upon $L_B \gg 1$ and $g = 2$ formulas (13), (14), (17), and (19) agree with the expressions given by Valles and Macosko.²³

When calculating L , analogously with the calculation of the average molecular weight,¹⁴ it is necessary to take into account the probabilities that any molecule chosen at random is a molecule of B_g or A_f . These probabilities are equal to the mol % of B_g and A_f in the reaction mixture. Therefore, the average maximum chain length will be equal to

$$L = L_B x_B + L_A x_A \\ = [L_B + (g/f)\beta L_A] / [1 + (g/f)\beta] \quad (21)$$

The procedure of summing the series in eqs. (17) and (18) requires large expenditures of computer time. However, the calculations can be significantly accelerated if the sums are substituted by integrals, which, in turn, are expressed analytically. To increase accuracy, it is preferable to sum up several first terms of the series by a direct method. So, we represent eqs. (17) and (18) as follows:

$$\bar{L}_B^{\text{in}} = 2 \sum_{N=1}^{J-1} P_B^{\text{in}}(L_B^{\text{in}} \geq N) + 2I_1 \quad (22)$$

$$\bar{L}_A^{\text{in}} = 2 \sum_{N=1}^{J-1} P_A^{\text{in}}(L_A^{\text{in}} \geq N) + 2I_2 \quad (23)$$

where I_1 and I_2 are integrals, which are taken analytically, and J is a number determining the accuracy of the calculation of \bar{L}_B^{in} and \bar{L}_A^{in} .

Let us denote $z_N^{(1)} = P_B^{\text{in}}(L_B^{\text{in}} \geq N)$, $z_N^{(2)} = P_A^{\text{in}}(L_A^{\text{in}} \geq N)$. Expanding the right parts of eqs. (14) and (16) in the Taylor series and omitting

the terms higher than the second power, we obtain

$$z_{N+1}^{(i)} \approx (1 - G)z_N^{(i)}(1 - H_i z_N^{(i)}) \quad (i = 1, 2)$$

where

$$G = 1 - \beta p^2 (f - 1)(g - 1)$$

$$H_1 = p[(f - 2) + p\beta(g - 2)(f - 1)]/2$$

$$H_2 = p\beta[(g - 2) + p(f - 2)(g - 1)]/2$$

It is convenient to introduce the new variable $y = N - J$. Let us assume that the discrete functions $z_N^{(i)}$ are approximately equal to the continuous functions $z_i(y)$ of y , i.e., $z_N^{(i)} \approx z_i(y)$ ($i = 1, 2$) with $y = N - J$.

Substituting the finite increments by derivatives, we obtain the following differential equations:

$$z_{N+1}^{(i)} - z_N^{(i)} \approx dz_i/dy \\ = (1 - G)z_i(1 - H_i z_i) - z_i \quad (i = 1, 2) \quad (24)$$

with the boundary conditions:

$$z_i(0) = z_i^{(j)} \quad (i = 1, 2)$$

$$z_i|_{y \rightarrow \infty} = 0 \quad (i = 1, 2)$$

Solving eqs. (24), we find for integer y ($y = 0, 1, 2, \dots$) the following estimation:

$$z_{J+y}^{(i)} \approx z_i(y) = z_j^{(i)} / \{\exp(Gy) \\ + H_i z_j^{(i)}(1 - G)[\exp(Gy) - 1]/G\} \\ (i = 1, 2) \quad (25)$$

Functions (25) are easily integrated analytically:

$$I_i = \sum_{N=J}^{\infty} z_N^{(i)} \approx \int_0^{\infty} z_i(y) dy \\ = [1/(1 - G)H_i] \ln\{1 + (1 - G)H_i z_j^{(i)}/G\} \quad (26)$$

EXPERIMENTAL

Novolac phenol-formaldehyde resin (PhFR, Kemerovo, Russia) with an average-weight molecular weight ≈ 500 and boron oxide obtained by the tempering of boric acid (pure for analysis) in a porcelain crucible for 2 h at 600°C are used as the reagents. When H_3BO_3 is used instead of B_2O_3 ,

an isolation of the gas (H_2O) in the polymer mass is observed, which hinders the reproducibility of the viscosity measurements. At the same time in the case of B_2O_3 , the polymer melt remains practically homogeneous up to the point of gelation.

The viscosity measurements were accomplished using a rotation viscosimeter^{25,26} made on the basis of an asynchronous executive engine-generator with a hollow rotor.²⁶ Viscosity was studied at a constant deformation rate, i.e., at a constant rate of rotations of the stress transducer ($\approx 2/\text{s}$). The latter was made as a cone of 0.13 radians, 40 mm height. The viscosimeter was calibrated by the viscosity of solutions of sugar in glycerin and the viscosity of Canadian balm, which, in turn, were measured by the absolute Stokes method. Upon constant rotations, the voltage on the driving winding of the engine depends linearly upon the viscosity.²⁵

In the experiment, a composition was used which consisted of 20% by weight of B_2O_3 and 80% by weight of PhFR. The reagents were mixed in a quartz cuvette at $\approx 120^\circ\text{C}$ for 3 min. During this time, B_2O_3 has time to become dissolved in the resin. The extent of conversion of the curing reaction at 120°C for 3 min is so small that it can be neglected. Then, the cuvette was immersed in a bath with silicon oil, heated to the temperature of measurements ($\approx 180\text{--}230^\circ\text{C}$). To avoid oxidation of the resin by air oxygen, the free room of the cuvette was filled by Ar. Heating of the cuvette proceeded for ≈ 30 s. This time is not long in comparison with the moment t_r of the gel formation.

At the initial moment, a viscosity of the system is so small (we suppose $\approx 0.5\text{--}5$ Pa-s) that at the beginning of the measurements it is not possible to balance the voltage on the winding of the engine. However, after reaching some threshold of viscosity ($\approx 20\text{--}50$ Pa-s), as a result of the curing reaction, the measurements become stable. A region of the viscosity chosen (see below) for the quantitative analysis (100–3000 Pa-s) corresponds to the stable measurements. The upper limit of the measured viscosity (≈ 3000 Pa-s) is determined by the power of the engine. After reaching the upper limit of viscosity, the rotations of the stress transducer first slow down and then stop.

RESULTS AND DISCUSSION

The Calculation of a Length of an Average Longest Linear Chain

At the point of gelation, the series in eqs. (17) and (18) must diverge, i.e., $\bar{L}_B^{\text{in}} \rightarrow \infty$ and $\bar{L}_A^{\text{in}} \rightarrow \infty$.

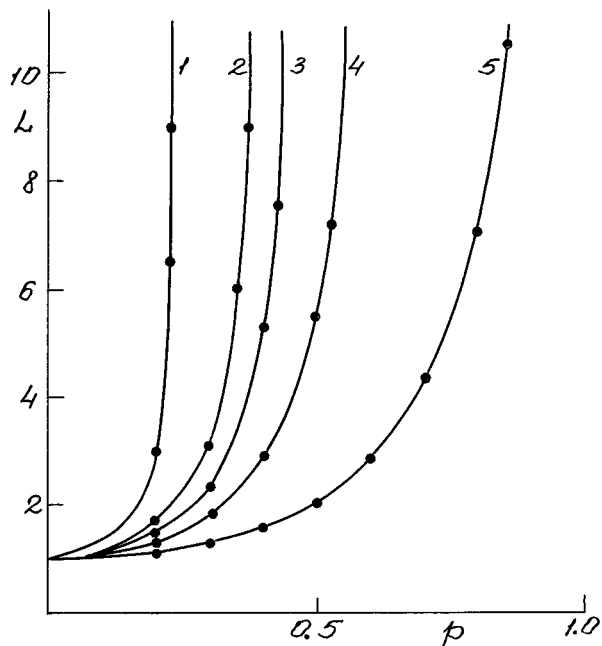


Figure 1 The dependence of the maximum length of the polymer chain upon the conversion degree for the component B_g with the functionality $g = 2$ upon different functionalities f of the component A_f : (1) 20; (2) 8; (3) 6; (4) 4; (5) 2. The points and the solid lines are the results of calculations using eqs. (17) and (18) and eqs. (22) and (23), respectively.

However, it is rather difficult to find a criterion of the divergence directly from eqs. (17) and (18). On the other hand, one can expect that the accuracy of eq. (24) will be greater the larger are the values of \bar{L}_B^{in} and \bar{L}_A^{in} . Therefore, eqs. (17) and (18) and eqs. (22) and (23) have common asymptotes. This conclusion is confirmed by numerical calculations.

The numerical results show that with $J = 5$ (see Figs. 1 and 2) an error of the L calculation by using eqs. (22) and (23) instead of eqs. (17) and (18) does not exceed 1% for all p values. One can see from eq. (26) that $I_i \rightarrow \infty$ ($i = 1, 2$) and, respectively, $L \rightarrow \infty$, when $G \rightarrow 0$. Thus, the criterion of gelation corresponding to eq. (5) is common for both M_w and L .

In the proximity of the gel point ($p \rightarrow p_r$, $G \rightarrow 0$), the function $L(p)$ has the following asymptotic form:

$$L(p) \approx c_1 - c_2 \ln(G) \quad (27)$$

where c_1 and c_2 ($c_2 > 0$) are some constants. Equation (27) agrees with the result of Zimm and Stockmayer,²⁷ obtained for the hydrodynamical

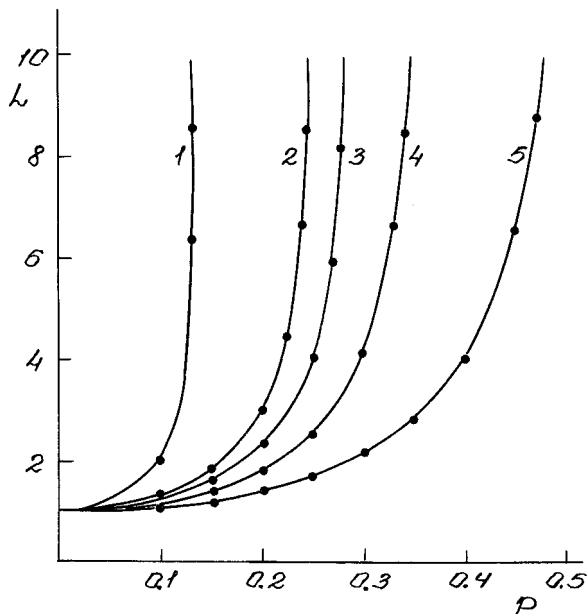
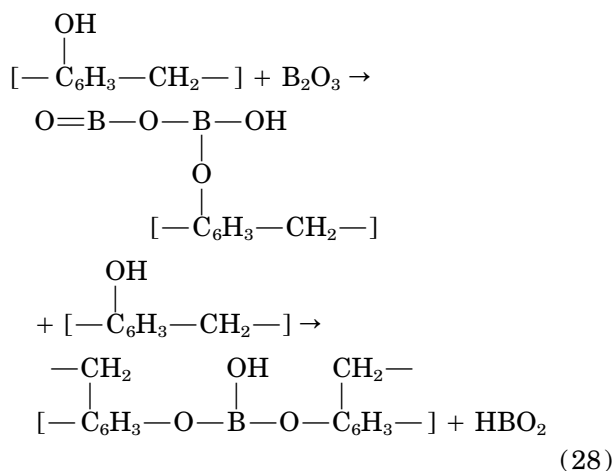


Figure 2 The same as in Figure 1 with $g = 3$ and f : (1) 30; (2) 9; (3) 7; (4) 5; (5) 3.

radius of the branching molecules. Similar to the maximum length of the chain L , as $p \rightarrow p_r$, the hydrodynamical radius becomes linearly dependent upon $\ln(G)$. Thus, it can be expected²³ that the formulas for the hydrodynamical radius and the formulas for L in treating the experimental data will lead to similar results.

Analysis of the Cure Kinetics in the System: Phenol-Formaldehyde Resin + B_2O_3

Solidification in the system under consideration takes place as a result of the formation of ether bonds. We shall assume the following formal scheme of the reaction of interaction of B_2O_3 with PhFR:



The molecule HBO_2 can be connected with the resin again. The coordination-unsaturated derivatives of boric acid are strong Lewis acids.²⁸ Thus, in principle, the reaction of B_2O_3 with hydroxyl-containing compounds like ROH, where R is an organic radical, can proceed up to the formation of the anion $[\text{B}(\text{OR})_4]^-$. However, if R is a fragment of novolac resin, as is the case in scheme (28), the formation of spatial structures with the coordination 4 of boron atoms is hardly possible due to sterical hindrances. We shall assume that the functionality of boron atoms is equal to 3 ($g = 3$). Thus, the molecule B_2O_3 can be considered as a unity of the two particles with the functionality of 3 and the molecular weight of $M_B = \frac{1}{2}M_{\text{B}_2\text{O}_3} = 34.8$ g. The novolac resin used in the experiments represented an oligomer with a degree of polymerization of 5. We assumed in the calculations that $M_A = 518$ g, $f = 5$.

The measurements of viscosity in the system were carried out by a rotation viscosimeter at four temperatures (see Fig. 3). In the experiments, a composition consisting of 20% by weight of B_2O_3 + 80% by weight of PhFR was used. It is noteworthy that this composition is optimal for the foaming of the coating.⁴ With our assumptions, it corresponds to the stoichiometric coefficient $\beta = 0.45$.

While using H_3BO_3 instead of B_2O_3 , an isolation of the gas (H_2O) in the polymer mass is observed, which hinders the reproducibility of measurements, whereas in the case of B_2O_3 addition, the polymer melt remains practically homogeneous up to the point of gel formation.

The activation energy of the curing reaction was determined by the method of a best matching of the curves $F(p)$ for different temperatures in

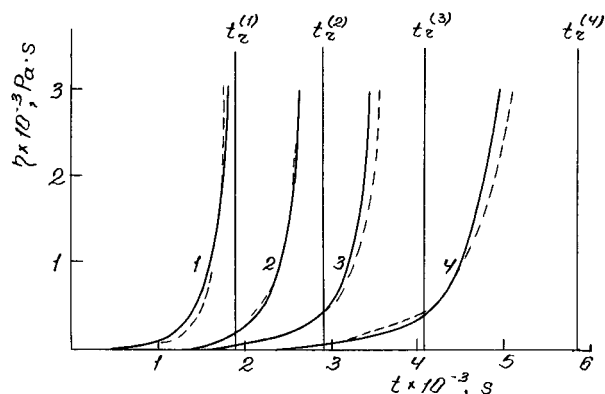


Figure 3 The dependence of viscosity upon time for the phenol-formaldehyde resin with 20% by the weight addition of B_2O_3 at T ($^{\circ}\text{C}$): (1) 225; (2) 208; (3) 195; (4) 182.

the scale of the reduced time. The structure factor $F(p)$ was calculated as $\eta \exp(-E_s/RT)$, where $E_s = 10$ kcal/mol. The dependence of $\ln F$ on the time at four temperatures is presented in Figure 4. On each of those dependencies $j = 1, 2, 3, 4$, there were chosen 5 points t_i ($i = 1, 2, \dots, 5$) with the equal ordinates. The value of E_s was calculated by the minimizing of the following function:

$$\Delta(E_s) = \sum_{i=1}^5 \sum_{j=1}^4 [t_i^{(j)} \exp(-E_s/RT_j) - \bar{\tau}_i]^2$$

where $\bar{\tau}_i = (\frac{1}{4}) \sum_{j=1}^4 t_i^{(j)} \exp(-E_s/RT_j)$. The procedure of the minimizing leads to $E_s = 11.8$ kcal/mol. Having calculated the average values of the reduced time for each coordinate, one can return to the scale of dimensional time $t_i^{(j)} = \bar{\tau}_i(E_s/RT_j)$ and build the curves corresponding to the best matching of the functions $\ln F$ in the scale of reduced time (see the dotted lines in Fig. 4).

The time of gel formation is the moment of infinite growth of the viscosity. It seems that the time moments when viscosity reaches the values of $\approx 3 \times 10^3$ Pa·s are close to the time of gel formation. Multiplying these by $\exp(-E_s/RT)$, according to eq. (8), one can obtain the τ_r value. For curves 1–4, the following τ_r are obtained, s: 0.127^{-1} , 0.113^{-1} , 0.111^{-1} , and 0.107^{-1} . The spread of these values is small ($\approx 20\%$). Thus, any τ_r (or an average τ_r) can be used for the calcu-

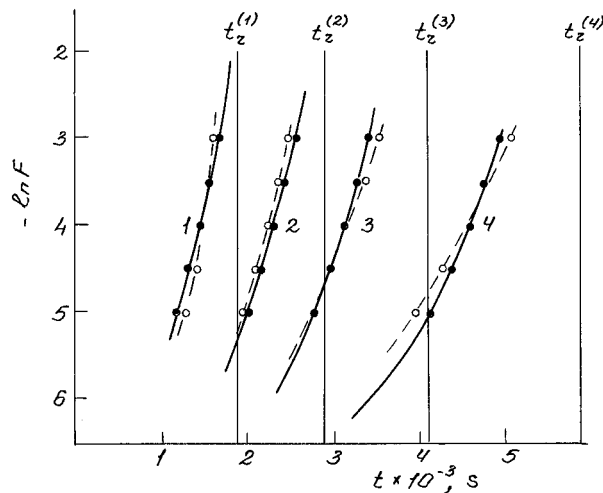


Figure 4 The dependence of the structure factor logarithm upon time at the temperatures corresponding to Figure 3. The solid curves are plotted on the basis of interpolated original values of viscosity. The dotted curves correspond to the best matching of the solid curves in the scale of the reduced time.

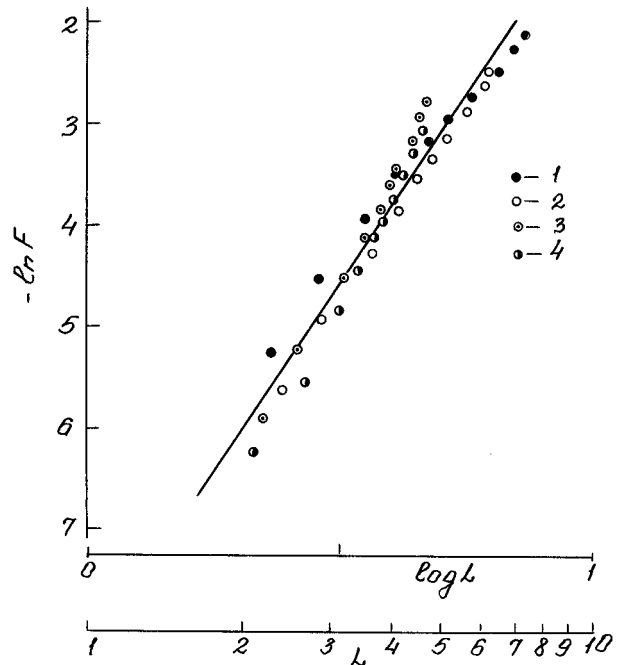


Figure 5 The dependence of the structure factor logarithm upon the maximum length of the polymer chain at T (°C): (1) 225; (2) 208; (3) 195; (4) 182.

lation of the rate constant of the curing reaction. However, to avoid the intersection of the kinetic curves $\eta(t)$ with the abscissas corresponding to gel transitions, we took a maximum of these values in the calculations: $\tau_r = 0.127^{-1}$ s, which corresponds to the maximum temperature of 225°C. Then, the values $t_r^{(j)}$ for the other temperatures (see Fig. 3) were calculated by the formula $t_r^{(j)} = \tau_r \exp(E_s/RT_j)$.

The reduced rate constant \bar{k}_s , calculated in accordance with eqs. (6) and (7), is equal to 68.4 s $^{-1}$. The dimensional constant k_s with $d_A = 1$ g/cm 3 and $d_B = 1.8$ g/cm 3 is equal to 3614 (mol/cm 3) \times s $^{-1}$.

Having calculated \bar{k}_s , one can find from eq. (3) the p value for each time moment and then by using eq. (21) calculate the maximum length of a polymer chain. By estimating a slope of the dependence $\ln F$ upon L (see Fig. 5), we are able to find the constant α in eq. (12). The calculations led to $\alpha = 3.26$. This value unexpectedly corresponds well to the known coefficient 3.4. When extrapolating the straight line to the value of $L = 1$, the constant $\ln \eta_0 = -8.35$ is determined.

Using the obtained constants, it is possible to build theoretical dependencies of the viscosity on the time. As seen from Fig. 3, the approximation is fulfilled quite satisfactorily.

CONCLUSIONS

Although the linear dependence of the viscosity logarithm upon the logarithm of the average longest linear chain in a branching molecule has semiempirical sense, this dependence can approximate well the viscosity of thermosets over a wide range. For instance, for the considered system, phenol-formaldehyde resin and boron oxide, a satisfactory approximation is observed within the range of viscosity $\approx 100\text{--}3000$ Pa-s. It is noteworthy that the calculated coefficient of the slope of the above dependence of 3.26 is very close to the well-known value of 3.4.

The best matching of the structure factor corresponding to different kinetic viscosity isotherms gives a fast and simple method of finding the activation energy of the curing reaction. The considered relationships approximate with a satisfactory accuracy the series of isotherms and not only one isotherm. Therefore, one can expect that at least within a reasonably narrow range of temperature it enables the viscosity to be predicted under nonisothermal conditions as well.

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