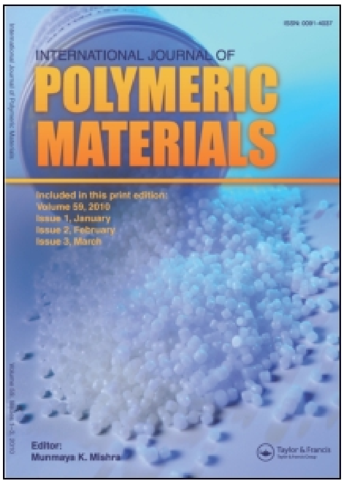

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A. E. Arinshtein[a]; S. M. Mezhikovskii[a]
[a] N. N. Semenov institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

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Some Problems of Structure Formation in Self-organizing Liquid Oligomer Systems

II. Theoretical Models for Formation of Supermolecular Structure of Oligomer Systems*

A. E. ARINSHTEIN and S. M. MEZHIKOVSKII[†]

*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 Kosygin st., 117334 Moscow, Russia*

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The driving force for self-organization are the fundamental laws of thermodynamics. We consider some theoretical models which qualitatively explain anomalous properties of these systems.

Keywords: Self-organizing systems; liquid oligomers; theoretical models; structure formation

1. INTRODUCTION

In this section we will consider some theoretical models which can explain qualitatively the reason for anomalous properties of oligomer liquids observed experimentally (see, for example, [1–20]). In particular, we substantiate peculiarities of rheological properties of oligomer liquids which demonstrate even temperature hysteresis of viscosity in a series of experiments [4, 19, 20]. Besides, in the framework of the

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[†]Corresponding author.

phenomenological aggregation models represented below one can find the explanation for extraordinary high relaxation times in non-equilibrium oligomer liquids (taking place in some situations), which are exceptional for liquid systems [1, 3, 10–13]. Finally, taking into account the inner structure of aggregates (assuming aggregates in oligomer liquids to be formations with increased orientation order of anisotropic oligomer molecules) has also allowed the theoretical explanation of some experimental kinetic anomalies, taking place at the initial stage of oligomers polymerization [1, 3, 7, 8, 16, 17]. Thus, our theoretical representations based on the assumption that complex supermolecular formations exist in oligomer systems make it possible to account for many unusual properties of oligomer liquids.

When theoretically considering the aggregation processes we shall base on the modified Beker-Döring-model offered in [21] for the description of terminationless radical polymerization:

$$\dot{u}_n = -vk_n u_n + vk_{n-1}u_{n-1} + q_{n+1}u_{n+1} - q_n u_n, \quad n \geq 2, \tag{2.1}$$

$$\dot{u}_1 = -vk_1 u_1 + q_2 u_2, \tag{2.2}$$

$$\dot{v} = -v\sum_{n=1}^{\infty} k_n u_n + \sum_{n=2}^{\infty} q_n u_n, \tag{2.3}$$

where u_n is the concentration of aggregates consisting of n molecules; v is the concentration of single molecules (a single molecule and an aggregate consisting of 1 molecules are the objects of different physical nature); k_n is the constant of the rate of single molecules addition to an aggregate of the size n; and q_n is the constant of the rate of single molecules splitting out of an aggregate of the size n.

The analysis of properties of Eqs. *set* (2.1)–(2.3) of the modified Beker-Döring-model shows that the dependence of the addition and splitting out constants k_n and q_n on aggregates size n only weakly influences the character of the solution of these equations. Therefore we can further believe that these constants do not depend on the aggregates sizes n.

2. THE ACTIVATION MODEL

This theoretical model of formation of oligomers supermolecular structure is based on the following postulates [22]:

- the system consists of aggregates and "disorganized" molecules;
- there is a distribution function for such aggregates based on their number and sizes, determined by the pre-history of the system;
- to attain thermodynamically equilibrium function of number and sizes distribution of aggregates, independent on the initial conditions, the system should previously overcome some energy barrier which is determined by the nature of the components;
- activation of molecules allowing them to form aggregates occurs due to thermal or mechanical (deformation) energy "pumping" into the system from outside;
- either external mechanical effect or temperature increase may result in activation of "disorganized" (not incorporated into aggregates) molecules only, but it cannot influence the aggregates themselves;
- increase of aggregates sizes occurs only due to addition to them of activated "disorganized" molecules;
- neither dissociation of aggregates, nor molecules splitting out of them is possible;
- the number of aggregates is invariable in the process.

Within the framework of these restrictions, the kinetics of formation of aggregates numbers and sizes distribution is described by the following equations set in which, for simplicity, the rate constants k do not depend on n:

$$\dot{u}_n = -kvu_n + kvu_{n-1}, \quad n \geq 2, \tag{2.4}$$

$$\dot{u}_1 = -kvu_1, \tag{2.5}$$

$$\dot{v} = -vk\sum_{n=1}^{\infty} u_n + p\left(c - \sum_{n=2}^{\infty} nu_n - v\right), \tag{2.6}$$

where u_n is the concentration of aggregates consisting of n molecules; v is the concentration of activated molecules; k is the constant of the rate of an activated molecule addition to aggregates; p is the constant of the rate of molecules activation; c is the total concentration of molecules in the system, including molecules both activated and incorporated into aggregates; the point over a symbol means derivative with respect to the time. Eqs. *set* (2.4)–(2.6) follows from Eqs. (2.1)–(2.3) of the modified Beker-Döring-model, putting $q_n \equiv 0$ and adding into Eq. (2.3) the addend describing the process of activation of inert molecules.

To solve Eqs. *set* (2.4)–(2.6) let's introduce the generating function

$$F(z,t) = \sum_{n=1}^{\infty} z^n u_n(t). \tag{2.7}$$

Multiplying Eqs. (2.4) by z^n and Eq. (2.5) – by z and summing these equations over n we shall obtain the equation for the generating function $F(z,t)$:

$$\frac{\partial}{\partial t} F(z,t) = (z-1)kv(t)F(z,t). \tag{2.8}$$

Equation (2.6) for the function $v(t)$ is also expressed using the generating function and it's derivative with respect to z at $z = 1$:

$$\dot{v}(t) = -kv(t)F(1,t) + p\left[c - \frac{\partial}{\partial t} F(z,t)|_{z=1} - v(t)\right]. \tag{2.9}$$

The solution of Eqs. (2.8), (2.9) under the initial conditions

$$v(t=0) = v_0, \quad F_0(z) = F(z,t=0) = \sum_{n}^{\infty} z^n u_{n0}, \tag{2.10}$$

has a simple form

$$F(z,t) = F_0(z)\exp[(z-1)kw(t)], \tag{2.11}$$

where the function $w(t)$ is connected with the activated molecules concentration $v(t)$ by means of the relationships $dw(t)/dt = v(t)$, $w(0) = 0$. In conformity with Eq. (2.9) it is equal to

$$w(t) = \frac{c - F_{z0}}{kN(p-kN)}\left\{\left(p - \frac{v_0 kN}{c - F_{z0}}\right)[1 - \exp(-kNt)] - \right.$$
$$\left. - kF\left(1 - \frac{v_0}{c - F_{z0}}\right)[1 - \exp(-pt)]\right\}, \tag{2.12}$$

where $F_{z0} = dF_0(z)/dz$; $\Sigma u_n = N = const$ is the total number of aggregates in the system.

The dependence $u_n(t)$ is easily developed using contour integration in the complex plane

$$u_{n},(t) = \frac{1}{2\pi i}\oint_{|z|=1}\frac{F(z,t)}{z^{n+1}}dz. \tag{2.13}$$

As a result we shall get that

$$u_n(t) = \exp[-kw(t)]\sum_{m=1}^{n}\frac{u_{m0}}{(n-m)!}[kw(t)]^{n-m}, \tag{2.14}$$

and that

$$v(t) = \frac{c - F_{z0}}{(p - kN)}\left[\left\{\left(p - \frac{v_0 kN}{c - F_{z0}}\right)\exp(-kNt) - \right.\right.$$
$$\left.\left. - p\left(1 - \frac{v_0}{c - F_{z0}}\right)\exp(-pt)\right\}\right]. \tag{2.15}$$

Using these expressions, the additional contribution to the viscosity $\Delta\eta$ which arises due to aggregates growth can easily be calculated in the approximation of low concentrations of aggregates. Assuming the ag-gregates to be rigid impermeable structures [23], the contribution of an aggregate to the system viscosity is proportional to its volume, which in the case of usual close packing is proportional to the number of mole-cules incorporated into the aggregate. Averaging over aggregates sizes and taking into account Eqs. (2.11) and (2.12), we obtain the following:

$$\Delta\eta(t) \propto \left\{kF_{z0} + \frac{c - kF_{z0}}{p - kF_1}\left[\left(p - \frac{v_0 kF_1}{c - F_{z0}}\right)[1 - \exp(-kF_1 t)] - \right.\right.$$
$$\left.\left. - kF_1\left(1 - \frac{v_0}{c - F_{z0}}\right)[1 - \exp(-pt)]\right]\right\}\eta. \tag{2.16}$$

The analysis of the expression (2.16) shows that two characteristic time scales are present in the system: $\tau_1 = 1/kF_1$ is the characteristic time of addition of activated molecules to aggregates and $\tau_2 = 1/p$ is the characteristic time of molecules activation.

Let's consider the possible situations.

If $\tau_1 < \tau_2$, *i.e.*, if the process of molecules addition to aggregates is fast, activated particles do not build up in the system. Thus, no system relaxation is observed after the external action ceasing.

If $\tau_1 > \tau_2$, *i.e.*, if activated molecules addition to an aggregate proceeds slower than their activation, there should be some time period over which the system contains significant number of "disorganized" activated particles. Their influence on the viscosity increase is determined by the relationship between the time moments t_1 (time moment of external effect ceasing) and τ_1 (time moment of complete exhaustion of the "disorganized" activated molecules in the system). Indeed, when $\tau_2 < t_1 < \tau_1$, since some number of "disorganized" activated particles has built up in the system, during the time period from t_1 upto τ_1 the mass of aggregates will rise. As a result, viscosity should increase. However, when $t_1 > \tau_1$, since almost all the activated molecules have managed to join the aggregates, no viscosity increase is observed.

In mathematic terms, this may be taken into account, assuming $p = 0$ in Eq. (2.6). After performing the necessary calculations, we shall derive that after the external effect ceasing the viscosity time dependence is as follows

$$\Delta\eta(t) \propto \{F_{z0} + kF_1 w(t_1) + v(t_1)(1 - \exp[-kF_1(t - t_1)])\}\eta, \quad (2.17)$$

where $w(t_1)$ and $v(t_1)$ are determined by the expressions Eqs. (2.12) and (2.15) at $t = t_1$.

When $t_1 < \tau_1$ the term $v(t_1)$ is significant. As a result, according to Eq. (2.17), the relaxation process takes place in the system. Its characteristic time is τ_1. When $t_1 > \tau_1$ the term $v(t_1)$ is, according to Eq. (2.15), exponentially small and its change amplitude $\Delta\eta$ in Eq. (2.17) is likewise exponentially small. The changes of this kind are negligible.

It should be noted that the presented patterns will be qualitatively valid even in the case when the contribution of aggregates size growth into viscosity of the system is non-linearly dependent on the particles concentration. The dependence of such a type takes place, for instance, in the case of non-trivial packing of molecules in aggregates (when aggregates are fractal objects) [24].

The model considered describes adequately some other features of oligomer rheological properties (*see* below, as well as [1, 2, 19, 20]). However, this model does not take into account the possibility of aggregates disintegration and, consequently, it cannot explain a number of other oligomer systems properties, such as, for example, unusually high relaxation times towards the equilibrium in the systems of this type [10 – 16].

3. THE RELAXATION MODEL

This model not only takes into account the possibility of aggregates growth but also assumes their disintegration. Within the model, besides the first four postulates accepted for the activation model, the following conditions are entered additionally, taking into account some peculiarities of relaxation of the aggregate-size distribution function towards the equilibrium [25]:

- on the way to the equilibrium the aggregate-size distribution formed in the system after the external effect ceasing varies both due to addition of separate activated molecules to the aggregates and due to molecules splitting out of aggregates;
- the number of aggregates in the process does not vary, *i.e.*, generation of new aggregates and disintegration of large aggregates into smaller ones do not occur. Splitted out separate activated molecules cannot be nuclei of a new aggregate, they may only join already existing aggregates.

The relaxation kinetics of the generated earlier aggregates distribution is described by Eqs. *set* (2.1) – (2.3) of the modified Beker-Döring-model in which, for simplicity, we shall consider the constants of activated particles addition and splitting out of aggregates as independent of an aggregate size, *i.e.*, $k_n \equiv k$ and $q_n \equiv q$:

$$\dot{u}_n = -vku_n + vku_{n-1} + qu_{n+1} - qu_n, \quad n \geq 2, \qquad (2.18)$$

$$\dot{u}_1 = -vku_1 + qu_2, \qquad (2.19)$$

$$\dot{v} = -vk\sum_{n=1}^{\infty} u_n + q\sum_{n=2}^{\infty} u_n, \tag{2.20}$$

where, as in Eqs. (2.1)–(2.3), u_n is the concentration of aggregates consisting of n molecules; v is the concentration of activated molecules; k is the constant of the rate of an activated molecule addition to an aggregate of the size n; q is the constant of the rate of activated molecules splitting out of an aggregate; the point over a symbol means the derivative with respect to the time.

Equations *set* (2.18)–(2.20) describes two processes: addition of activated particles to aggregates with the rate constants k and splitting of activated molecules out of aggregates with the rate constants q.

Note that two conservation laws correspond to the entered Eqs. *set* (2.18)–(2.20).

$$\sum_{n=1}^{\infty} u_n = N = const \text{ and } \sum_{n=1}^{\infty} nu_n = M = const, \tag{2.21}$$

where N is the concentration of all the aggregates in the system, not depending on their sizes; M is the concentration of activated molecules in the system, including molecules incorporated into aggregates (the presence of inactive molecules is not important for this model). The existence of these conservation laws essentially facilitates solving the problem.

To solve Eqs. *set* (2.18)–(2.20), we shall introduce, as it was done above, the generating function $F(z, t)$ Eq. (2.7). In this case, the equations for the latter and for the function $v(t)$ contain the following form

$$\frac{\partial}{\partial t}F(z,t) = (z-1)\left\{\left[kv(t) - \frac{q}{z}\right]F(z,t) + qF_{0z}(t)\right\}, \tag{2.22}$$

$$v(t) = -kNv(t) + q[N - F_{0z}(t)]. \tag{2.23}$$

where $F_{0z} \equiv \partial F(z,\ t)/\partial t|_{z=0} \equiv u_1(t)$.

Note that the equations set developed Eqs. (2.22), (2.23) is not closed upon itself. The presence of the summand $F_{0z}(t)$ in these equations makes necessary to introduce an additional equation for its solution containing the term $F_{0zz}(t) \equiv \partial^2 F(z, t)/\partial t^2|_{z=0} \equiv u_2(t)$. For the latter it is also necessary to introduce a new additional equation containing the generating function derivative of the next order and so on. However, it turns out, that the existence of the conservation law expressed by means of the generating function

$$\partial F(z,t)/\partial t|_{z=1} + v(t) = M, \tag{2.24}$$

permits to obtain the necessary information concerning the system without using any "cutting" procedure of an infinite equations chain.

For reversible processes the balance between forward and reverse processes has to be attained in the system, and Eqs. *set* (2.22), (2.23) should have the steady-state solution, *i.e.*, $\partial F(z,t)/\partial t = 0$ and $dv(t)/dt = 0$.

As the right parts of Eqs. (2.22), (2.23) are equal to zero, we shall obtain the steady-state solution

$$F_{st}(z) = \frac{zF_{0zst}}{1 - z(1 - F_{0zst}/N)}, \tag{2.25a}$$

$$v_{st} = \frac{q}{k}\left(1 - \frac{F_{0zst}}{N}\right), \tag{2.25b}$$

where the stationary value of F_{0zst} is determined using the conservation law Eq. (2.24). In fact, substituting Eq. (2.25a) into Eq. (2.24), we shall obtain a square equation for the term F_{0zst}, the positive root of which is

$$F_{0zst} = \frac{N}{2}\left[\sqrt{\left(1 - \frac{k}{q}M\right)^2 + 4\frac{k}{q}N} + 1 - \frac{k}{q}M\right]. \tag{2.26}$$

Thus, Eqs. (2.25) and (2.26) describe completely the steady-state of the system under consideration.

To obtain the steady-state aggregates concentration distribution it would be sufficient to expand Eq. (2.25a) as a geometrical power series

$$u_{nst} = F_{0zst}\left(1 - \frac{F_{0zst}}{N}\right)^{n-1}. \tag{2.27}$$

In particular, at $q \to 0$ (the disintegration processes are suppressed) the concentration of the activated molecules not incorporated into aggregates also approaches to zero: $v_{0st} \to 0$, while

$$F_{0zst} \approx \frac{N^2}{M}, \tag{2.28}$$

and

$$u_{nc} \approx \frac{N^2}{M}\left(1 - \frac{N}{M}\right)^{n-1}. \tag{2.29}$$

On the other hand, assuming $q \equiv 0$ in Eqs. (19), (20), the direct integration of these equations gives:

$$v(t) = v_0 \exp(-kNt), \tag{2.30}$$

$$F(z, t) = F_0(z) \exp\left\{(z-1)\frac{v_0}{N}[1 - \exp(-kNt)]\right\}, \tag{2.31}$$

where $v_0 = v(t = 0)$ and $F_0(z) = F(z, t = 0)$.

At large t values ($t \gg 1/kN$) we develop from Eqs. (2.30) and (2.31) that, respectively, $v(t) \to 0$ and

$$F(z, \infty) = F_0(z) \exp\left\{(z-1)\frac{v_0}{N}\right\}, \tag{2.32}$$

whence it follows that the asymptotic aggregate-size distribution at $p \equiv 0$ has the form:

$$u_n(\infty) = \exp\left(-\frac{v_0}{N}\right)\sum_{m=0}^{n-1}\frac{u_{n-m}(t=0)}{m!}\left(\frac{v_0}{N}\right)^m. \tag{2.33}$$

Comparing Eqs. (3.33) and (3.29) one can see that these two distributions do not coincide fundamentally. It means, that at small values of the constant q of molecules splitting out of aggregates, *i.e.*, when this process is suppressed substantially, the kinetics of the formation of equilibrium aggregate-size distribution consists of two stages. At the first stage, due to addition of activated molecules to existing aggregates some quasi-stable aggregate-size distribution is reached relatively quickly. (This distribution is determined by the initial system state.) Then, due to splitting of separate molecules out of aggregates, slow redistribution of molecules between aggregates occurs. As a result, the system relaxes to its true steady-state.

To estimate the system relaxation time to its true steady-state let's integrate formally Eq. (2.22):

$$\begin{aligned} F(z,t) &\\ = F_0(z)\exp\left\{(z-1)\left[k\int_0^t v(t')dt' - \frac{qt}{z}\right]\right\} &+ \\ + (z-1)q\int_0^t F_{oz}(z,t')\exp\left\{(z-1)\left[k\int_{t'}^t v(t'')dt'' - \frac{q(t-t')}{z}\right]\right\}dt'. \end{aligned} \tag{2.34}$$

Equation (2.34) is very inconvenient for the analysis. However, after performing the necessary calculations, we shall obtain that the function $F(z,t)$ relaxes at small value of constant q ($q \ll kM$) to its steady-state as

$$\begin{aligned} F(z,t) &\\ \approx F_0(z)\exp\left[\frac{-q\left(\frac{N}{M}\right)^2 t}{2\left(1-\frac{N}{2M}+\sqrt{1-\frac{N}{M}}\right)}\right]\frac{z\mathrm{e}^{(z-1)\frac{v_0}{N}[1-\exp(-kNt)]}}{\sqrt{\pi}qt\left(1-z\sqrt{1-\frac{N}{M}}\right)} &+ \\ + F_{st}(z)\left\{1-\frac{z}{\sqrt{\pi}qt\left(1-z\sqrt{1-\frac{N}{M}}\right)}\exp\left[\frac{-q\left(\frac{N}{M}\right)^2 t}{2\left(1-\frac{N}{2M}+\sqrt{1-\frac{N}{M}}\right)}\right]\right\}. \end{aligned} \tag{2.35}$$

Thus, in the case when for the rate constants of the forward (addition) and reverse (splitting out) processes k and q the strong inequality $q \ll kM$ is valid, (*i.e.*, the reverse process is substantially suppressed) it appears that the time evolution of the generating function $F(z,t)$ has two characteristic stages. The first initial stage lasts for a characteristic time of the order

$$\tau_1 = 1/kN, \tag{2.36}$$

and it is described by means of Eq. (2.31). At this stage, the process of addition of active molecules to aggregates prevails and some quasi-steady-state aggregate-size distribution is reached, depending on the initial state of a system. At the second stage, lasting for the characteristic time of the order

$$\tau_2 = (1/q)(M/N)^2. \tag{2.37}$$

this quasi-steady-state distribution (due to the processes of the molecules redistribution between aggregates) relaxes to the true steady-state distribution, which depends neither on the initial state of the system and nor on its intermediate quasi-steady-state. The dependence $F(z, t)$ is described at this stage by Eq. (2.35).

Note a very important, in our opinion, feature of the process being studied. The characteristic time of relaxation towards the equilibrium can be very large in our system. This fact is related not so much to assumed small value of the constant q (if M is reasonably large the numerical value of constant q can be reasonably large too), as to the presence of the square factor $(M/N)^2$ in Eq. (2.37) for the characteristic relaxation time τ_2. The quantity M/N is the average size of aggregates, and, as a rule, it is large when the aggregates formation processes are essential. Therefore, the existence of this factor leads to the anomalously large value of the system relaxation time.

4. TEMPERATURE HYSTERESIS OF VISCOSITY

Above, we have considered two theoretical models for evolution of aggregative structure of oligomer liquids: the activation model and the relaxation one. It is apparent that both activation and relaxation can take place simultaneously, therefore it is necessary to consider a model which would take into account both these processes [26]. We shall supplement the assumptions formulated above by several more ones:

- activation of inert molecules because of an external action (temperature, for example) happens according to the Arrhenius mechanism with the rate constant k;
- activated molecules can relax to their initial state;

- beginning from some critical value N_{cr} of an average aggregates size N, the possibility for free molecules to join aggregates sharply increases;
- the temperature action results in a build up of k and growth of N_{cr};

"Combining" Eqs. *sets* (2.3)–(2.5) and (2.18)–(2.20) we shall obtain the following system of the kinetic equations:

$$\dot{u}_n = -vku_n + vku_{n-1} + qu_{n+1} - qu_n, \quad n \geq 2, \tag{2.38}$$

$$\dot{u}_1 = -vku_1 + qu_2, \tag{2.39}$$

$$\dot{v} = -vk\sum_{n=1} u_n + q\sum_{n=2} u_n + Pc - Rv, \tag{2.40}$$

$$\dot{c} = -Pc + Rv, \tag{2.41}$$

where k is the constant of the rate of activated molecules addition to aggregates; q is the constant of the rate of activated molecules splitting out of aggregates; p is the constant of the rate of inert oligomer molecules activation; R is the constant of the rate of activated oligomer molecules relaxation; c is the concentration of inert molecules; v is the concentration of activated molecules; u_n is the concentration of aggregates consisting of n molecules.

Using the generating function (2.7), one can easily obtain the steady-state of Eqs. *set* (2.38)–(2.41). Indeed, the quantities $F_{st}(z)$, u_{1st}, c_{st}, and v_{st} are connected by three algebraic relations

$$F_{st}(z) = \frac{zu_{1st}}{1-(k/q)zv_{st}}, \; c_{st} = (R/P)v_{st}, \; u_{1st} = [1-(k/q)v_{st}]N, \tag{2.42}$$

which allow (taking into account the second one of the conservation laws (2.21), having in this case the form ($\sum nu_n + v + c = M$) finding any quantity being of interest for us.

In particular, by means of following equation one can find the magnitude of F_{1zst} (stationary value $\partial F/\partial z$ at $z = 1$) through which the viscosity increment ($\Delta\eta/\eta = F_{1zst}$) is determined:

$$1 - \frac{N}{F_{1zst}} = \frac{k(F_{1zst})/q}{1+R/P}(M - F_{1zst}), \tag{2.43}$$

here we have shown that, according to our assumptions, the aggregation rate constant k depends on the average aggregates size which is proportional to their total mass F_{1zst}.

It is convenient to search the solution of Eq. (2.43) graphically (a step-like dependence $k(F_{1zst})$ was approximated with the help of a hyperbolic tangent). The analysis of the obtained solutions has shown that with raise of temperature T, depending on whether the ratio $(k/q)/(1+R/P)$ increases or decreases, the value of F_{1zst} and, correspondingly, of the viscosity increment $\Delta\eta/\eta$ may either increase or decrease. In the first case, when with raise of temperature the quotient $(k/q)/(1+R/P)$ increases, while the amplitude of the k constant change with the F_{1zst} build up is reasonably high, there are three steady-states in the system. Two of them are stable and the third one is unstable, *i.e.*, bistability arises, the situation being possible when with temperature raise the value of all the three steady-states increases (see Fig. 2.1).

Hence, the situation is possible when the bifurcation diagram of viscosity (with temperature taken as a controlling parameter) has the form presented in Figure 2.2. In such a case, a change in the state of a system can proceed as follows. If the initial state of the system is

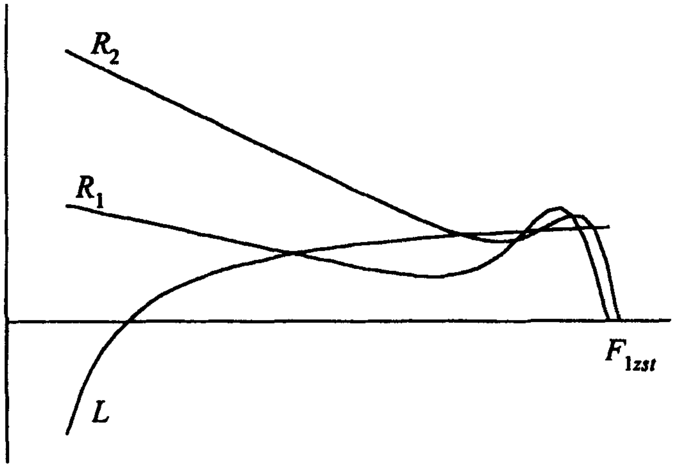

FIGURE 2.1 The graphic solution of Eq. (2.43) in the case, when with raise of temperature the ratio $(k/q)/(1+R/P)$ increases. The curve L corresponds to the left part of Eq. (2.43), and the curves R_1 and R_2 correspond to its right part at T_1 and T_2 $(T_1 < T_2)$.

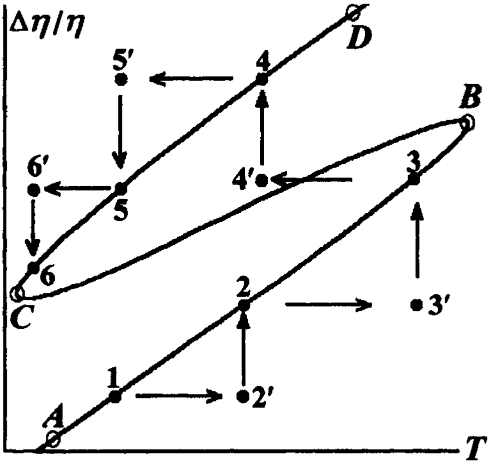

FIGURE 2.2 The bifurcation diagram for a system with bistability, demonstrating the mechanism of hysteresis wherein a transition from one branch of stable states to another happens within a range of temperature values where there exist both branches of stable states, without disappearance of one of them, *i.e.*, it happens not abruptly. The branches *AB* and *CD* are stable, and the branch *BC* is unstable.

located on the branch *AB* (points 1 and 2), then with increase of temperature T with any step ΔT the system always will appear in an intermediate nonequilibrium state which is located below the curve *AB* (points 2′ and 3′). It can relax only to the state which also lies on the branch *AB* (points 2 and 3). However, when decreasing temperature T with a rather large step ΔT, the system can appear in an intermediate nonequilibrium state which is located over the curve *CB* (the point 4′). From this point relaxation is possible only to a state which is located on the branch *CD* *via* the path $4' \rightarrow 4 \rightarrow \cdots \rightarrow 6$. As a result, at the reverse temperature path the phenomenon of hysteresis can be observed.

Such a mechanism of hysteresis arising leads to the fact that in the case of forward temperature path no abrupt change of the state occurs corresponding to a transition from a disappearing branch of steady-states to another one (see Fig. 2.3). On an experimental curve the jump would manifest itself in that the last point (or several last points) located on a curve 1–2 (corresponding to the forward temperature path) would go to the curve 3–4 (corresponding to the reverse temperature path). But in such a case the experimental curve presented

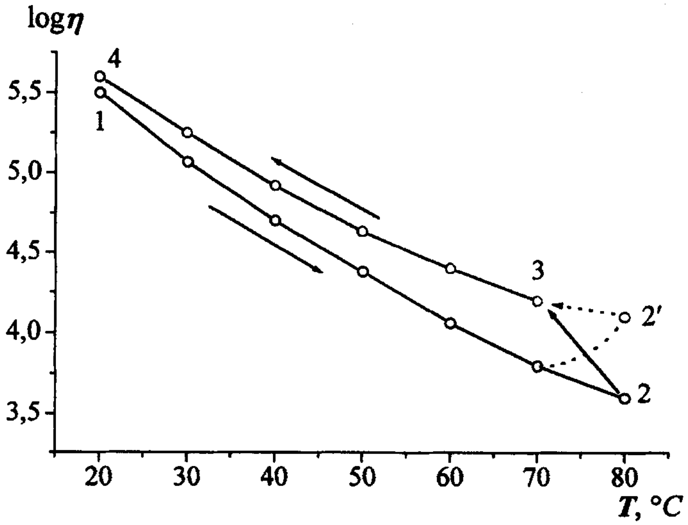

FIGURE 2.3 Hysteresis of viscosity at the forward (1 – 2) and reverse (3 – 4) paths in a rheological experiment. By the dotted line, it is shown how a hysteresis dependence of viscosity would appear at the forward (1 – 2') and inverse (2' – 4) temperature paths in the case of the standard mechanism of bistability.

in Figure 2.3 would appear somewhat different. In particular, the point 2 would shift upwards and lie on the prolongation of the line 3 – 4, having occupied the position of the point 2'. It is such a situation that takes place in the experiment described in [19, 26].

5. THE KINETICS OF THE BIMOLECULAR CHEMICAL REACTION OF AN ENSEMBLE OF ANISOTROPIC MOLECULES

As mentioned above, within the framework of the considered models we do not take into account peculiarities of oligomer aggregates structure. However, when it is assumed that aggregates in oligomer liquids are formations with increased orientation order of anisotropic oligomer molecules one can explain unexpectedly high initial rate of polymerization observed experimentally in these systems.

In the description of the chemical reaction kinetics of an anisotropic reactant we shall take into account that, due to anisotropy of reacting molecules, the constant of the rate of their reaction depends on their mutual orientation [7, 16, 27]. It is evident that relative orientation of reacting molecules can be different, thus resulting in the existence of a spectrum of the rate constants in the system. In the case that reactive centres are located only at one end of a molecule (*i.e.*, the molecule is a vector) it is necessary to distinguish between the parallel and antiparallel relative orientations of molecules.

Let us introduce the concentration $c(\varphi, t)$ of molecules having the orientation φ relative to an arbitrarily specified direction (for the director, the orientation φ corresponds to a double angle). The total concentration $c_\Sigma(t)$ of a substance can be expressed in terms of $c(\varphi, t)$ by the expression

$$c_\Sigma(\varphi, t) = \int_0^{2\pi} c(\varphi, t)d\varphi.$$

If the rotational mobility of anisotropic molecules is not taken into consideration (it is the situation which is of most interest for us), a standard kinetic equation of a second-order reaction can be written for the function $c(\varphi, t)$ in the approximation of point systems

$$\frac{\partial c(\varphi, t)}{\partial t} = -c(\varphi, t)\int_0^{2\pi} K(\varphi - \varphi_1)c(\varphi_1, t)d\varphi_1, \tag{2.44}$$

here $K(\varphi - \varphi_1)$ is the reaction rate constant for two anisotropic molecules with orientation φ and φ_1, respectively.

The kernel $K(\varphi - \varphi_1)$ of the integral operator must obviously be symmetric about the rearrangement of arguments, *i.e.*, it must be an even function with a maximum at $\varphi - \varphi_1 = \pi$ and a minimum at $\varphi = \varphi_1$. Besides, it must be a nonnegative periodic function with a cycle of 2π.

The exact solution of Eq. (2.44) can be obtained when the concentration $c(\varphi, t)$ is represented in the form

$$c(\varphi, t) = \exp\left[-\int_0^{2\pi} K(\varphi - \varphi_1)\alpha(\varphi_1, t)d\varphi_1\right], \tag{2.45}$$

and for $\alpha(\varphi, t)$ shall be used a Fourier-series expansion

$$\alpha(\varphi, t) = \frac{\ln A_0(t)}{2\pi k} + \frac{1}{\pi}[A_1(t)\cos(\varphi - \varphi_0(t)) + \cdots]. \tag{2.46}$$

The kernel $K(\varphi-\varphi_1)$ can also be represented as a Fourier-series expansion. We restrict our consideration only to the first harmonic:

$$K(\varphi-\varphi_1)=k[1-\lambda\cos(\varphi-\varphi_1)], \tag{2.47}$$

here λ is the parameter characterizing the degree of anisotropy of the reaction rate constant, $0\leq\lambda\leq 1$. If $-1\leq\lambda\leq 0$, the maximum of the reaction rate constant corresponds to the parallel orientation of reacting molecules.

As a result we obtain the equations convenient for further analysis

$$\begin{cases}\frac{dA_0(t)}{dt}=2\pi k I_0\big(k\lambda A_1(t)\big),\\ \frac{dA_1(t)}{dt}=\frac{2\pi}{A_0(t)}I_1\big(k\lambda A_1(t)\big).\end{cases} \tag{2.48}$$

Here $I_n(x)$ are the Bessel functions of imaginary argument, and the function $\varphi_0(t)$ appears to be a constant: $\varphi_0(t)=\varphi_0=const.$

The reactant concentrations $c(\varphi,t)$ and $c_\Sigma(t)$ are expressed in terms of functions $A_0(t)$ and $A_1(t)$ as

$$c(\varphi,t)=\frac{1}{A_0(t)}\exp\left\{k\lambda A_1(t)\cos(\varphi-\varphi_0)\right\},$$

$$c_\Sigma(t)=\frac{2\pi}{A_0(t)}I_0\big(k\lambda A_1(t)\big).$$

In the case of weak orientation order of reacting anisotropic molecules the time dependence of $c_\Sigma(t)$ was found to correspond to the common kinetics of a second-order reaction:

$$c_\Sigma(t)=\frac{c_\Sigma(0)}{1+kc_\Sigma(0)t}, \tag{2.49}$$

here we denote $c_\Sigma(0)=2\pi/A_0(0)$ as the initial total concentration of a reactant.

But, as the reaction proceeds, the degree of orientation order of anisotropic molecules in the system increases. Eventually, the point in time $t_{or}(1/t_{or}\sim c_\Sigma(0)[k\lambda A_1(0)]^{2/\lambda})$ comes, from which the degree of orientation order of anisotropic molecules can not be considered as small and the dependence (2.49) breaks down.

Note that in the case when the maximum of the reaction rate constant corresponds to the parallel orientation of reacting molecules ($\lambda < 0$), orientation self-organization does not occur in the system.

Let us consider now the opposite limiting case for which the degree of orientation order of anisotropic reacting molecules is high. At $1 - \lambda \ll 1$, which is indicative for the maximum anisotropy of the reaction rate constant, we obtain

$$c_\Sigma(t) \approx \frac{c_\Sigma(0)}{1 + 2c_\Sigma(0)t/A_1(0)}, \tag{2.50}$$

here the parameter $A_1(0)$ characterizes the initial degree of orientation order of anisotropic reacting molecules.

At $\lambda = -1$, similar calculations result in another type of the function $c_\Sigma(t)$, namely,

$$c_\Sigma(t) = \frac{c_\Sigma(0)}{1 + 2kc_\Sigma(0)t}. \tag{2.51}$$

In its form, Eq. (2.51) is coincident with Eq. (2.49) which fits the common (nonpoly-chronic) kinetics. However, in the case, for which the degree of orientation order of anisotropic reacting molecules is high the effective rate constant at $\lambda = -1$ is twice as high as when any orientation ordering is absent. It is the effect that was observed experimentally in a number of works [1, 3, 17].

One can arrive to the same conclusions from more general considerations, examining the mutual influence of the chemical reaction kinetics and of structural organisation of the reaction medium [28, 29].

The models considered above describe satisfactorily some peculiarities of rheological and relaxation behaviour of oligomer systems. But they are far from explaining all the inherent anomalies of oligomers. It is connected with the fact that the models do not take into account some processes which, under specific conditions, can essentially affect oligomer liquids properties. First, these are the processes of new aggregates nucleation (associates and cybotaxes), taking into account their inner structure (anisotropy), effects of hydrodynamic interaction of associates, correlation in their spatial arrangement, influence of aggregates sizes on the constants of their growth and disintegration, *etc.* All these factors may be included in a subsequent consideration within the framework of the main postulates of the aggregative model of supermolecular structure formation in oligomer liquids. However, although bringing some additional information and refining the consequences, taking account of the above factors must not influence radically the validity of the conclusions following from the models considered above.

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