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INFLUENCE OF KINETIC FACTORS ON THE DISTINCTIVE FEATURES OF THE RHEOLOGICAL BEHAVIOR OF OLIGOMER SYSTEMS

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The distinctive features of the rheological behavior of oligomer liquids have been considered within the framework of the concept of the aggregative nature of their supermolecular structure. It has been shown that the dependence of the rheological properties of oligomers on the temperature–time and deformation prehistory is a consequence of the system's nonequilibrium at the instant of measurement. Theoretical models quantitatively describing the evolution of the system to thermodynamic equilibrium have been proposed. Account for the kinetics of formation of the supermolecular structure of oligomer liquids enables one to correctly explain certain experimental "anomalies," thus transferring them to the class of fundamental physicochemical regularities.

In recent years, a number of reports on the influence of the temperature–time and deformation prehistory of oligomer systems on their rheological properties have appeared (see, for example, [1–3]). In particular, for oligobutadieneurethane acrylates (OBUAs) it was shown [1, 2] that: a) even small (compared to the loads developing in experimental deformation regimes) *preliminary* shear actions on the oligomer liquid irreversibly and significantly (by a decimal order) reduce the time of reaching the steady-state regime of flow with a viscosity η_s; b) the quantity η_s becomes appreciably higher if the liquid, after predeformation, is "resting" for a certain time between measurements; c) the time of "rest" τ_r upon reaching which η_s ceases to depend on τ_r is defined as τ^{cr}; d) when $\tau_r < \tau^{cr}$, the oligomer is flowing as a non-Newtonian fluid, and when $\tau_r > \tau^{cr}$ the system passes to the regime of Newtonian flow. Furthermore, it has been disclosed that the identical OBUA samples but having dissimilar temperature prehistories (some are heated to the test temperature, others are cooled to this temperature) are characterized by dissimilar viscosity indices. However these differences are counterbalanced after the shear action on them: the system "forgets" its temperature prehistory. The viscosity significantly grows.

These unusual results can be explained variously. Since the chemical transformations in the system were excluded [2], it was natural to analyze the experiments enumerated above within the framework of the concept of flow of the so-called "structurized" liquids. Each individual experiment can logically be interpreted in the variant of "linkage" network and flow of dilatant systems [4–8]. However, it is impossible to explain the entire experiment in this context. For example, if we assume that the linkage network (or other supermolecular structures of the liquid) is broken after the intense premixing, the change observed experimentally in the character of oligomer flow is a natural outcome. But it remains unclear why changes do not occur (in any case, they are not recorded in the rheological experiment) as a result of the analogous or even much larger deformations developing in the course of the experiment itself. Or if we have the destruction of the linkage network, why is the viscosity in a "structureless" liquid higher than that in a "structurized" liquid? These and many other questions arising from such consideration of the above set of experiments are unanswered by the existing models.

The situation is the reverse if we allow for the possible influence of the kinetics of formation of supermolecular structures on the rheological properties of oligomer systems even within the framework of the model of a "structurized" liquid. It is taken that: 1) the formation of supermolecular structures in oligomer liquids is an activating process; 2) the times of reaching equilibrium in the system are comparable to or exceed the time of the rheological experiment; 3) rheological methods are sensitive to changes in the supermolecular structure which occur in the system as the equilibrium state is approached.

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In this context, we can logically explain the above-mentioned set of experimental observations at a qualitative level. For example, to form the equilibrium supermolecular structure of an oligomer liquid offering stable rheological properties to the liquid it is necessary, first of all, to overcome a certain energy barrier required not only for destruction of the structure formed by the beginning of measurement but also for activation of the processes of formation of the "intermediate products" of the future supermolecular structure (aggregates of oligomer molecules carrying out the act of mass transfer). This precisely occurs under the corresponding thermal and mechanical actions on the system. The number and quality of these "intermediate products" depend of the nature of the oligomer and on the kind and quantity of energy added in the process of destruction. Then the oligomer liquid needs a certain period of "rest" during which the stresses are relaxed and the intermediate products reach a thermodynamically equilibrium level which is determined by the parameters of state of the system. If the number or size of the aggregates increases during the period $\tau_r = \tau^{cr}$, this must result in a viscosity growth. When the time of reaching the equilibrium state is shorter than or equal to τ_r, the rheological experiment reflects an equilibrium situation; if the interval between the completion of the preliminary action on the liquid and the beginning of measurements is shorter than the time of reaching equilibrium, the result of the experiment is influenced by both the equilibrium structures and structures that had no time to become equilibrium by the instant of the measurements. The uncertainty in selection of τ_r in different experiments is, apparently, responsible for the spread in the values of the viscosity characteristics given by different authors [2, 7–9].

However, such a qualitative consideration leaves unanswered many questions which inevitably arise in thorough analysis of these experiments. For example, why does the dependence of the viscosity on τ_r manifest itself in some experiments [1–4], while in other, no less precise experiments, one has not found such a dependence [7–10]? Why are the values of τ^{cr} abnormally (for liquid systems) high (according to some data [11], they can be as high as several days)?

Together with A. É. Arinshtein and V. I. Irzhak [12–15] the author has proposed several theoretical models that describe the dynamics of formation of the equilibrium structure of high-viscosity oligomer systems and enable one to quantitatively explain the unusual character of their macroscopic properties, including rheological ones.

Common to the theoretical models is the assumption that the supermolecular structures of oligomer liquids are formed and evolve as a result of the processes of aggregation of oligomer molecules. All of them are based on the following physically substantiated postulates:

(a) the system consists of aggregates (associates, clusters, etc. — the terms can be different) and "disorganized" molecules;

(b) the random distribution function of these aggregates by number and size is determined by the prehistory of the system;

(c) for the thermodynamically equilibrium (independent of the initial conditions) distribution function of the aggregates by number and size to be attained, the system must overcome in advance a certain energy barrier determined by the nature of the components;

(d) activation of the molecules (naturally, not in a chemical sense) which enables them to form aggregates is due to the temperature or mechanical (deformation) "pumping" of energy into the system from the outside;

(e) the size of the aggregates increases only due to the attachment of activated "disorganized" molecules to them;

(f) the number of aggregates remains constant in the course of the process.

We introduced additional limitations for different models: in the first model, detachment of the oligomer molecules from the aggregates was abandoned; in the second model, it was permitted; in the third model, it was taken that the rate constant of attachment of the molecules to the aggregates increases with increase in their total mass; in the fourth model, analysis was made of the variant of the aggregation model in which no limitations were imposed on the number of aggregates, etc.

Within the framework of the indicated postulates, the kinetics of formation of the size distribution of aggregates is described by the following system of equations:

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

$$\dot{u}_1 = -kvu_1 ; \tag{2}$$

$$\dot{v} = -vk\sum_{n=1}^{\infty} u_n + p\left(c - \sum_{n=2}^{\infty} nu_n - v\right). \tag{3}$$

A point above a symbol denotes the time derivative.

By solution of this system, which was performed within the framework of a modified Becker–Döring model [16] we, in particular, obtained the expression for calculating the additional contribution to the viscosity $\Delta\eta$ occurring due to the growth of the aggregates. Under the assumption that the aggregates are rigid impermeable formations, it has the form

$$\Delta\eta\,(t) \propto \left\{kF_{z0} + \frac{c - kF_{z0}}{p - kF_1}\left[\left(p - \frac{v_0 kF_1}{c - F_{z0}}\right)[1 - \exp(-kF_1 t)] - kF_1\left(1 - \frac{v_0}{c - F_{z0}}\right)[1 - \exp(-pt)]\right]\right\}\eta\,, \tag{4}$$

where F_{z0} and F_1 are the generating functions of two variables $F(z,\,t) = \sum_{n=1}^{\infty} z^n u_n(t)$ at $t = 0$ and $z = 0$ respectively.

An analysis of expression (4) shows that in the system there are two characteristic time scales: $\tau_1 = 1/kF_1$ is the characteristic time of attachment of the activated molecules to the aggregates and $\tau_2 = 1/p$ is the characteristic time of activation of the molecules.

If $\tau_1 < \tau_2$, i.e., the process of addition of the molecules to the aggregates is rapid, the activated particles are not accumulated in the system, and no relaxation of the system occurs during the period $t = \tau_r$ after the cessation of the external action.

If $\tau_1 > \tau_2$, i.e., the attachment of the activated molecules to an aggregate is slower than their activation, there must exist a certain time interval during which the system contains a considerable number of "disorganized" activated particles. Their influence on the viscosity increment will be determined by the relation of the times t_1 and τ_2, i.e., the relation between the time from the instant of cessation of the external action and the time of complete exhaustion of the "disorganized" activated molecules in the system. Indeed, during the period $\tau_2 < t_1 < \tau_1$, since a certain number of the activated particles has been accumulated in the system, the aggregate mass will increase during the time from t_1 to τ_1, which must lead to a viscosity increase; however if $t_1 > \tau_1$, no viscosity increment is observed since all the activated molecules have had time to attach themselves to the aggregates by the instant t_1. Mathematically, this is expressed as

$$\Delta\eta\,(t) \propto \left\{F_{z0} + kF_1 w\,(t_1) + v\,(t_1)\,(1 - \exp[-kF_1\,(t - t_1)])\right\}\eta\,, \tag{5}$$

where the function $w(t_1)$ is related to the concentration of activated particles $v(t_1)$ by the relation $dw(t_1)/dt = v(t_1)$.

If $t_1 < \tau_1$, then $v(t_1)$ is substantial and, according to (5), we have relaxation with a characteristic time τ_1. If $t_1 > \tau_1$, then $v(t_1)$ will be exponentially small and the amplitude of change of $\Delta\eta$ in (5) will also be exponentially small. This change in $\Delta\eta$ can be disregarded.

Furthermore, it follows from the theory that the constant p and accordingly τ_2 are related to the energy of the external action, for example, to the value of the rate of shear γ or to the time of application of the external action τ_t, and that there must exist the limit values γ^{cr} and τ_t^{cr} ensuring an activation of the "disorganized" molecules maximum for these compounds, whereupon η ceases to depend on γ and τ_t.

Summing up what has been said above, we note that to create an equilibrium structure involving all thermodynamically allowed states of supermolecular formations (it is precisely such a structure that will reflect the true rheological properties of the system) first it is necessary to overcome a certain (inherent in this system) energy barrier required for activation of the entire fraction of the "disorganized" molecules that are capable of entering the organized structures (aggregates) after the activation. Under the action of the corresponding thermal and mechanical actions whose limit values are determined by the quantities T^{cr}, γ^{cr}, and τ_t^{cr} for each specific system, such activation occurs with a rate constant p. After the cessation of the energy action, if $k < p$, the oligomer liquid needs some time (this is precisely the time τ^{cr} during which a thermodynamically equilibrium aggregate-distribution function determined by the parameters of state of the system is spontaneously formed.

If the time of reaching equilibrium is shorter than τ_{r}, the rheological experiment (or any other test responding to changes in the supermolecular structure) reflects an equilibrium situation. If the interval between the completion of the preliminary action and the beginning of measurement is shorter than the time of reaching equilibrium, the experiment records the distribution function which has been obtained by this instant.

The model considered takes no account of the possibility of destruction of aggregates; therefore, it cannot explain a number of other properties of oligomer systems, for example, the anomalously long times of relaxation of these systems to equilibrium.

We can also theoretically substantiate this anomaly of oligomer systems by introducing an additional condition in which the aggregate-size distribution obtained in the system on the road to equilibrium after the cessation of the external action changes both due to the attachment of single activated molecules to the aggregates and the detachment of them.

According to this model, the kinetics of formation of the aggregate-size distribution is described by the following system of equations:

$$\dot{u}_n = -\,vku_n + vku_{n-1} + qu_{n+1} - qu_n\,, \quad n \geq 2\,; \tag{6}$$

$$\dot{u}_1 = -\,vku_1 + qu_2\,; \tag{7}$$

$$\dot{v} = -\,vk \sum_{n=1}^{\infty} u_n + q \sum_{n=2}^{\infty} u_n\,. \tag{8}$$

The system of equations (6)–(8) describes two processes: the attachment of activated particles to aggregates with rate constants *k* and the detachment of active molecules from an aggregate with rate constants *q*. Similarly to the previous case, we solved this system, with allowance for the fact that it corresponds to two conservation laws

$$\sum_{n=1}^{\infty} u_n = N = \mathrm{const} \quad \text{and} \quad \sum_{n=1}^{\infty} nu_n = M = \mathrm{const}\,, \tag{9}$$

using the generating function $F(z,\ t)$.

It turned out that the function $F(z,\ t)$ relaxes to its steady state according to the following law:

$$F\,(z,t) \approx F_0\,(z)\exp\left[\frac{-\,q\left(\dfrac{N}{M}\right)^2 t}{2\left(1-\dfrac{N}{2M}+\sqrt{1-\dfrac{N}{M}}\right)}\right]\frac{z\exp\left\{(z-1)\,\dfrac{v_0}{N}\,[1-\exp\,(-\,kNt)]\right\}}{\sqrt{\pi}\,qt\left(1-z\sqrt{1-\dfrac{N}{M}}\right)}+$$

$$+\,F\,(z)\left\{1-\frac{z}{\sqrt{\pi}\,qt\left(1-z\sqrt{1-\dfrac{N}{M}}\right)}\exp\left[\frac{-\,q\left(\dfrac{N}{M}\right)^2 t}{2\left(1-\dfrac{N}{2M}+\sqrt{1-\dfrac{N}{M}}\right)}\right]\right\}. \tag{10}$$

When a strong inequality ($q << kM$) holds between the rate constants of direct (attachment of single activated molecules to aggregates) k and inverse (detachment of the molecules from an aggregate) q processes, i.e., the inverse process is substantially suppressed, the time change of the generating function $F(z, t)$ has two characteristic stages.

The initial stage lasts for a characteristic time of the order of $\tau_1 = 1/kN$. At this stage, the acts of attachment of the activated molecules to aggregates prevail over the acts of detachment since the number of free activated molecules is still large. Here we have the formation of a quasi-steady-state aggregate-size distribution which depends on the initial state of the system.

The second stage of evolution of the system begins when the number of free activated molecules has decreased as a result of the attachment acts so that the rates of the processes of molecular attachment and detachment become comparable. The stage lasts for a characteristic time of the order of $\tau_2 = (1/q)(M/N)^2$. At this stage, the quasi-steady-state distribution begins to relax to the true equilibrium state. Unlike the first stage at which the evolution of the system is target-oriented, at the second stage the evolution is combinatorial, i.e., it occurs due to the "exhaustion" of numerous random acts of detachment and attachment. Naturally, the time of establishment of equilibrium is determined by the number of all possible variants of "exhaustion" and it will be the longer, the larger the average aggregate size obtained in the quasisteady state. Since the quantity M/N, being the average aggregate size, is rather large, as a rule, for aggregation-prone liquids, the presence of the square multiplier substantiates the fact that the time of relaxation from the quasiequilibrium state to an equilibrium state in such systems can turn out to be anomalously long.

In closing, we note that all the above reasoning concerning the influence of the temperature–time prehistory on the properties of a system are suitable and even compulsory not only for oligomer systems but also for any systems. However, for the first systems they are of fundamental importance, since the times of establishment of thermodynamic equilibrium in them can be comparable to the time of observation of the system [17]. Indeed, whereas we have $\tau_a < \tau_i < \tau_e$ in low-molecular-weight liquid systems and $\tau_i >> \tau_e$ in liquid polymer systems, we have $\tau_i \cong \tau_e$ and $\tau_a \cong t^*$ for oligomer systems. This means that low-molecular-weight liquids are usually equilibrium at the instant of measurement and their physicochemical properties are independent of the temperature–time (in the general case, energy) prehistory as a rule. The native polymer samples are thermodynamically nonequilibrium but kinetically stable; therefore, one cannot correctly evaluate the influence of the kinetics of establishment of equilibrium on the dependence of the macroscopic properties on the prehistory in reasonable observation times. For oligomer liquids the probability that the dependence of the macroscopic properties on the prehistory will manifest itself multiply increases, since it is not improbable that the property measured will be recorded under different starting conditions or at different distances from the equilibrium state.

NOTATION

η, viscosity; η_s, viscosity in the steady-state regime of flow; $\Delta\eta$, viscosity increment; t, time; t_1, fixed time by a certain instant; t^*, resolution of the method (instrumental resolution); τ_r, time of "rest" between the instant of cessation of the external action and the beginning of measurement; τ^{cr}, critical value of the time of "rest" upon reaching which η_s ceases to depend on τ_r; τ_t, time of application of the external action; τ_r^{cr}, critical time of application of the external action, which ensures the maximum activation of molecules at γ = const and T = const; τ_a, average lifetime of an aggregate; τ_i, average time of relaxation of an aggregate to the equilibrium state; τ_e, time of exposure, time of observation of an object; γ, rate of shear; γ^{cr}, critical value of the rate of shear, which ensures the maximum activation of molecules at τ_t = const and T = const; T, temperature; T^{cr}, critical value of the temperature, which ensures the maximum activation of molecules at τ_t = const and T = const; c, total concentration of molecules in the system; N, concentration of aggregates irrespective of their size (number n in the aggregate); M, concentration of activated molecules including those involved in the aggregate; u_n, concentration of the aggregates consisting of n molecules; u_1, concentration of the aggregates of a single molecule; ν, concentration of the activated molecules; ν_0, concentration of the activated molecules at $t = 0$; k, rate constant of attachment of the activated molecules to the aggregates; p, rate constant of molecular activation; q, rate constant of detachment (separation) of the active molecules from the aggregates; F, generating function; z, "silent" variable of the generating function. Subscripts and superscripts: r, "rest"; cr, critical; e, exposure; a, aggregate; t, tests.

REFERENCES

1. S. M. Mezhikovskii and E. I. Vasil’chenko, *Dokl. Ross. Akad. Nauk*, **339**, No. 5, 627–630 (1994).
2. S. M. Mezhikovskii, E. I. Vasil’chenko, and T. B. Repina, *Vysokomolek. Soed. B*, **37**, No. 5, 887–891 (1995).
3. S. M. Mezhikovskii, in: *Ext. Abstr. of Papers presented at Proc. 21st Symp. on Rheology* [in Russian], Ostashkov (2002), p. 68.
4. V. P. Budtov, *Physical Chemistry of Polymer Solutions* [in Russian], St. Petersburg (1992).
5. G. V. Vinogradov and A. Ya. Malkin, *Rheology of Polymers* [in Russian], Moscow (1977).
6. F. Bueche, *Physical Properties of Polymers*, Interscience, New York (1967).
7. J. D. Huhler, I. F. Makdonald, E. Ashare, T. W. Spriggs, and R. B. Bird, *Trans. Soc. Rheol.*, **11**, 181–185 (1967).
8. Yu. S. Lipatov, in: *Proc. I All-Union Conf. on Chemistry and Physical Chemistry of Oligomers* [in Russian], Vol. 1, Chernogolovka (1977), pp. 59–86.
9. A. A. Berlin, A. G. Kondrat’eva, N. N. Tvorogov, É. S. Pankova, and A. Ya. Malkin, *Vysokomolek. Soed. B*, **15**, No. 10, 740–744 (1973).
10. E. I. Vasil’chenko and S. M. Mezhikovskii, *Vysokomolek. Soed. A*, **31**, No. 7, 1362–1366 (1989).
11. S. M. Mezhikovskii, V. M. Lantsov, L. A. Abdrakhmanova, L. A. Zhil’tsova, and E. I. Vasil’chenko, *Dokl. Akad. Nauk SSSR*, **302**, No. 4, 878–882 (1988).
12. A. Arinshtein and S. Mezhikovskii, *Polym. Eng. Sci.*, **37**, No. 8, 1339–1347 (1997).
13. A. É. Arinshtein and S. M. Mezhikovskii, *Khim. Fiz.*, **16**, No. 5, 122–133 (1997).
14. A. Arinshtein and S. Mezhikovskii, *Int. J. Polym. Mater.*, Vol. 47, 249–269 (2000).
15. T. F. Irzhak, S. M. Mezhikovskii, and V. I. Irzhak, *Dokl. Ross. Akad. Nauk*, **379**, No. 5, 628–630 (2001).
16. A. É. Arinshtein and V. I. Gol’danskii, *Dokl. Ross. Akad. Nauk*, **352**, No. 2, 312–315 (1997).
17. S. M. Mezhikovskii, *Physical Chemistry of Reactive Oligomers* [in Russian], Moscow (1998).