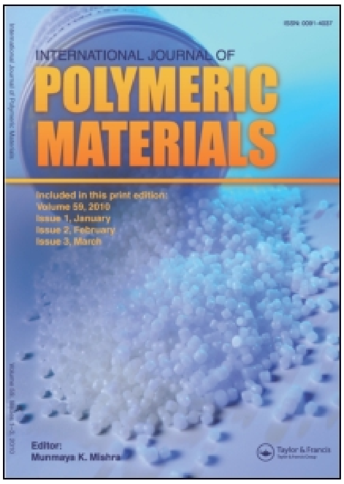

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Some Problems of Structure Formation in Self-Organizing Liquid Oligomer Systems

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Synergetic processes in liquid polymer systems have been studied intensively in the last decades. Nowadays, numerous experiments have proved the presence of self-organizing formations of various structure forms in polymer and oligomer systems.

The driving forces for the processes of self-organization are the fundamental laws of thermodynamics. But these processes proceed in time, obeying the kinetic regularities. The author consider self-organization as the processes of relaxation to the thermodynamic equilibrium going with different rates at the different levels of structure – the molecular, supermolecular, topological and the phase one.

Keywords: Oligomer systems; structure formation; process kinetics; self-organization; liquid phase

0. INTRODUCTION

The thermodynamics of oligomers is covered adequately in [1-6], also voluminous literature is dedicated to their phase-formation (see, for example, [7-10]). In the present work, in its first part the terminology is refined used for description of oligomer systems, but, generally, experimental data on the kinetics of the processes of self-organization at the level of supermolecular structure are considered and also topology of these processes is partially touched. In its second part, written in collaboration with Prof. A. E. Arinstein, theoretical models are presented which describe the processes of self-organization in liquid oligomer systems. The third part (in collaboration with Dr. A. V. Kotova) is devoted to the analysis of the kinetics of chemical transformations taking place during radically initiated polymerization of reactive oligomers.

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1. TERMS, DEFINITIONS, STARTING PRINCIPLES

First, let us determine the terms and concepts used in the present work. Some of them are evident, others are universally accepted and some are still open for discussion. In order to exclude possible variant readings, we will refine their physical meaning.

A great variety of definitions of the concept "self-organization", sometimes even mutually exclusive, are known (see, for example, [11–16]). In the context of the present review we accept that self-organization is a spontaneous (occurring due to internal causes) process of ordering of a system structure.

According to the paradoxical definition of [15, 16], ordering, *i.e.*, generation of order in structure, is a symmetry violation in the following sense. For example, an isotropic (a uniform in any direction inside the body) liquid is more symmetric than anisotropic one: local order appearing leads to violation of structure of a macroscopic system as a whole.

Local order manifests itself as structure inhomogeneity in the macroscopic body of a liquid.

The causes for structure inhomogeneities appearing in a liquid in general and in liquid oligomers in particular, can be various. They can arise as a result of phase transitions, form due to strong dipole–dipole interactions, hydrogen or complementary-group bonds, van der Waals forces of interaction between molecules, as a result of existence of large-scale fluctuations in the metastable region or at the critical point, and also of the "tails" of the random fluctuations distribution *etc*. In other words, inhomogeneities can be generated by forces of different energy-richness, it is the fact that, in general, controls geometrical sizes and the range of lifetimes of inhomogeneities of different nature.

In particular, fluctuations of concentration and density arising because of thermal motion of particles are considered as some structure formations (aggregates), which are characterized by finite sizes and finite lifetimes [16]. The dimensional and time ranges of such fluctuations in liquids may vary over very wide limits [16–21]. Besides, fluctuations can be distinguished by the degree of local anisotropy: according to [16] spatial and orientation arrangement of particles inside a fluctuation is not equiprobable; in turn, in different fluctuations belonging to the same macroscopic body the orientation directions may not coincide.

Inhomogeneity can be an element both of a homogeneous (one-phase) and of heterogeneous (two-, multiphase) structures (in the latter case inhomogeneities can arise in each of co-existing phases). It depends on the variables of state determining a system belonging to one region of the phase diagram or another. The presence of inhomogeneities in solutions and melts of oligomers does not necessarily mean heterogeneity of these systems, in the sense that a phase transition has happened there. Also, it does not points to the fact of "microphase" separation, as it is said sometimes. Not arguing here with representatives of other points of view [22], we will emphasize only that, according to the classical definition done by Gibbs, "a phase is a set of homogeneous parts of a system, equal in their composition and in their chemical and physical properties not depending on amount of a substance, and bounded by an interface from other parts of the system". Only the simultaneous set of these two criteria – independence of properties from the amount of a substance and the presence of an interface – is a necessary and sufficient condition for the existence of a thermodynamical phase, that dis tinguish between it and other types of inhomogeneity of a liquid.

The ideology of aggregation in liquid systems has a long history (see, for example, monographs and reviews [17–19, 24, 25]), the trials of its quantitative expression in the framework of the "colloidal approximation" ascending to the works of Smoluchowsky [26] and Oswald [27]. The concept of local order of molecules in a liquid (as opposed to the "gas structurelessness") arose in 1920s, when Stewart coined a term "cybotaxis region" for explanation of the diffraction patterns of X-rays scattering which was obtained in the experiments with various types of organic liquids [28]. The term "cybotaxis" (χιβωτοζ means "ark") [28], has been completely approved in science due to fundamental generalizations of Ya. I. Frenkel [18]. Now it is widely used for description of structure not only of common low-molecular, but also of metallic liquids [29]. The appearing later and presently wide-spread term "cluster" approaches to the term "cybotaxis" in its meaning, but its definition does not take account of a possibility of spatial orientation of initial particles forming a given structure unit.

In the literature on polymers one can meet many terms for determination of supermolecular inhomogeneities: agglomerates, aggregates, ensembles, associates (homo- or self-associates), blobs, domains, templates, clusters, complexes (heteroassociates), micelles, segregates, cybotaxes *etc.* Having a strictly specified meaning, each of these terms is valid. However, since sometimes the same terms are provided with different interpretations in different publications, it is necessary to revise the physical meaning of some of them.

For the description of supermolecular structure of liquid oligomer systems we use mainly the terms "aggregate", "associate" and "cybotaxis". The notion "aggregate" is more general, involving both associate and cybotaxis structures. The terms "associate" and "cybotaxis" related to the liquid state of oligomers reflect the distinct types of long-living (comparable with resolution of the experimental methods) supermolecular structure formations (aggregates). They differ in their spatial arrangement and orientation of molecules inside the body of local inhomogeneity of a liquid. Cybotaxes are characterized by different degree of anisotropy in the spatial arrangement of molecules, while associates are always isotropic [3, 18, 29]. The lifetime of the *i*th cybotaxis or of the *i*th associate depends on the composition and the temperature of a system and is controlled by the energy of intermolecular bonds. Given proper conditions, associates can transform into cybotaxes, and *vice versa.* In an equilibrium macroscopic system an increase in order (formation of aggregates, the transition "associate-cybotaxis" *etc.*) in one place is inevitably followed by disordering in another one.

A macroscopic closed system can be represented as a sum of microscopic subsystems (elements of a system) which in the process of attaining the equilibrium continue to exchange the matter and energy between themselves and the environment. Not only phase inclusions but also supermolecular structures, for example, fluctuations of oligomer molecules concentration with distinct time and dimensional parameters, can play the role of such subsystems.

Various forms of the distribution functions of such fluctuations by number, sizes and lifetimes $\mathbf{f}(n)$, $\mathbf{f}(r)$ и $\mathbf{f}(\tau_0)$ are postulated for liquids – the Boltzman, Gibbs distribution and others [17, 18, 30] and corrections to them [30–32]. In any case, the distribution functions change in the time of relaxation τ_i on the path of a system from the initial (most often random) state $\mathbf{f}_0$ towards its equilibrium (not depending on initial conditions) state $\mathbf{f}_e$. It is rarely feasible to calculate $\mathbf{f}_0(n, r, \tau_0)$ and $\mathbf{f}_e(n, r, \tau_0)$ accurately, therefore in practice the mean values of n, r, τ_0 are used.

The rate of relaxation represents a function of many variables. First of all [30], τ is determined by the scaling factor:

$$\tau_i = L/\nu_i, \qquad (I-1)$$

where τ_i is the characteristic time of relaxation, L is the linear dimension of a system, ν_i is the rate of approaching the equilibrium with respect to the ith parameter.

The rate of relaxation depends on the variables of the state of a system and, in the general case, the time of the equilibrium establishment in a macroscopic system is controlled by the slowest of the relaxation processes at the level of subsystems.

The time of relaxation of a single fluctuation (its lifetime) or, in the general case, the average time of relaxation of all the fluctuations determine the choice of the experimental technique for the study of a system. τ_0 must exceed the resolution of a method (instrument) t^*, while the average time τ_i of fluctuations relaxation to equilibrium determines the choice of the exposure time τ_e (the time of the object observation from the moment of a sample preparation to the beginning of its properties registration in the experiment).

Formation of supermolecular structure of liquid oligomer systems has an essential peculiarity, differentiating them from low-molecular and polymer liquids. The times of relaxation to equilibrium of supermolecular structures of low-molecular liquids are usually very small and, as a rule, the inequalities $\tau_0 < \tau_i$ и $\tau_i < \tau_e$ are obeyed. (Numerical estimations and special cases are presented in [17, 30]). Therefore the kinetics of the process of the fluctuations Gibbs equilibrium establishment does not limit the total rate of attaining the equilibrium in macroscopic systems (exceptions are considered in the framework of non-equilibrium thermodynamics [15, 33, 34]). Polymer systems are characterized by a broad spectrum of relaxation times and their upper limit times are so high that they exceed observation times by many orders [18], *i.e.*, $\tau_i \gg \tau_e$. Therefore, although a system does not attain equilibrium, the exact influence of the kinetics can not be detected in reasonable observation times and, hence, the role of the equilibrium attaining kinetics can not be correctly estimated experimentally [18, 35–38].

In liquid oligomer systems, due to their molecular structure specificity [3], lifetimes of supermolecular formations and resolution of experimental methods and also the time of the equilibrium establishment and the observation time may appear to be of the same order: $\tau_0 \cong t^*$, and $\tau_i \cong \tau_e$. Therefore, on one hand, the set of methods allowing correct investigation of oligomers expands [39], but, on the other hand, macroscopic properties of oligomers may manifest dependence of the time and temperature (generally, energetic) pre-history of a system. It is not inconceivable that registration of a property being measured will take place at different starting conditions or at different distance from the equilibrium state.

Unfortunately, no unambiguous experimental criteria have been yet in literature allowing reliable judging whether a system has attained the thermodynamic equilibrium by the moment of testing. It is likely to be a consequence derived from the classical expression (I-1), which involves the value of ν_i – the rate of attaining the equilibrium with respect to the ith parameter, but, as mentioned above, the rates may be different.

Thus, the thermodynamic equilibrium of a macroscopic system as a whole is preceded by the processes of the local equilibrium establishment at the level of subsystems (structure hierarchies). In other words, the establishment of the concentration equilibrium (equilibrium with respect to the molecular composition) still does not mean that the equilibrium function is attained for the distribution by number and sizes, all the more by their inner structure (topology). Clearly all this is a consequence of the kinetic peculiarities of attaining the thermodynamic equilibrium.

2. ANISOTROPY IN LOCAL ORDERS

The question about inner structure of supermolecular formations of oligomer liquids and the problem of anisotropic packing of molecules inside aggregates arose as early as in 1960s in connection with anomalies revealed for the values of initial rates of curing W_0 of some oligoesteracrylates [40, 41]. It turned out that it was impossible to account for the whole complex of experimental observations of the kinetics of unsaturated oligomers polymerization not only by means of the classical laws of the radical polymerization kinetics [42–46], but also by the concept of presence of usual random associates in a reactive liquid, *i.e.*, by existence of local microparcels in the system, with increased concentration of functional groups within them. Therefore, additional assumptions were required, one of which provided a possibility of anisotropic packing of reacting molecules inside fluctuations of a liquid system concentration.

In particular, anomalously, high values of the constants of the rates of polymer chain growth K were observed during iniciated polymerization of anisovtric oligomers like α,ω-dimethacrylate-n –tetramethyleneglycols at the degrees of polymerisation $\Gamma \rightarrow 0$, which appeared to be essentially (in a number of cases an order of magnitude) higher than K_g of monomeric methylmethacrylate. For the explanation A. A. Berlin and G. V. Korolev [40, 47] suggested that in liquid oligomers aggregates (supermolecular formations) exist in which spatial orientation of molecules is not random but anisotropic. Molecules are oriented within them so that double bonds of methacrylic groups are brought close together and in the kinetically favourable order (see Fig. I-1 (I)). It was assumed that, when lifetimes τ_p of such labile templates (in our terms, cybotaxes) are comparable or exceed the time of an elementary act of a chemical reaction τ_c (the lifetime of an active center or of the transition state), they must provide W_0 increase as compared with the "normal" rate of polymerization (controlled by reactivity of the methacrylic bond in the processes of methylmethacrylate polymerization), due to an increase of the pre-exponent in K_g.

This idea about determining role of supermolecular aggregates in the processes of *liquid* systems polymerization, in which molecules are oriented predominantly in a certain direction, probably, "was in the air" at that time, because at about the same time it was used

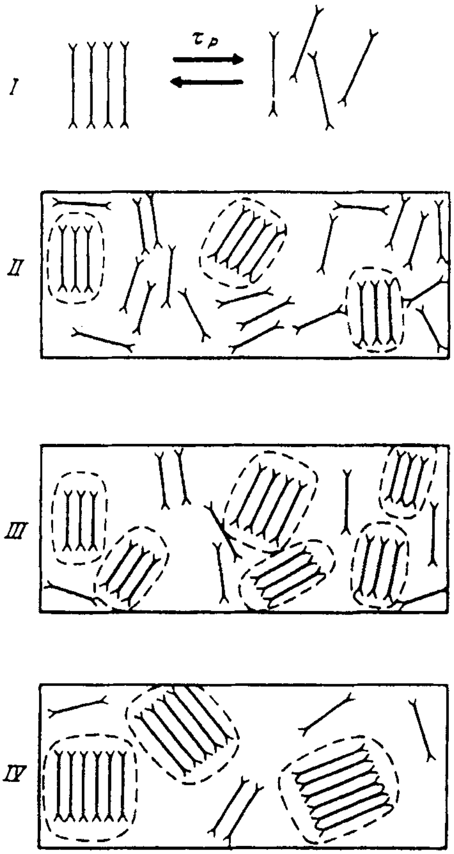

FIGURE I-1 The scheme of the cybotaxic model of liquid oligomers structure. >—< – a molecule of a telechelate oligomer; τ_p – lifetime of a cybotaxis. I – formation and disintegration of a cybotaxis ("kinetically favourable order"). Cybotaxic liquids may differ in lifetimes of cybotaxes (τ_p - var), in the number of cybotaxes in a volume unit (II И III), in the sizes of cybotaxes (II И IV).

independently, in one or another form (as orientation on substrates, smectic structures *etc.*) in the works of various author groups [*i.e.*, 41, 48–53].

Since that time, numerous circumstantial evidences of the hypothesis about existence of regions with spatial anisotropy of molecules in oligomer liquids have been obtained. In addition to the compact analysis of early works having allowed formulating and evaluating the hypothesis about particles anisotropy inside aggregates of liquid oligoesteracrylates, which is presented in the monograph [54], let us consider the result obtained recently, for the explanation of which there have been apparently no any alternative to the cybotaxis model.

In [55, 56] the initial stages of the polymerization process were investigated for one-phase solutions of tetramethylene-α,ω-dimethacrylate (MB), whose characteristic viscosity $\eta \approx 5$ cP, in unreactive oligomers of various viscosity – in bis-(dioxyethylenephtalate)-α,ω-diisobutyrate (IDF), ($\eta \approx 1000$ cP); in trioxyethylen -α,ω-diisobutyrate (TGI), ($\eta \approx 10$ cP) and in the fully saturated analogue of MB tetramethylene-α,ω-diisobutyrate (IB), ($\eta \approx 5$ cP). The obtained results were compared with the kinetics of polymerization of methylmethacrylate (MMA), dissolved in the same unreactive oligomers.

In Figure I-2 one can see the dependencies of the values of MB polymerization rate W_0 extrapolated to the initial point of time on the weight fraction φ_1 of MB in these solutions. In the given case the rate value is normalized to the concentration of methacrylic groups in the

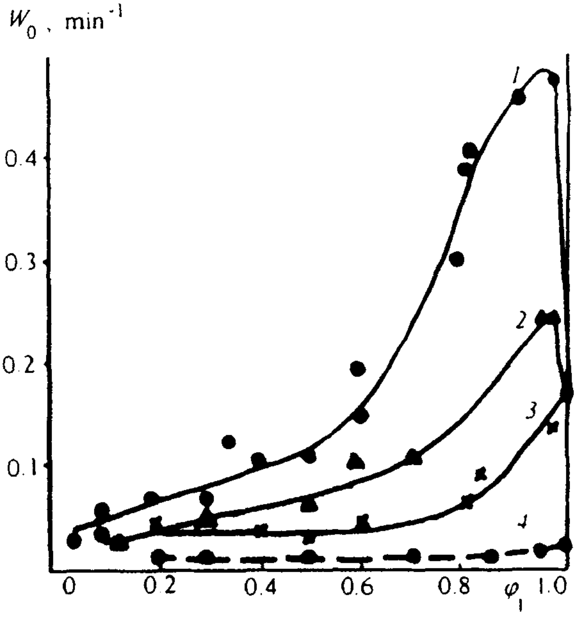

FIGURE I-2 The dependence of ω_0 on φ_1 for the blends of MB with IDF (1), TGI (2), IB (3) and the blend of methylmethacrylate with IB (4).

solution. In the same coordinates (except that ϕ_1 is the weight fraction of MMA) the data are presented for the polymerization of methylmethacrylate blended with IB (MMA blended with TGI and IDF give the same picture). It can be seen that, for the solutions of MB in a highly viscous solvent the curve $W_0 = f(\varphi_1)$ has a maximum in the region of higher concentration of oligoesteracrylate (Curve 1). As an unreactive solvent viscosity decreases, the rate peak magnitude diminishes gradually (Curve 2) and for the blend of component with close values of characteristic viscosity W_0 dropped at once with increase in weight fraction of the unreactive analogue (Curve 3). For the solutions of methylmethacrylate the dependence of W_0 on concentration was not observed at all (Curve 4).

The analysis of these data first requires the answer to the fundamental question – why addition of an "ideal" diluent (IB does not differ from MB in its chemical structure, except the double bond substituted by the saturated one) or a thickener (viscosities of MB and IDF differs by more than two decimal orders) to a reactive oligomer results in corresponding drop or growth (but always change) in W_0.

Accounting for this experimental phenomenon in the framework of the classical "gel-effect" [57] (increase of viscosity leads to decrease in the constant of the kinetic chain termination rate and in turn to growth of W_0) can interpret the only region on the Curve 3 in Figure I-2 – where W_0 grows with adding more viscous IDF to MB. But it leaves unexplained the rate diminution observed during the further thickening of the reaction system. Other common in chemical kinetics assumptions considered, for example, in [54, 58], also can not offer reasonable explanation of the whole complex of the effects revealed. For instance, the W_0 values operated in [55, 56], are normalized. They are related to the total quantity of reactive groups in the system and hence in the kinetic sense should not depend on the MB concentration in the solution. In other words, for all the oligomer systems (Curves 1–3) a picture should be observed identical to that for monomeric methylmethacrylate (Curve 4). Nevertheless, as it follows from Figure I-2, for the solutions of anisometric telechelate oligomers the experiment indicates a rather complex dependence W_0 on φ_1, which is seemingly not to be expected if to adhere to traditional schemes. The interpretation of the above data logically fits in the scheme of the cybotaxis model of an oligomer liquid (see. Fig. I-1).

Accepting existence of some distribution of cybotaxes by number, sizes and lifetimes in an oligomer system [55, 59], accepting W_0 growing with increase in the number of cybotaxes (templates with kinetically favourable orders), increase of their lifetimes and of reactive molecules number in a single cybotaxis (*i.e.*, its size), the explanation of the regularities considered above leads to the following.

The initial W_0 growth in thickened systems comparing with the W_0 observed in the "pure" MB is a consequence of increase in number and lifetimes of cybotaxes taking place in the case of adding highly viscous components. It is in agreement with the idea considered in [54, 60].

The W_0 drop observed for the systems with close viscosities of components is a result of "embedding" of an unreactive component into the structure of the "kinetically favourable order" of a reactive oligomer (see Fig. I-3), which is not restricted thermodynamically. It is quite evident that even when structure parameters of cybotaxes of type B forming in a blend system do not differ from the corresponding characteristics of cybotaxes forming from the molecules of oligoesteracrylate only (type A), even so the number of elementary acts of chemical interaction at the initial point of time will be less in the cybotaxes of type B than in the cybotaxes of type A. Hence, W_0 must decrease. It follows from Figure I-3 that in the case of a blend system the rate of W_0 decrease may vary not in direct proportion to the diluent concentration. Moreover, at the equimolar ratio between reactive and unreactive molecules in a solution the role of supermolecular structure in polymerization processes is bound to be no more affecting. In such a case pair neighboring of two methacrylic groups and of one methacrylic and one isobutyrate groups inside a

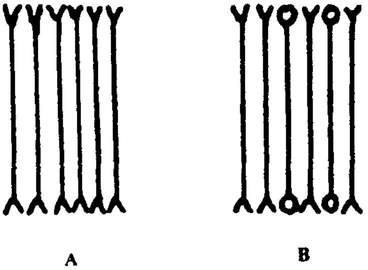

FIGURE I-3 The scheme of cybotaxes consisting of molecules of oligoesteracrylate (A) and of the mixture of molecules of oligoesteracrylate and its saturated analogue (B).

cybotaxis becomes equiprobable. Therefore, at such concentrations the classical kinetics laws are expected to start functioning. As it is seen from Figure I-2 (Curve 3), it is $\varphi_1 \approx 0{,}5$ when the rate ceases to depend on φ_1.

One can easily account for the fact that for the systems with high viscosity of the unreactive component an extremum on the curve $W_0 = f(\varphi_1)$ is observed in the experiment. It is due to a competition between the positive effect of the second component on the polymerization process as of a thickener (the number of cybotaxes grows which have lifetimes comparable with the times of elementary acts) and its negative effect (at the same time, because of "embedding" of unreactive molecules into the structures with the "kinetically favourable order", the number of elementary acts in a unit time decreases). It is evident that at a low dosage of a thickener the first factor prevails, while at a high dosage – the second one.

The considered above, as well as many other [5, 53, 55, 56, 58, 61 – 65] experimental testimonies to the anisotropic arrangement of molecules in supermolecular structures of liquid oligomers are actually circumstantial evidences. It is probably the reason for a certain skepticism in respect to the associate-cybotaxis model of oligomer systems structure and to the role of anisotropic structure of aggregates in thermodynamics, kinetics and mechanisms of macrostructure formation in such systems and also in their physical and chemical properties. Omitting the discussion on this problem [53, 54, 58, 61, 62], we will note only that if leaving aside terminological distinctions, thecurrent concepts of existence of long-living supermolecular formations in oligomer liquids, including anisotropic ones, not only quite conclusively account for many anomalies of dynamic and stationary macroscopic properties of oligomers [31, 40, 41, 54, 58, 63, 66], but also recently were substantiated theoretically.

We will consider in detail the theoretical model of the kinetics of a chemical reaction with anisotropic aggregates and its substantiation in [67]. Here, let us note that in the works of A. E. Arinstein [68, 69] for the description of chemical processes in liquid condensed systems in the framework of the polychronic kinetics model [70, 71] the notion was introduced about a spectrum of the constants of elementary chemical reactions rates. This spectrum is a consequence of different degrees of relative orientation of reacting molecules. The level of structure organization is characterized by the parameter of orientation order α. The latter may vary from 0 (the system is fully isotropic) to 1 (the maximum degree of anisotropy, molecules are parallel).

In the framework of these postulates the kinetics of, for example, a bimolecular reaction is described by the equation

$$dC(t)/dt = K_{ef}(\alpha)C^2(t), \qquad (\mathrm{I}-2)$$

where $C(t)$ is the function of the current concentration of a reactant.

In the linear approximation

$$K_{ef}(\alpha) = K_{ef}(0) + dK_{ef}(0)/d\alpha(1-\alpha) = k_1\alpha + k_2(1-\alpha). \qquad (\mathrm{I}-3)$$

Here k_1 and k_2 are the constants of the rates of chemical reactions in the ordered and disordered subsystems, correspondingly.

The evolution of the order parameter is expressed as

$$d\alpha/dt = W_{Th}(\alpha) + W_{Ch}(C,\alpha). \qquad (\mathrm{I}-4)$$

The function $W_{Th}(\alpha)$ determines variation of order in a system in the absence of a chemical reaction, and the function $W_{Ch}(C, \alpha)$ – in the process of chemical transformations. According to [69]

$$W_{Th}(\alpha) = -(\alpha - \alpha_{Th})f_{Th}(\alpha) = -k_3(\alpha - \alpha_{Th}), \qquad (\mathrm{I}-5)$$

where α_{Th} is the value of the order parameter corresponding to the thermodynamical equilibrium of the system.

The last equality in (I–5) corresponds to the situation when f_{Th} (α_{Th}) = Const. In the general case, $\alpha_{Th} \rightarrow 1$ or $\alpha_{Th} \rightarrow 0$, *i.e.*, in the process of attaining the equilibrium in the system both self-organization in the relative arrangement of molecules and disordering can occur.

In the consideration presented above the only essential approximation used is that the spectrum of the kinetical constants of a chemical reaction is not self-averaged, as it is accepted in the classical gas kinetics. It is presented in the form of a function of distribution of the orientation parameter of reactive molecules, because of high times of structure relaxation in condensed media. Thus, from this consideration, it follows that the rate of a chemical reaction must *naturally* depend on this function of distribution, both in the equilibrium and on the path to the equilibrium. In other words, the rate of a chemical reaction *must* depend on what part of reactive molecules has managed to form supermolecular structures with the "kinetically favourable" order or, in our terms, what fraction of associates has managed to relax into cybotaxes. The experimental data [55, 56] confirm this conclusion.

3. LIFETIMES OF SHORT ORDERS

It was noticed earlier that short orders in oligomer liquids may be generated by the forces of various nature and energy-richness.

If supermolecular structures form due to thermal fluctuations, then, according to [18], the transition of a liquid particle from one equilibrium state to another is an activation process. So the time of "settled life" of a particle near the point of equilibrium is determined by the Arrhenius function of temperature:

$$\tau = \tau_0 e^{w/kT}, \qquad (I-6)$$

where τ_0 is the mean time of a particle stay in a given fluctuation, up to its disintegration or "splitting out" of it, and w is the activation energy of the disintegration or splitting out process. In the simplest case $\tau_0 \sim$ the period of atomic vibrations $\approx 10^{-12}$ sec. It is apparent that the lower the temperature, the more τ. For T, corresponding to the liquid state of a system, the lower limit of τ usually does not exceed 10^{-7} – 10^{-9} sec. However, when a system enters the metastable region in the process of lowering the temperature (for blend systems also in the process of varying the concentration), lifetimes of fluctuations essentially increase [72], and at the critical point $\tau \rightarrow \infty$ [30, 72].

Note two circumstances. On one hand, the temperature (and concentration) range corresponding to the critical point is very narrow [73, 74], and "falling into it" is an extremely difficult experimental task [30, 72, 74]. But, on the other hand, for oligomers which are characterized by a broad MMD [75], in the case of aggregation *due to weak forces* the probability of lifetimes increase for some fluctuations becomes many times higher. It is connected with the fact that for polydisperse systems the *local* "critical" and "metastable" states may appear at any point of the phase diagram, *i.e.*, at various T values [22, 76–78]. Although not apparent, this assumption is used in the works of many authors for explanation of some features of translational diffusion of oligomers [1], their rheological behaviour [66, 79, 80], of the processes of phase separation during curing [77, 78] *etc.*

The other situation is in the case of formation of oligomer supermolecular structure due to appearing of rather strong dipole–dipole, hydrogen *etc.*, bonds. Recently G. V. Korolev [39] has conducted, in the framework of the physical networks ideology [58, 81], the analysis of a possibility to realize and detect interaction between atomic groups (centers of intermolecular interaction – IICs) characterized by different bond energy (see Tab. I-1).

In [39] the process of molecules binding into aggregates is considered as the process of equilibrium polycondensation, with the only difference that, in contrast with the chemical reactions of step-by-step addition, which are finished by the formation of stable (under real conditions) covalent bonds between molecules, "physical polycondensation" leads to the formation of a final product characterized under the same conditions by lability of bonds between II*Cs*.

The mechanism of bonds formation is described by a simple kinetic scheme of reversible polycondensation:

$$\Gamma + \Gamma \xrightarrow{k2} \Gamma_2 \tag{I – 7}$$

$$\Gamma_2 \xrightarrow{K1} \Gamma + \Gamma \tag{I – 8}$$

TABLE I-1 The bond energies of II*Cs* formed by different atomic groups

Atomic group	*E, kcal/mol*	*Atomic group*	*E, kcal/mol*
—C=O | OH	10,8	—C=O | H	4,3
—C_6H_5	7,6	> C=Or	3,6
—OH	7,3	—NH_2	3,6
—O—C—O— ‖ O	6,6	—O—	1,5
—CN	6,3	—C=C—	0,7
—C=O | OR	4,4	≡C—H	0,5

Note. E were calculated basing on the data of the evaporation heats measurements [1.82].

Here, Γ is the atomic group carrying an IICs, Γ_2 is the intermolecular bond, K_1 and K_2 are the constants of the rates of the bond dissociation and regeneration (of the forward and reverse processes).

The Γ_2 lifetime is connected with the monomolecular constant K_1 of the rate of this bond dissociation by the relation [39]:

$$\tau = 0,69/K_1 \qquad (I-9)$$

In turn,

$$K_1 = k_{01}e^{-E_1/RT}, \qquad (I-10)$$

where $K_{01} \approx 10^{12}\,\text{sec}^{-1}$ (the frequency of atomic groups vibration), and E_1 is the dissociation energy of the corresponding IIC (see Tab. I-1).

Similarly to the case of thermal fluctuations, the lifetime τ of bonds formed by IIC obeys the Arrhenius law.

The equilibrium concentration of intermolecular bonds v grows with lowering the temperature up to its limit value v_0 corresponding to the total content of all the potential IIC capable of bonds forming. The quantity v/v_0 has the meaning of the equilibrium degree of aggregation, it is the fraction of the potential IICs conversion into intermolecular bonds

$$v/v_0 = (1+\gamma) - \sqrt{(1+\gamma)} - 1, \qquad (I-11)$$

$$\gamma = K_1/8K_2v_0 = K_{01}\cdot\exp[(E_2-E_1)/RT]/8K_{02}v_0, \qquad (I-12)$$

where K_{01}, K_{02}, E_1 and E_2 are the pre-exponents and activation energies of the corresponding reactions. Since several potential IIC may be in an oligomer molecule (in the general case n), then

$$v = n\cdot C, \qquad (I-13)$$

where C is the concentration of oligomers molecules.

According to the estimations of [39], at $n > 2$ almost all the liquid molecules appear to be bound with each other and are the components of aggregative structure. Needless to say that situation of this type can be detected experimentally only in such a time scale of observing the system t^* which is comparable with lifetimes of these bonds.

In Figure I-4, the dependencies of v/v_0 and τ_a on E/T are presented [39]. Their correlation with the resolution of different methods (Tab. I-2)

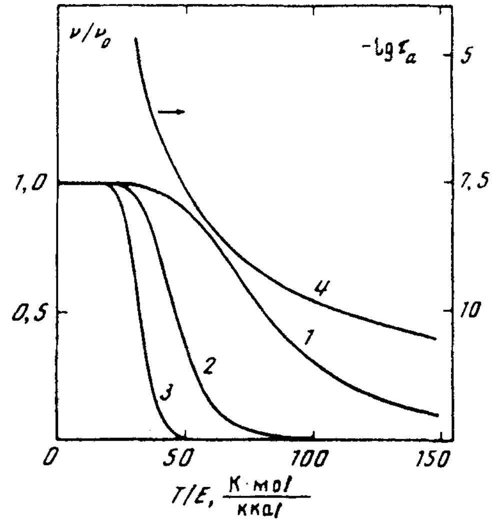

FIGURE I-4 The generalized by T/E dependence of the degree of association (v/v_0) and a lifetime (τ_a) of an associative bond. The values of $K_{01}/(K_{02}v_0)$, used in the course of calculations, are equal to 10^3 (1), 10^5 (2) and 10^7 (3).

TABLE I-2 Time resolution of different experimental techniques [39]

Technique	*t^*, sec*
Efficiency of radical initiation	10^{-10}– 10^{-9}
ESR in the spin-probe variant	
3 cm range (without saturation transfer)	$5 \cdot 10^{-11}-10^{-7}$
3 cm range (with saturation transfer)	$5 \cdot 10^{-8} - 10^{-4}$
2 cm range	$\geq 4 \cdot 10^{-10}$
NMR	
high resolution	$\sim 10^{-10}$
in the impulse method variant	10^{-6}– 10^{-5}
Kinetic parameters of radical polymerization	$> 10^{-4}$
Relaxometry	
dielectric	10^{-6}– 10^{-3}
mechanical	$> 10^{-1}$
Thermomechanics	> 1

allows *a priori* determination of the condition of correctness ($\tau_0 > t^*$) of the methods application for the study of oligomers containing functional groups with different values of E_1, in various temperature ranges and under various model conditions corresponding to the curves 1 – 3 in Figure I-4.

It follows from this analysis, that in the temperature region 20–80°C where in the experiment the anomalies of dynamic and stationary properties of oligomer liquids, attributed to their supermolecular structure specificity, manifest themselves [3, 7, 40, 41, 47, 54–56, 64–66], lifetimes of the Γ_2 formed by the IIC with bond energies of 0,5–10 kcal/mol (see Tab. I-1) appear to be $< 10^{-5}$– 10^{-6} sec. In other words, if the above considerations [39] are valid, then the anomalies of oligomer liquids seemingly are not related to the peculiarities of their supermolecular structure, since aggregates lifetimes are smaller than the resolution of the methods that detected them (see Tab. I-2).

This contradiction is resolved when taking account of the following considerations [39]. The estimations show that for the τ of aggregates being $> 10^{-4}$ sec., *i.e.*, sufficient to be detected by the methods pointed out, it is necessary that E_1 should be ≥ 12 kcal/mol. Molecules of oligomers, in particular, oligoesteracrylates, contain several II*C*s in one molecule with $E_1 = 3-9$ kcal/mol. Let us assume that separate bonds interaction is not isolated but correlated and a supermolecular aggregate is held by the interaction of a "bundle" of *n* II*C* bonds. Then, for an aggregate to dissociate or even for only two "bound" molecules to move away from each other due to translational diffusion, it is necessary that all *n* bonds connecting adjacent molecules dissociate *simultaneously*. For these events the energy fluctuation is required essentially greater than 12 kcal/mol. In other words, in order to provide aggregates with $\tau > 10^{-2} - 10^{-4}$ sec. it is sufficient that in the process of intermolecular interaction the *sum* of bond energies of *n* of II*Cs* of one oligomer molecule would be > 12 kcal/mol. For the most oligomers the condition of $\Sigma E_1 \geq 12$ kcal/mol is fulfilled. (See also [13, 81)].

4. THE KINETICS OF FORMATION OF EQUILIBRIUM SUPERMOLECULAR STRUCTURE IN HOMOGENEOUS OLIGOMER SYSTEMS

It is a well-known fact [1, 22, 83, 84], that in oligomer systems attaining the equilibrium state is diffusion limited, proceeds step-by-step and is protracted. It was shown in [56, 85–87] that the concentration equilibrium establishment in co-existing phases of heterogeneous oligomer systems is followed by further rearrangement of molecules which is presumably [84] related to the process of attaining the equilibrium with respect to structure parameters of supermolecular formations. This latter stage appeared to be unexpectedly slow, limiting the whole process of the thermodynamic equilibrium establishment in oligomer systems.

For the first time the hypothesis about protraction of the process of supermolecular structure rearrangement in oligomer blends was proposed in [85] because of absence of alternative ideas capable of accounting for the dependence of the initial rate W_0 of oligoester-acrylates curing on time pre-history of rubber-oligomer systems. Later this hypothesis was confirmed by means of the direct study of the relaxation kinetics of a blend components which was conducted using the impulse NMR method [87, 88] and IR-spectroscopy [89]. For instance, in IR spectra of solutions of oligoisoprenedihydrazone and diisocyanates blends to which proton acceptors (dioxane, acetone) were added, besides the band of free NH-bonds υ_{NH} in the region of $3400-3450\,cm^{-1}$, after 2–60 days of storage the band of associated NH-bonds $(\upsilon_{NH})_a$ appears in the region of $3300-3350\,cm^{-1}$. Diluting or heating a solution results in a decrease in the band intensity, but after ceasing the action its intensity rises again and reaches its initial magnitude in 40–60 days [89].

4.1. Relaxation to Equilibrium According to the NMR Data

In Figure I-5 [87] the dependencies of T_2 – times of spin-spin relaxation characterizing the modes of motion of the corresponding components of a system – and of their fractions P (in the total sum of fractions of all the T_2 which is equal to (1) on the exposure time τ_e are presented, for tetramethylene-α,ω-dimethacrylate (MB) and *cis*-polyisoprene prior to blending and for their blend after reaching the equilibrium swelling of the rubber in the oligomer. (The exposure time is a time from the moment of a sample preparation to the beginning of a measurement). One can see that the characteristic times of relaxation T_2^0 of the oligomer and $(T_2^r)'$ and $(T_2^r)''$ of the rubber measured in each of the components prior to blending do not depend on τ_e (Curves 1–3). Two characteristic times found in the rubber reflect existence of domains with distinct densities of molecular packing there.

The situation changes after swelling. Three times T_2 are revealed in the swelled system, of which one – $(T_2^0)_c$ – is assigned to the oligomer and the other two – $(T_2^r)'_c$ and $(T_2^r)''_c$ – to the rubber. First, these three

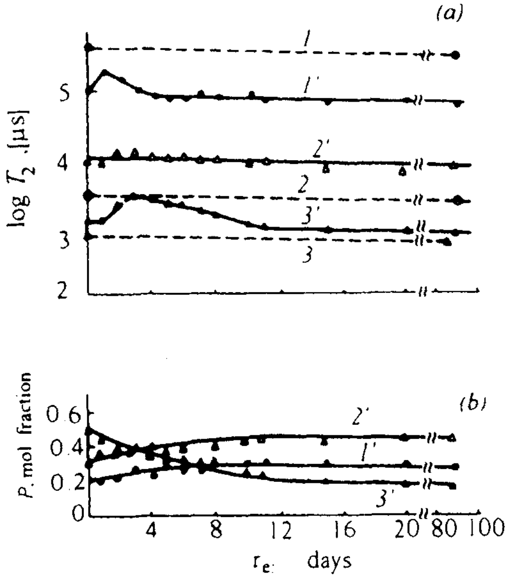

FIGURE I-5 The dependence of lg T_2 (a) and P (6) on τ_e for tetramethylene-dimethacrylate (1), *cis*-isoprene (2, 3) and *cis*-polyisoprene swollen in tetramethylene-dimethacrylate (1′ – 3′).

times differ from the corresponding times of individual components in their magnitude. Second, in spite of the fact that no visible changes happen during the exposure period, they manifest dependence on τ_e.

Indeed, $(T_2^0)_c < T_2^0$, it is natural, since the oligomer molecules mobility is retarded in the presence of the rubber. $(T_2^r)'_c > (T_2^r)'$ and $(T_2^r)''_c > (T_2^r)''$, it is natural too, since mobility of the rubber molecules (segments) increases due to plasticization. These effects are expected. Unexpected was the fact that while the characteristic times of nuclear relaxation of the individual components before blending do not depend on τ_e, after swelling T_2 of each component in the blend varies as a function of τ_e. In the same period the ratio of the protons fractions P corresponding to each of the three characteristic times of relaxation changes permanently. The complete cessation of changing of all the nuclear relaxation parameters as a function of the time exposure occurs only at $\tau_e \geq 12$ days. The analogous in their meaning results were obtained when investigating relaxation characteristics of other polymer-oligomer and oligomer-oligomer systems [88, 90 – 92].

Not discussing here the thorough information containing in the data presented in Figure I-5, we will emphasize only two following from this information consequences which are important for the problem under consideration:

(1) After reaching the limiting swelling, *i.e.*, in the systems called swollen to equilibrium, the structure rearrangement continues within them, which causes the dependence of T_2 and P on τ_e. Since chemical reactions proceeding is impossible during this period, the macroscopic concentration in the system does not change, as well as other parameters of its state do not change, it is natural to connect the mentioned variations of T_2 and P with rearrangement of supermolecular structure of the system. The rearrangement take place during the exposure because of redistribution of molecules between the elements of the subsystems.

(2) Approaching the limit by all the curves $T_2 = f(\tau_e)$ and $P = f(\tau_e)$, *i.e.*, cessation of the processes of supermolecular structure rearrangement in swollen samples in the given systems, happens at 10–12 day of exposure (τ_e^{cr}). It is 30–50 times greater than the time of equilibrium swelling (τ_S^{cr}), equal to 6–8 hours for the systems under study. This critical time of approaching the limit τ_e^{cr} is taken as the time of the thermodynamic equilibrium establishment at the level of supermolecular organization of a system. The value $\tau_e^{cr} \approx 12$ days determined using the nuclear relaxation test coincides with the estimations of the times of attaining equilibrium in analogous systems fulfilled in [85, 86], using the test of exposure time independence of kinetic characteristics of curing.

In other systems, the time of attaining equilibrium may be different. For example, in epoxide blends (also using the NMR measurements test) it extends to even several months [92].

4.2. Relaxation to Equilibrium According to the Data on the Kinetics of Curing

For the same system as considered in the previous section (MB in the *cis*-polyisoprenematrix) in connection with the peculiarities of its relaxation to equilibrium, in [86, 93] the dependence of the kinetics of the chemical reactions of curing on the exposure time τ_e

was investigated. The kinetics curves of polymerization (degree of conversion Γ – time t) were obtained by the method of calorimetry with variation of τ_e. The samples for testing, similarly to [87], were prepared by swelling of the rubber films in the oligoesteracrylate up to the limiting weight, that took no more than 8 hours at room temperature. Then the swollen films were withdrawn from the liquid and stored in contact with air, fixing τ_e. Neither chemical nor any other visible changes had not happened for the time of storage: no weight and volume changes, no oligomer oozing out to the film surface was detected *etc.*

In Figure I-6, the kinetic curves of polymerization in the coordinates $\Gamma = f(t)$ are presented for three series of samples (see Tab. I–3): I. – All other conditions being equal, the time swelling τ_S was varied from 6 to 240 hours; II. – At τ_S = Const τ_e was varied from 0 min to 90 days; III. – Swollen samples (τ_S^{cr} = 8h) stored in contact with air for 240 h were repeatedly placed in contact with 4 – IMM, in which the film swelled earlier. After 8 h of the repeated storage in the oligomer, which did not lead to any change in weight, the films were withdrawn

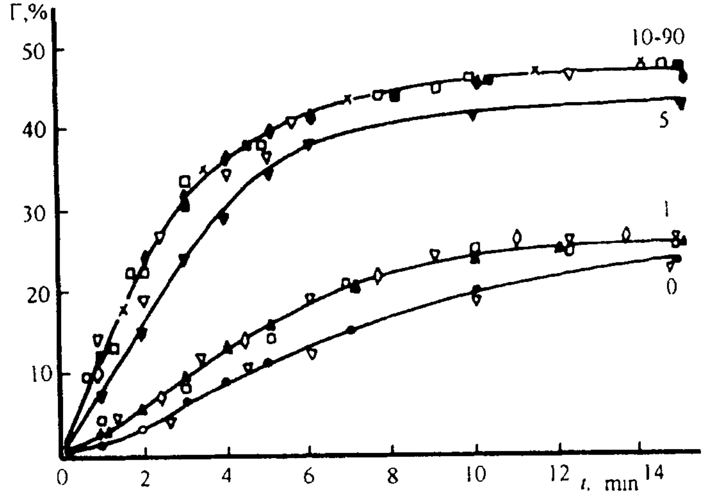

FIGURE I-6 The kinetic curves of polymerization of tetramethylene-dimethacrylate in the *cis*-isoprene matrix at different values of τ_e (figures at the curves are days) И τ_S : 8 (°), 24 (×), 48 (◊) и 240 (∇) hours. Shaded symbols mean samples after the repeated swelling. The explanation is in the text, see Table I–3.

TABLE I-3 The samples of the *cis*-polyisoprene-tetramethylene-dimethacrylate system prepared by primary and repeated swelling

The sample type	*Notation in Figure* I-6	τ_S, *h*	τ_e, *days*	*The curve number*	τ_S, *h*	τ_e, *days*	*The curve number*
		Primary swelling			*Repeated swelling*		
A	1	8	0	I	–	–	–
		8	1	II	–	–	–
		8	5	III	–	–	–
		8	10	IV	–	–	–
		8	90	IV	–	–	–
B	2	24	0	I	–	–	–
		24	10	IV	–	–	–
	3	48	1	II	–	–	–
		48	5	III	–	–	–
	4	240	0	I	–	–	–
		240	10	IV	–	–	–
C	5	8	10	–	8	0	I
		8	10	–	8	1	II
		8	10	–	8	10	IV

from the liquid and the procedure was repeated in the manner used in the series II.

The analysis of the data presented in Figure I-6 indicates:

(1) The increase of $\tau_S > 8\,\mathrm{h}$ does not affect the kinetics of curing at $\tau_e = \mathrm{Const.}$ *i.e.*, in the case the concept about the connection between W_0 and structure order in the liquid phase [40, 54–56, 61] is valid, then no changes occur in supermolecular structure of a system during the period of swelling $\tau_S > \tau_S^{cr} = 8\,\mathrm{h}$. Even in the case changes happen they are beyond the limit of the given method sensitivity.

(2) Within the interval $\tau_e = 0-10$ days the rate of curing and the limiting degree of polymerization grow with τ_e growth. At some critical value of the exposure time τ_e^{cr}, which in the given case is ~ 10 days, further τ_e increase does not influence the kinetics of curing. In other words, the molecular structure rearrangement, to which the kinetics of chemical transformations is sensitive, occurs during the sample storage period and ceases at $\tau_e = \tau_e^{cr}$. This time is assumed to be the time of a system relaxation to the thermodynamic equilibrium at the level of supermolecular structure organization.

(3) Swollen films stored earlier at $\tau_e \geq \tau_e^{cr}$ "forget" about their kinetic stability after the secondary contact with the oligomer (samples of

the series III). Their kinetic behaviour resembles that of samples after the primary swelling, *i.e.*, they manifest the dependence of the constants of the polymerization rate on τ_e. In other words, changes in supermolecular structure taking place in the period τ_e are reversible: after the secondary contact with the oligomer the supermolecular structure of a system returns to its original state.

It follows herefrom that the spontaneous formation of the equilibrium supermolecular structure of a system providing the stability of the kinetics of curing not depending on time pre-history, occurs after the swelling process has finished, in the exposure period $0 < \tau_e \leq \tau_e^{cr}$, and in the absence of a contact of a swollen film with the liquid phase. During this period, in the macroscopic body of a sample local redistribution of the oligomer concentration takes place, as well as spontaneous formation of the supermolecular structure elements (cybotaxes and associates). Their lifetimes, radii of correlation, physical bonds strength *etc.*, differ from those of the original oligomer and of a polymer-oligomer film in contact with the liquid.

What are the driving forces leading to so essential rearrangement of a system structure in the period τ_e which proceeds seemingly for no apparent thermodynamic reasons? Indeed, while at the stage of swelling averaging the concentration over the macroscopic volume of a system takes place by means of diffusion, due to the natural minimization of the internal energy of a blend [1], in systems swollen to the constant weight the chemical potential gradient approaches to zero within the error of experimental measurements [94, 95]. Since the macroscopic state variables (temperature, concentration, pressure) do not vary during the exposure period, the thermodynamic nature of the process of supermolecular structure rearrangement and even the fact of the rearrangement may be thought as doubtful. To settle these dobuts two versions of qualitative considerations are used.

According to the first one [39] anisotropic structures with strictly ordered packing of oligomer molecules are assumed to form from chaotic disorder as a result of strong bonds generation between II*Cs* of different oligomer molecules in local microparcels of concentration fluctuations. (In our terms, the associate → cybotaxis transition occurs.) The more the number of II*Cs* in a molecule, the more the possibility of this process. The entropy loss (the disorder → order transition) therewith is compensated by the energy gain (the strong intermolecular bonds formation). This consideration is supported, first, by the thermodynamic data [5, 63] which show that the redistribution of the entropy and enthalpy components of free energy and the mutual compensation of combinatorial and non-combinatorial parts of the total entropy take place in oligomer systems; second, by the fact, that for liquid oligomers the coefficient of molecular packing (CMP) is higher than that for low-molecular liquids. For instance, for oligoesteracrylates CMP = 0.639 – 0.702 [54], while for common liquids the maximum value of CMP = 0.58 [96]. Assuming the process of the associate → cybotaxis transition proceeding in time, the version that strong intermolecular bonds formation facilitates the generation of order appears to be realistic. Nevertheless, it can not explain the reasons for extended time of this transition. Also the question is left unexplained why strong intermolecular interactions take place only after a variation in the conditions of storage of the rubber-oligomer system, *i.e.*, why the equilibrium is broken only after the rubber-oligomer film is withdrawn from the liquid.

The second version gives the explanation to the latter fact as well. It was supposed in [86] that the driving forces for spontaneous proceeding of the processes of supermolecular structure rearrangement are the disturbances caused by molecular forces of interaction in the superficial layer being not compensated and the change of the concentration profile, as a consequence.

The qualitative interpretation of this idea is as follows. The system in which the limiting value of swelling is reached is considered as a two-phase one, where a film swollen to the limit (a solution of the oligomer in the rubber) is one phase and a very diluted solution of *cis*-polyisoprene in the oligomer (up to 0,1 – 0,3% of *cis*-polyisoprene molecules dissolve in the oligoesteracrylate in the process of swelling [63]) is the other one. It is this macroscopic system, in which the contact of a film with the liquid takes place and the phase boundary is permeable for gradientless migration of components, that should be considered as equilibrium one.

After a film swollen to the limit is taken from a solution and the remains of the liquid are removed from its surface, the thermodynamic equilibrium is broken, since the contact "film – liquid" is replaced by the contact "film – air". Clearly the surface tension at the boundaries "film – liquid" and "film – gas" are distinct. Hence [97], the local concentrations and the degrees of orientation of molecules are to differ in superficial layers and in the bulk. Therefore, as soon as a film is withdrawn from the liquid, the equilibrium established earlier is broken and a new one is formed, with its own concentration profile. Note, that formation of a concentration profile (*i.e.*, appearing of differences in the values of concentration in superficial layers and in the bulk) itself could not affect the values of the constants of oligoesteracrylates polymerization determined experimentally but for at the same time it caused variation of the degree of anisotropy in the newly formed elements of supermolecular structure. (Let us remind that in the given experiment W_0 was normalized to the total concentration of the oligomers.) Beginning within superficial layers, the supermolecular structure reorganization propagates then into the body of the system. The process of averaging the number and sizes of associates and cybotaxes proceeds comparatively slow because of high viscosity of the system and is characterized by the time τ_e^{cr}. Another matter is the case when a swollen film has been stored in air for a time $\tau_e \geq \tau_e^{cr}$ (*i.e.*, when the equilibrium supermolecular structure has already formed within it) and then is again put in contact with an oligomer. In other words, when the phase boundary is then open for migration of components, this will finally lead to the re-establishment of the "status quo" – *i.e.*, of the previous supermolecular organization. It is supposedly the reversibility that is responsible for the identical kinetics of curing for the samples of the II and III series (Fig. I-6).

To confirm the possibility of execution of such a scenario let us refer to some works on the problem of phase equilibria in the neighbourhood of the interface (see the review [98–102] and the literature therein). In these works it was shown for a large number of different objects (magnetics, low-molecular liquids, solutions and blends of polymers) that structure rearrangements in the bulk and the processes taking place near the substratum surface are related to each other intricately. This sometimes leads to quite unexpected effects, in particular, to initiation of anisotropic structures formation in the bulk [101, 102]. Of the whole variety of theoretical and experimental results obtained in this direction, let us consider, for instance, the quantitative dependencies of the concentration dispersion as a function of the distance from the surface which were derived in the scaling approximation by de Gennes [103]. Examining the behavior of a semi-diluted solution in contact with an impermeable wall, he showed that

$$\Phi_1 \approx \Phi^{9/4}, \qquad (I-14)$$

$$\Phi(z) = \Phi f(x^m), \qquad (I-15)$$

where Φ_1 is the concentration in the first layer, Φ is the bulk concentration, $\Phi(z)$ is the concentration at the distance z from the wall, $x = z/\xi$, at the layer thickness ξ. If $x > 1$, then $m =$ In the case $x < 1$ $m = 3/5$. The power function of the concentration profile becomes more complex while taking into account long-range van der Waals forces which are different for different components. In the general case, the index of a power at Φ in the Eq. (I-15) may have values both more and less than.

Being applied to the experiments presented in [86] and confirmed later in [91], it probably means that reorganization of supermolecular structure occurring in the period τ_e in some cases must result in increase in the degree of order, while in other – in disordering of a system. It is also in agreement with the consequences of the theory [69] considering the dynamics of molecules anisotropy in condensed media in another aspect. Should this be the case then disordering of molecular structure (decrease of the degree of anisotropy in cybotaxes or decrease of the number of cybotaxes or of their sizes, that is equivalent to lowering the number of anisotropic molecules in a separate cybotaxis) must lead to a drop in W_o, while increase of order – to its growth. The experiment has supported this consequence. It was shown in [85] that for the films of butadiene-nitryl rubber swollen in tetramethylene-dimethacrylate, which are characterized by better thermodynamic affinity of components ($\chi = 0{,}012$) than the films of *cis*-polyiscoprene swollen in the same oligomer ($\chi = 0{,}136$), the initial rate of polymerization decreases as a function of τ_e, while for the swollen *cis*-polyisoprene films it grow (Fig. I-7). This is the consequence of the fact that in the case of low affinity of unlike components the dominating tendency in the period τ_e is the segregation of like molecules (formation of cybotaxes), while in the opposite case it is the molecular dispersion (disintegration of aggregates).

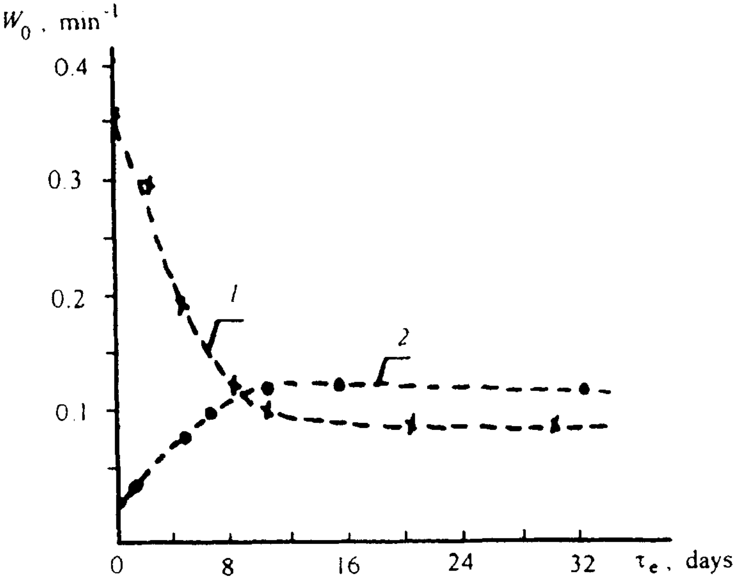

FIGURE I-7 The dependence of W_0 on τ_e for the polymerization of tetramethylene dimethacrylate in the matrices of polybutadiene-nitryl (1) and *cis*-polyisoprene (2) rubbers.

4.3. Relaxation to Equilibrium According to the Data of Rheological Tests

In Figure I-9, the dependencies of viscosity η, registered by a rotational viscosimeter, on the time of testing τ_t are presented, at 20°C and at the shear rate $\gamma_t = 54$ sec^{-1} in the course of testing. They were obtained in [104] for a sample of oligobutadieneurethaneacrylate (OBUA) using different procedures of its pre-treatment. The Curve 1 reflects the dependence $\eta = f(\tau_t)$ of the original sample; the Curve 2 – of the same sample, but after the preliminary shear action at $\gamma_p = 2$ sec^{-1} for 90 min; then immediately at $\gamma_p = 6$ sec^{-1} for further 90 min (Curve 3) and, finally, the same sample after the "rest" in the measurement cell of the instrument of 15 h (Curve 4).

One can see that (a) even small (in comparison with loads devloping within the experimental regimes of deformation) *preliminary* shear actions on an oligomer liquid irreversibly and essentially (a decimal order of magnitude) reduce the times of approaching the steady regime of flow (the regime within which $\eta = \eta_S$, where η_S does not depend

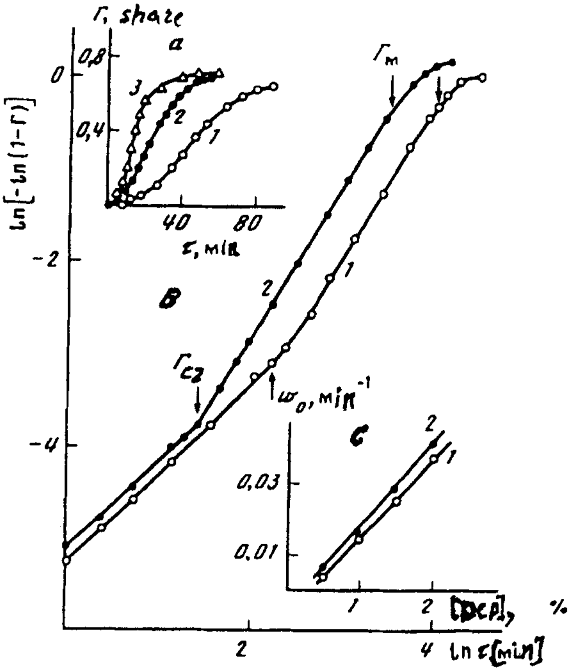

FIGURE I-8 The kinetic curves in the coordinates "degree of polymerization Γ – time of heating τ" (a), their anamorphoses in the coordinates of the Avraami equation (b) and the dependence of the initial rate of polymerization W_0 on the initiator concentration (c) in the process of block polymerization of trioxyethylene-Dimethacrylate at 110°C and at the initiator concentration equal to 0,5% of DCP (a, b), the inhibitor (hydroquinone) concentration equal to 0,007% (a, b, c), at exposure times $\tau_e = 0$ (1), 5 (2) и 20 days(3). The arrows on the curves are the values of the degrees of converstion Γ_{cr} and Γ_M, corresponding to the beginning of phase separation and phase inversion.

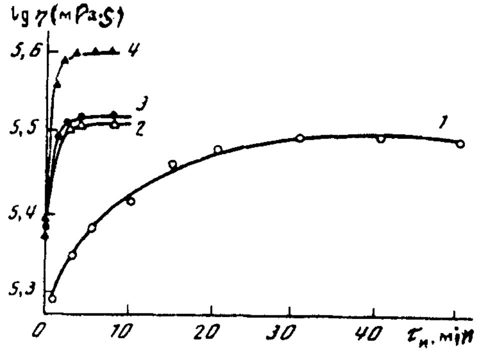

FIGURE I-9 The dependence of lg η on τ_S at 20° and $\gamma = 54$ c^{-1} for a sample of OBUA, stored before testing at room temperature. The tests without pre-deformation (1), after the pre-deformation at $\gamma = 2$ c^{-1} (2), at $\gamma = 6$ c^{-1} (3) and after $\tau_0 = 15$ h (4).

on τ_t); (b) within the investigated interval of γ_p values, the magnitude of η_S virtually does not depend on γ_p, but it rises drastically in the case when after the pre-deformation the liquid "is resting" for some time between measurements.

In Figure I-10, the dependencies $\eta_S = f(\gamma_t)$ are presented obtained for the OBUA sample at variation of the "rest" time τ_r. The latter was determined as a time between the moment of the sample pre-deformation (for example, the end of measurements in a previous experiment) and the beginning of η_S registration in a current experiment.

It follows from Figure I-10 that τ_r controls not only the value of η_S but also the character of flow. Indeed, at $\tau_r \leq 30$ min OBUA flows as a non-Newton liquid (η depends on γ), while at $\tau_r > 30$ min the system goes to the regime of Newton flow. It is important for the problem under consideration that within the interval $0 < \tau_r \leq 30$ min the magnitudes of η_S grow with τ_r, while at $\tau_r > 30$ min viscosity does not depend on τ_r. The time of "rest" at which η_S ceases to depend on τ_r is taken as the critical τ_r^{cr}. It is given the same physical meaning as τ_e^{cr}, *i.e.*, it is the time of attaining the equilibrium state, but here – by the viscosity test.

Let us emphasize that it was shown in [105] by special tests that neither during rheological testing nor during the period of pre-deformation and during the period of "rest" OBUA did not undergo

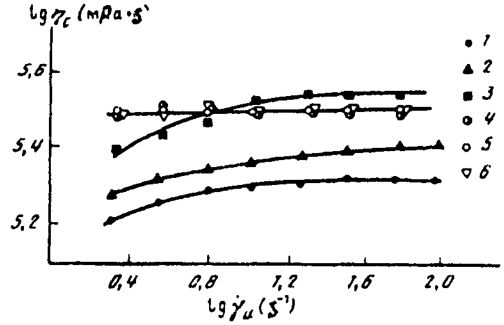

FIGURE I-10 The dependence of $\lg \eta_c$ on $\lg \gamma_{\text{И}}$ for OBUA at $\tau_0 = 0$ (1), 15 (2), 30 (3), 60 (4), 90 (5) and 120 min (6).

any chemical transformations, also no phase transitions were detected. Hence, all the noticed changes of rheological properties of the oligomer are connected with rearrangement of not molecular or phase but of supermolecular structure.

These structure rearrangements take place not instantaneously but proceed in time comparable with the time of a rheological experiment. The time of "rest" of a system after ceasing mechanical actions τ_r is one of the most important characteristics of the process, since during this period formation of the structure responsible for rheological properties of a liquid occurs. There exist the limiting values $\tau_r = \tau_r^{cr}$ at which the rheological parameters reach their steady values.

The common models of a "structurized liquid", for example, in the variant of a network of hookings [106], can not explain the above experimental facts comprehensively. For instance, the fact that the character of flow changes after the servere mechanical action at $\gamma 90$ $\sec^{-1}$ could be explained by destruction of a network of hookings (or of other supermolecular structures). But in such a situation the question is left unanswered why the same structure changes do not occur (at least, they do not manifest themselves on the experimental curves $\eta = f(\gamma)$) as a result of similar and even essentially greater deformations developing in the course of the rheological experiment itself. Or, if a network of hookings breaks down at γ_{cr}, why viscosity in a "structureless" liquid appears to be higher than in a "structured" one? The known models can not clearly answer these and many other questions.

The situation changes when one takes account of a possible effect of the kinetics of supermolecular formations development on rheological properties of oligomer liquids in the framework of the aggregative model. In doing so it is assumed that (1) formation of equilibrium supermolecular structure of liquid oligomers is a process including activation. For the creation of equilibrium structure providing the stable rheological properties of a system, first, it is necessary to overcome an energy barrier which enables the system to begin the process of evolution to equilibrium for its structure having formed to a given moment; (2) the rate of equilibrium supermolecular structure formation in oligomers is lower than that in low-molecular liquids. The times of attaining equilibrium are comparable or exceed the time of a rheological experiment; (3) the rheological methods are sensitive to variations of supermolecular structure occurring on the path of approaching the equilibrium state. If the time of attaining equilibrium $\tau_e \leq \tau_r$, then the rheological experiment reflects the equilibrium situation. In the case $\tau_r \leq \tau_e$ the experiment detects the superposition of equilibrium and not-equilibrium structures.

Note, that the values τ_r^{cr} obtained studying OBUA rheological properties and τ_e^{cr} found when examining the kinetics of curing of rubber-oligomer systems differ even in order of magnitudes (minutes in one case, days in the other one). It may be due to the fact the reactivity and transport properties of oligomers are "limited" by different parameters of supermolecular structure, the equilibrium state of which is attained for different times. The inner arrangement of a structure inhomogeneity probably does not play a crucial role in the acts of transfer (rheology), only such parameters as a number and a size of aggregates, strength of bonds between them are important. But for the kinetic experiments of oligomers curing, besides, orientation of molecules inside the body of a supermolecular formation is essential - generation of the "kinetically favourable orders" [47, 54, 56, 61]. It is evident that equilibrium in respect to relative arrangement of molecules inside an aggregate can be completed only after averaging the external structure parameters of aggregates themselves. Therefore, although relaxation rearrangement inside the body of a supermolecular structure may be not finished yet, it does not influence the value of viscosity being measured. Probably, that is why η reaches its steady value earlier than W_0, all other conditions being equal. A circumstantial evidence to the above consideration is the fact that the unreactive analogue embedding into the structure of a oligoesteracrylate cybotaxis results in decrease of the initial rate of polymerization W_0 (Fig. I-2, Curve 3), but it does not affect the rheological characteristics of the blend [63]. The noticed fact may manifest itself in the experiment only when the polymerization constants are sensitive to the inner structure of a supermolecular formation, *i.e.*, to the associate ↔ cybotaxis transitions, while the rheological constants are indifferent to it.

Thus, the testings of equilibrium of oligomers supermolecular structure obtained by different experimental methods may not coincide, since they may reflect distinct levels of approaching the thermodynamic equilibrium.

5. THE CORRELATION BETWEEN THE KINETICS OF CURING AND DURATION OF THERMODYNAMIC EQUILIBRIUM ESTABLISHMENT IN AN INITIAL SYSTEM

The dependence of macroscopic properties of materials based on oligomers and their blends on the time pre-history of an initial system was noted repeatedly (*i.g.*, see [3, 69, 89, 107]). In particular, it was shown [63], that for achieving identical (reproducible) kinetic curves of curing of reactive oligomer systems in identical runs (the same composition, the same regimes *etc.*), besides meeting all the common methodical standards, the following procedure is *necessary in addition*. After a composition preparation (adding initiators, curing agents, inhibitors, catalysts, plasticizers, thickeners *etc.*), every sample is required to be preliminary (yet before switching the mechanism of curing) stored at rest for no less than a certain, sometime quite extended time. For different oligomers this time τ_e^{cr} (when the kinetics of curing no longer depends on the time pre-history of a system) essentially differ, it may range from several minutes-hours up to many days. The lower limit may be much less. If it is small (fractions of second, seconds – the possibilities of its reliable registration are determined by the methodical features of an experiment and by technical parameters of instruments used for measuring the degrees of conversion) then in actual practice the time of pre-storage of samples is not essential. But for the practice much more important is the upper limit, since the time pre-history of a system is often not taken into account. This may lead to principal errors: the polymerization process may begin at different distances from the state of thermodynamic equilibrium.

In the general case, the reasons determining the dependence of the kinetic parameters of a curing process on the time of storage (exposure) τ_e may be related both to the structure peculiarities of reactive systems, *i.g.*, duration of attaining equilibrium during formation of elements of the "kinetically favourable and unfavourable orders" spoken above, and to the kinetical effects themselves, such as proceeding in time redistribution of a polymerization initiator in the body of a system. Another example is the process of concentration variations in the course of a sample storage taking place for inhibitors or admixtures which activate or passivate network formation (peroxides accumulated during storage [108], oxygen absorbed by a system [109]) *etc.*

For example, in [110], when studying the kinetics of high-temperature curing of trioxyethylene-dimethacrylate in the presence of 0,5% of dicumyl peroxide (DCP) and the residual content of the inhibitor (hydroquinone) equal to 0,007% it was found (Fig. I-8a), that the value of the induction period τ_{ind} of the polymerization process, which is about 20–30 min at $\tau_e = 0$, decreases with the exposure time buildup and reaches zero at $\tau_e \geq 5$ days. This effect was interpreted as slow "eating away" of the inhibitor due to its interaction with the products of the initiator decomposition which partly breaks down during the period τ_e. To confirm this conclusion, the following facts were presented. First, clearly W_0 grows with increase of τ_e, second, both at $\tau_e = 0$ and $\tau_e = 4$ days W_0 is proportional to the first power of the initiator concentration (Fig. I-8c), third, at the thermal initiation in the absence of DCP τ_{ind} increases to 2–3 h and virtually does not depend on τ_e within the range $0 < \tau_e < 20$ days.

The role of the kinetic factors is undoubtedly important and in a number of cases is given priority for explanation of some features of oligomers curing. However, only on these concepts many other experimental observations are left unclear which were carried out when studying the kinetics of curing of oligomer systems. The dissimilar run of curves $W_0 = f(\tau_e)$ for different systems (Fig. I-7) discussed earlier [85] is an example. For accounting for those data it may be assumed by analogy with the version of [110] that the growth of W_0 with increasing τ_e observed for the polyisoprene rubber- oligoesteracrylate system is a consequence of decrease in the inhibitor concentration during the exposure period. Also another "kinetic" version may be accepted about this effect stemming from gradual accumulation of peroxide compounds in those samples during storage that, in principle, the procedure of the experiment used in [85] did not exclude. But in these cases the reasons for the drop of W_0 in the related experiments with butadiene-nitryl rubber-oligoesteracrylate blends would be left unexplained. On the contrary, for the latter system it may be supposed that the decrease of W_0 as a function of τ_e is related to oxygen accumulation during the storage period, that is expected to result in reducing the initial rate of polymerization [109]. But such a consideration would be inconsistent with the described above growth of W_0 found for the other rubber-oligomer system in which oxygen can dissolve too. When searching distinctions between isoprene and nitryl rubbers in the processes of oxygen sorption and in their oxidation mechanisms, which may lead to the contrary dependencies $W_o = f(\tau_e)$ during oligoesteracrylates curing in their matrices, no strong arguments were found to confirm such a possibility. Other presumptive explanations of the results presented in [110], which were based on the use of the classical principles of the kinetic effects analysis [42–45], have appeared to be contradictory in the same extent.

In the considered experiments the method (mechanical blending, swelling, *via* simultaneous solutions) and the order (into the oligomer, rubber, into a blend) of adding the initiator did not affect neither the character of kinetic curves of both the systems, nor the values of τ_e^{cr}. The systems were carefully purified from the inhibitors, no chemical transformations were revealed within them during the storage period. Therefore, it was supposed in the given case that the most probable causes for existence of the time-pre-history dependence of the kinetics of curing were variations in the structure organization of system occurring within the period $0 < \tau_e < \tau_e^{cr}$. The differences in the character of the function $W_o(\tau_e)$ for the above systems were supposed to result from the contrary tendencies in the change of the parameters of their supermolecular structure.

Starting from the considered above regularities of formation of thermodynamically equilibrium structure in oligomer systems, one can assume that the formation of equilibrium structure proceeds step-by-step: averaging over concentration of components (the molecular level), averaging over associate-cybotaxis composition (the supermolecular and topological level), and for heterogeneous mixtures also averaging over the morphology parameters (the colloid level take place [9].

It is essential that the effect of τ_e spreads not only to the kinetic parameters of the initial stages of curing (τ_{ind} и W_o) but also to the mechanisms of structure formation at medium and deep stages of an oligomer conversion. In particular, it is confirmed by Figure I-8b where the kinetic anamorphoses of polymerization are presented in the coordinates of the Avraami equation, at $\tau_e = 0$ and 5 days. One can see that increasing τ_e results in a shift of the limits of the phase separation and monolithization beginning. (The comprehensive analysis of the polymerization kinetics in the framework of the Avraami model is presented in the third park of this work). The same

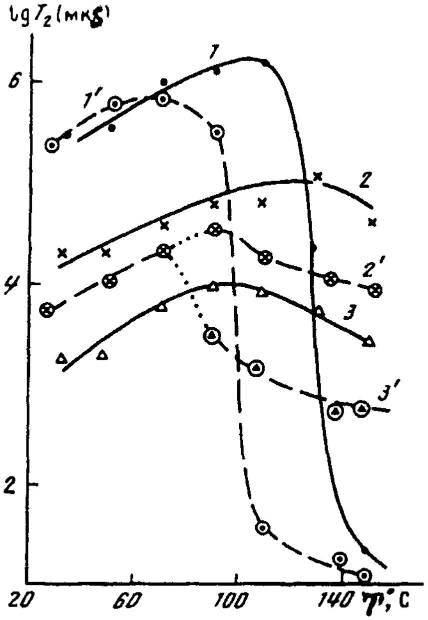

FIGURE I-11 The temperature dependence of lg T_2 for the polybutadiene-tetramethylene-dimethacrylate system at $\tau_e = 0$ (1–3) и 85 days (1′–3′).

conclusions follow from the analysis of Figure I-6: increasing τ_e leads to growth of the limiting degrees of conversion of tetramethylene-dimethacrylate in the *cis*-polyisoprene matrix. They are also confirmed by the results of the study of the nuclear relaxation processes at the thermal curing (heating in the presence of material initiators) of the polybutadiene-oligoesteracrylate system at $\tau_e = 0$ and 85 days. It is seen from Figure I-11 that increasing τ_e results not only in the significant decrease of the temperature of polymerization beginning but also in the fundamentally dissimilar relaxation behaviour of all the intermediate and final products of the chemical transformations.

6. THE RELATIONSHIP BETWEEN THERMODYNAMIC AND KINETIC FACTORS IN THE PROCESSES OF CURING

The possible correlations between thermodynamic and kinetic patterns of structure formation in original oligomer systems and in these

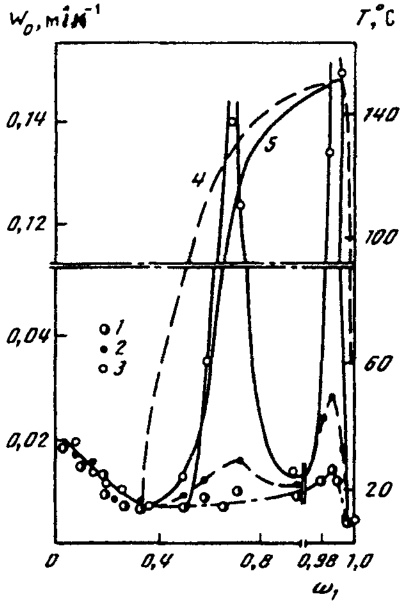

FIGURE I-12 The phase diagram (the binodal – 4 and the spinodal – 5) and the dependence of W_0 on ω_1 for the PVC-trioxyethylenedimethacrylate system at the curing temperature 110°C and the initiator concentration equal to 0,5% of DCP, at the exposure times τ_e = 1 (1), 5 (2) и 40 days.

systems in the process of curing have not been adequately studies yet. This may-sided problem has attracted the attention of scientists quite recently [3, 7, 8, 88, 111]. Let us consider only one of its aspects.

Comparing the influence of the thermodynamic and kinetic factors controlling the system approaching the equilibrium state on a variation of the magnitudes, *i.g.*, of the rates of curing, the experimental observations testify that the role of the thermodynamic factors seemingly dominates. Indeed, for example, in the framework of the one-phase state of a certain system a variation of such a kinetical factor as τ_e at the fixed thermodynamic variables (ω_1 и T = Const.) results in no more than 2–2.5 times change in W_0, if at all (see Figs. I-2, I-7). At the same time a variation of the thermodynamic variables of state ω_1 or T determining a system "falling" into one or another region at the phase diagram may lead to changes of W_0 by orders of magnitude [5, 9, 84–86]. But the point is that W_0 is determined by the time in which the structure reorganization proceeds to the thermodynamically permitted level. Will the reorganization of a system structure have had time to cease to the moment of W_o registration in an experiment and thus to provide the corresponding equilibrium value? Unfortunately, so far this question has been put in the experimental practice not often. But taking (or not taking) account of the kinetics of relaxation to equilibrium could change not only the numerical values of a measured property but also even the qualitative character of dependencies. The data of Figure I-12 may readily illustrate this principle. In Figure I-12, the dependencies of W_o on ω_1 for the trioxyethylene-dimethacrylate system obtained at τ_e variation are correlated with the phase diagram. One can see that at the transition to the metastable state and in the neighbourhood of the critical point W_o increases no less than 10–20 times. But (and it is of fundamental importance!) these bursts of the polymerization rate – the peaks on the curve $W_o = f(\omega_1)$ - can be revealed, only meeting the condition $\tau_e \geq \tau_e^{cr}$, *i.e.*, taking into account the kinetics of attaining the thermodynamic equilibrium. Indeed, at τ_e = 1 day (Curve 1) the extrema on the curve virtually do not reveal themselves, and at τ_e = 5 days (Curve 2) they are insignificant. Only at τ_e = 40 days (Curve 3) the picture corresponds to the described above. Indeed, as V. I. Irzhak said on another occasion, "thermodynamics proposes but kinetics disposes".

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