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# Kinetics of oligomer curing †

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**Abstract. Common and specific features of formation of polymer networks by addition polymerisation and polycondensation of oligomers are analysed. The kinetic peculiarities of these processes related to the structure of an oligomeric liquid and some aspects of the supramolecular organisation of polymers are considered. The bibliography includes 221 references.**

## I. Introduction

Information on changes in the concentrations of starting reactants and(or) reaction products in the course of chemical transformations of low-molecular-mass compounds to low-molecular-mass products with a different structure provides a comprehensive description of the kinetics of these processes.[1] Possible side reactions usually occur at lower rates and can be suppressed by choosing appropriate reaction conditions (in this case, the yield of the target product is an important parameter). Impurities can be removed in various ways and, in principle, it is possible to attain 100% purity of the reaction product. This refers to technological and economic considerations. It is important that the final low-molecular-mass product can be obtained as an individual compound with a predetermined chemical structure independent of reaction conditions.

A fundamentally different situation occurs if chemical transformations of low-molecular-mass reactants result in the formation of polymers (in particular, polymer networks). Due to statistical character of these processes, the products obtained from the same reactants can have different molecular structures and hence different physical properties. The 'heterounit structure of polymers' (the term introduced by Korshak [2]) manifests itself even in the simplest cases, *e.g.*, the 'head-to-head' and 'head-to-tail' addition of monomers, 1,2- and 1,4-addition of dienes, *cis*- and *trans*-isomerism, stereoisomerism, *etc*. Different units can show different types of distribution over a linear chain, different sequence and form blocks of different lengths. Thus, the same reactants form polymers with different molecular architectures; this level of molecular organisation is relevant to the description by chemical symbols. It is this structural level that determines the key properties of polymers, as demonstrated by the atomic group contribution methods by Askadskii [3] and van Krevelen.[4] Of course, it is possible to increase the yield of a product with a particular structure by varying the reaction conditions (temperature, pressure, catalysts, *etc*.), but a 100% yield is never attainable. Also, it is virtually impossible to separate a mixture of products into individual components. If a reaction results in the formation of a polymer network, an individual compound with a specified molecular architecture cannot be obtained at all.

The situation becomes even more complicated if polymers are synthesised from oligomers. On the one hand, a characteristic feature of synthetic oligomers is molecular heterogeneity,[5] that is, according to the molecular mass distribution (MMD) and the functional group distribution. Therefore, the molecular structures of the polymers synthesised from oligomers are characterised by an additional degree of uncertainty compared to the molecular structures of the polymers synthesised from low-molecular-mass compounds. On the other hand, a characteristic feature of liquid oligomeric systems is a specific type of intermolecular organisation,[6 – 10] namely, they contain various types of aggregates (molecular associates, nematic clusters, *etc*.). Both the presence and variety of such species not only influence the kinetic features of polymerisation, but can also be 'inherited' by polymeric products. Hence this offers prospects for variation of the supramolecular structure (here, this is meant the pattern of mutual arrangement of the chemi-

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cally identical fragments of macromolecules, which determines the close packing of a polymeric material).

The most important characteristic of polymerisation products is their topological structure.[11] The corresponding formalism ignores particular chemical structures of macromolecules and treats them as fibres, which can differ in length and MMD, be linear or branched and form complex cyclic structures (including chemically non-bonded ones, catenanes) up to a continuous (three-dimensional) network. On this level, the structure of a network polymer is represented by a graph[12] and described in terms of the distribution of knots with respect to the number and functionality (degree of branching), distribution of interknot chains according to length, ring size distribution, *etc*., also ignoring their chemical nature. Reaction conditions strongly influence this level of structural organisation.

The formation of a network polymer is accompanied by not only changes in the body of reactants, but also phase and aggregate transitions. Owing to microheterogeneous nature and specific features of phase separation, a 'liquid (monomer, oligomer) → solid (elastic) polymer' transition is followed by the formation of structures with different morphologies, *e.g*., with different size and composition distributions of inclusion phases. Therefore, the properties of the polymer depend on its morphology on the colloidal level of structural organisation, which is to a great extent determined by the curing conditions.[13]

Thus, characterisation of the kinetics of polymerisation processes requires not only knowledge of changes in the reactant concentrations, but also allowance for structural aspects. As a consequence, the processes should be treated in a more sophisticated manner than the formal kinetics of chemical reactions permits.

This first of all concerns the principles of formation of the polymer chain. There are two main types of processes,[11, 14, 15] a unit-by-unit chain growth and growth by virtue of coupling of larger fragments, which can be described as follows:

$$R_i + M \longrightarrow R_{i+1}, \quad (1)$$

$$R_i + R_j \longrightarrow R_{i+j}. \quad (2)$$

Here the subscripts denote then number of repeating units in the active chain R, and M is the monomer or oligomer that is converted into a repeating unit of the polymer.

In the first case, a characteristic feature consists in the constant number of chains irrespective of the type of the reactive centre (radical, ion, functional group). In the second case, the growing chains interact not only with the starting components. Indeed, smaller macromolecules can react with one another owing to the presence of reactive functional groups, this will result in the formation of larger macromolecules and in a decrease in the number of chains. Clearly, the kinetic descriptions of the two processes should be different.

The former case can be treated as addition polymerisation, while the latter, as stepwise polymerisation (polycondensation). These are essentially kinetic terms, and their interpretation differs from conventional chemical interpretation[16] that dates back to Carothers.[17] Addition polymerisation refers to reactions occurring without formation of side products, whereas polycondensation covers reactions accompanied by formation of low-molecular-mass products. In a monograph by Szwarc,[18] it was stated that in many polycondensation processes each formation of a new chemical bond was accompanied by simultaneous elimination of a small molecule. Earlier, such an elimination has been assumed to be the most characteristic feature of polycondensation, which differs it from addition polymerisation, but this point of view can no longer be considered correct.

The formation of a network structure goes beyond chemical reactions between the reactants. Chemical reactions are accompanied or followed (consecutively or competitively, simultaneously or with some delay) by physical processes that change the translational mobility of reactants and make the reaction centres less sterically accessible; this unavoidably affects the reaction rate. The aggregation state and phase state of the system can change during the chemical reaction. This is the reason for the multistage formation of a polymer network and for different kinetic laws in different stages of polymerisation process, the chemical and physical processes being interrelated.

In the present review, we analysed the common and specific features of addition polymerisation and polycondensation processes used to form network polymers from reactive oligomers with emphasis placed on the topological, supramolecular and colloidal levels rather than molecular level of structural organisation of polymers.

## II. Influence of supramolecular organisation of liquid oligomers on polymer network formation

### 1. On the supramolecular structure of oligomeric liquids

A macroscopic oligomeric system can be treated as the sum of microscopic subsystems (elements of the entire system) that participate in mass and energy transfer with one another and with the environment as they approach the equilibrium state.[8] The role of such subsystems is played by structural inhomogeneities, *e.g*., inclusion phases for heterogeneous systems, density fluctuations for homogeneous systems and fluctuations of the component concentrations with different temporal and spatial parameters for multicomponent systems. All oligomeric systems consist of 'organised' (aggregated) and 'non-organised' molecules. In turn, the aggregate subsystem can be divided into cybotaxes‡ and associates. These terms are used to describe the liquid state of oligomers and characterise different types of long-lived supramolecular structural formations that differ in spatial arrangement and orientation of the molecules confined within a local inhomogeneous region in the liquid.

The notions 'associate' and 'cybotaxis' have a number of common features and distinctions.[8, 20–22] Thus both supramolecular structures have the same compositions, they are not phase formations and their lifetimes depend to a larger extent, than those of statistically averaged thermal fluctuations, on the system composition and temperature, on the energy of intermolecular interactions and on molecular conformations. The distinctive feature of cybotaxes is some degree of anisotropy in

‡ The term 'cybotaxis' (from Greek χιβωτοζ) was introduced by Stewart[19] in the 1920s, but eventually had a strong presence in science owing to fundamental generalisations by Frenkel.[20] In the literature on polymers, such and related structural aggregates are often called 'clusters' (this term was introduced more recently). Both terms are similar in sense, but the latter ignores the possibility of spatial orientation of primary particles. Because of this the notion 'nematic cluster' relevant to the physical meaning was introduced. Yet another term for the description of cybotaxic regions in the liquid is 'anisotropic associate'. For more terminology details, see a monograph.[8]

the spatial arrangement of molecules, whereas associates are always isotropic. Under specific conditions, associates can undergo transformation into cybotaxes and *vice versa*. The ordering (aggregation, associate → cybotaxis transition, *etc.*) in a certain region of an equilibrium macroscopic system unavoidably causes disordering in another region. The direct and reverse transitions cybotaxis ⇄ associate can occur at the same or different rates. Cybotaxes can show various types and different extent of anisotropy. Non-organised molecules can attach to aggregates and detach from them. Aggregated liquids can differ in aggregate lifetimes, number of aggregates per unit volume, aggregate size and molecular orientations in different cybotaxes.

Structural inhomogeneity of liquid oligomers (and, generally, all liquids) is due to energy or entropy reasons. The supramolecular structure of oligomeric systems can be governed by strong dipole–dipole interactions, hydrogen or complementary group bonds and van der Waals forces of intermolecular interaction. Its formation is a result of fluctuations of thermal motion of particles; a considerable increase in the temporal and spatial scales of such fluctuations in the metastable region and at the critical point is due to the onset of a long-range intramolecular interaction (with the favourite relation between the molecular length and flexibility) and to static flexibility of the molecules.[8–10] Thus, the supramolecular structures of oligomeric systems can be formed under the action of forces of different nature, and this mainly governs the time scale of the lifetimes of various inhomogeneities.

Summing up, the macroscopic structure of liquid oligomeric systems can be treated as a conglomerate of aggregates of different sizes and lifetimes, with isotropically and anisotropically arranged molecules that are 'dispersed' (here we use quotation marks because aggregates are not phase formations) among 'non-organised' molecules. Theoretical models for the supramolecular structure of oligomers and experimental proofs of their correctness have been considered in detail in a monograph.[8]

## 2. Kinetic features of the early stages of polymerisation in curing of oligomers

### a. Relation between the curing kinetics and the supramolecular organisation of the starting systems

The influence of (i) internal structure of the supramolecular formations of oligomeric liquids and (ii) anisotropic packing of molecules within aggregates on the kinetics of polymer network formation attracted the attention of researchers in the 1960s in connection with the discovery of abnormally high initial curing rates of certain oligoester acrylates. Namely, the initial polymerisation rates $W_0$ (polymerisation rate at low conversions $\alpha \approx 0$) are much (several orders of magnitude) higher than 'normal' values.[23,24] However, in the course of polymerisation they rapidly decreased in a relatively narrow interval $\alpha \approx 1\% - 5\%$ and became comparable with the polymerisation rate of methyl methacrylate taken as the 'normal' value. This effect was not observed upon adding small amounts of solvents of low viscosity to the starting oligomer, but became more pronounced (abnormal increase in $W_0$ occurred) if solvents of high viscosity were added. Attempts to explain the phenomenon using the classical kinetic schemes failed.

Another experimental observation that contradicted the canonical viewpoint was reported by Gusakovskaya.[25] She discovered a temperature region corresponding to the liquid state of oligomer (here a regular, monotonic decrease in $W_0$ with a decrease in the curing temperature is not observed) and even a very narrow temperature interval in which the parameter $W_0$ increased as temperature decreased.

These and some other experimental observations of the kinetics of polymerisation of unsaturated oligomers (for review of studies in this field, see Refs 9 and 26) could not be explained not only in the framework of the classical kinetics, but also assuming the existence of local fluctuating microscopic volumes with increased concentration of functional groups in the reactive liquid consisting of conventional statistical associates. This required additional hypotheses, one of which assumed the possibility of anisotropic packing of the reacting molecules within the concentration fluctuation in the liquid system.

Berlin and Korolev[23] assumed the existence of supramolecular aggregates with anisotropic rather than random molecular orientation (kinetically favourable 'building blocks') in liquid oligomers. In such aggregates, the molecules are oriented in such a manner that the double bonds of the methacrylic moieties are brought closer together and arranged in a kinetically favourable order. It was also assumed that if the lifetimes $\tau_p$ of such labile 'building blocks' (cybotaxes) are comparable or longer than the time of elementary act in the chemical reaction (lifetime of active centre or transition state), an increase in the pre-exponent $A$ in the expression for the rate constant for chain propagation

$$k_p = A \exp\left(-\frac{E}{RT}\right)$$

should lead to an increase in the parameter $W_0$ compared to the 'normal' polymerisation rate determined by the reactivity of the double bond of the methacrylic moiety in the course of methyl methacrylate polymerisation. Of course, the temperature and viscosity of the system influence the $\tau_p$ value.

This concept also provided a reasonable explanation for the 'incorrect' effect of temperature on the reaction rate (see above), namely, the kinetically favourable 'building blocks' disintegrate as the temperature increases; otherwise their lifetimes increase. Naturally, if an oligomeric system contains cybotaxes, the $W_0$ value should decrease on raising the temperature. Moreover, a temperature range should exist in which the $W_0$ value should increase with a decrease in temperature. It seems appropriate to say that Semenov[27] was the first to substantiate in 1957 the possibility of the effect of ordered structures on chain processes and thus explained a dramatic increase in the polymerisation rate of crystallising monomers observed in very narrow temperature intervals near the phase transition temperature on lowering the temperature.

This approach makes it possible to explain not only the results mentioned above, but also many other results obtained in studies of different types of oligomers.

Convincing proofs of the effect of cybotaxes on the process kinetics were provided in studies[28,29] of the early stages of polymerisation of single-phase tetramethylene α,ω-dimethacrylate (viscosity $\eta \approx 5$ sP) solutions in non-reactive oligomers of various viscosity, namely, bis(dioxyethylene phthalate)-α,ω-diisobutyrate ($\eta \approx 1000$ sP), trioxyethylene α,ω-diisobutyrate ($\eta \approx 10$ sP) and tetramethylene α,ω-diisobutyrate ($\eta \approx 5$ sP). The results obtained were compared with the kinetic data for polymerisation of methyl methacrylate (MMA) dissolved in these non-reactive oligomers.

In Fig. 1 the rate of polymerisation of tetramethylene α,ω-dimethacrylate normalised to the concentration of methacrylic groups in solution and extrapolated to zero ($W_0$) is

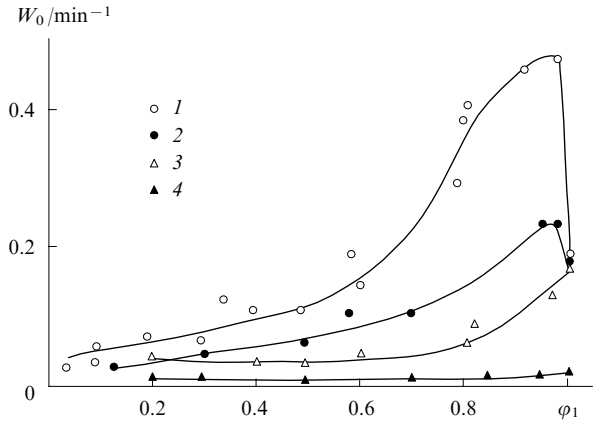



**Figure 1.** Initial polymerisation rate $W_0$ plotted *vs.* $\varphi_1$ for tetramethylene α,ω-dimethacrylate blends with bis(dioxyethylene phthalate) α,ω-diisobutyrate (*1*), trioxyethylene α,ω-diisobutyrate (*2*), tetramethylene α,ω-diisobutyrate (*3*) and a methyl methacrylate – tetramethylene α,ω-diisobutyrate mixture (*4*).

plotted *vs.* mass fraction of tetramethylene α,ω-dimethacrylate ($\varphi_1$), the dependences for the mixtures with trioxyethylene α,ω-diisobutyrate and bis(dioxyethylene phthalate)-α,ω-diisobutyrate being similar. The data for polymerisation of methyl methacrylate solution in tetramethylene α,ω-diisobutyrate are presented in the same coordinates ($\varphi_1$ is the MMA fraction). The $W_0 = f(\varphi_1)$ curve plotted for the tetramethylene α,ω-dimethacrylate solution in the highly viscous solvent shows a maximum in the region of high concentration of the oligoester acrylate (curve *1*). As the viscosity of the non-reactive solvent decreases, the magnitude of the maximum in the polymerisation rate curve gradually decreases (curve *2*); for the mixture of the components with similar characteristic viscosities the parameter $W_0$ decreases immediately as the fraction of the non-reactive oligomer increases (curve *3*). No concentration dependence of $W_0$ was observed for the methyl methacrylate solutions (curve *4*).

Assuming certain distributions of cybotaxes present in the oligomeric system over the number, size and lifetimes and an increase in the parameter $W_0$ with an increase in the number the lifetimes of the cybotaxes and the number of reactive molecules in a unit cybotaxis, the experimental facts mentioned above can be explained as follows.

The initial increase in $W_0$ in thickened systems compared to the $W_0$ value for 'pure' tetramethylene α,ω-dimethacrylate is due to an increase in the number and lifetimes of cybotaxes upon adding components of high viscosity. A decrease in $W_0$ observed for the systems with similar viscosities of the components is the result of 'incorporation' of the non-reactive component into the kinetically favourable structure of the reactive oligomer, there are no thermodynamic limitations on this process.

Considering a blend, the decrease in parameter $W_0$ is not necessarily proportional to the concentration (see Fig. 1). Moreover, if the reactive and non-reactive molecules are present in solution in an equimolar ratio, no effect of supramolecular structures on the polymerisation processes should be observed, because this case corresponds to equiprobable neighbourness of two pairs of functional groups (one pair consists of two methacrylate groups and the other pair consists of one methacrylate and one isobutyrate group) within the cybotaxis. Therefore, the laws of classical kinetics should be valid at these concentrations. In the experiments, the polymerisation rate becomes independent of $\varphi_1$ at $\varphi_1 \approx 0.5$.

An extremum in the $W_0 = f(\varphi_1)$ curves for the systems with high viscosity of the non-reactive component can be explained with ease by the competition between the positive and negative effects of the second component on the polymerisation process. In the former case, the non-reactive component acts as thickening agent and the number of cybotaxes whose lifetimes are comparable with the characteristic times of elementary acts increases. In the latter case the number of elementary acts per unit time simultaneously decreases due to incorporation of the non-reactive molecules into the kinetically favourable structures. Of course, the first factor dominates at low, while the second factor dominates at high, concentration of the thickening agent.

All these conclusions were confirmed recently [30–34] in similar experiments with other systems. It was found that the specific rate of polymerisation of alkyl acrylates decreases by several times upon dilution of the system with inert solvents due to disintegration of anisotropic clusters.[30] This is also the reason for the auto-retardation effect in deep stages of the polymerisation of alkyl acrylates.[31]

It should be emphasised that the ability of oligomers to form kinetically favourable aggregates depends not only on the molecular chain length, the nature of the molecular environment and the state parameters of the system, but also on the molecular structure of the oligomeric chain. Even minor changes in the molecular structure of the oligomer can make the formation of a cybotaxis diffucult or impossible. For instance, an 'abnormal' increase in the initial polymerisation rate observed in methacrylic systems was not observed in the acrylic systems under identical conditions.[32–34]

The aggregate size estimates made by different methods vary from ~5 to ~40 molecules per aggregate.[31,35–37] In particular, kinetic data[31] predict a nonyl acrylate aggregate size of 37 molecules at 50 °C.

A strong argument in favour of the existence of kinetically favourable associates was provided by the results of computer simulation of these structures by the molecular mechanics method.[38,39] It was shown that higher alkyl (meth)acrylates, starting from butyl esters, can form regular associates in which the oligomer molecules, their hydrocarbon fragments, ester groups and double bonds are ordered both positionally and orientationally. The energy of intermolecular interaction in the acrylate and methacrylate homologous series increases with an increase in the size of the alkyl fragment in the oligomer molecules.

To date, a large body of experimental data was accumulated (see Refs 7 and 40–42), which indicate that supramolecular organisation of the starting reactive oligomeric system may govern the curing kinetics; this concerns different classes of oligomers undergoing chemical transformations by both addition polymerisation and polycondensation mechanisms. Specific features of formation of polyurethane networks in the pre-gel state are due to the dependence of the rate of the chemical reaction between the isocyanate and hydroxyl group on the degree of self-association of alcohols and on the formation of complexes of different alcohols with one another and with other electron-donating molecules present in the reaction system. Considerable differences between the nucleophilic and electrophilic reactivities of associated and non-associated alcohol and isocyanate molecules and the molecules present in the structures with different degree of association

give rise to kinetic and structural heterogeneities in the early stage of curing process.[43]

In studies of urethane formation reactions[44,45] it was concluded that from the very beginning polymerisation occurs in the presence of microheterogeneities due to strong intermolecular interactions and polar and non-polar chain fragments. The reaction rate of NCO with OH groups is directly related to the conformational ordering of oligoesterdiol molecules that form supramolecular structures.[46] The formation of urethane groups in the reaction changes the system of intermolecular interactions and, eventually, the kinetic law, that is, the second-order reaction becomes a first-order one after 55% – 70% conversion.

In spite of all differences and even contradictory character of experimental results obtained in curing studies of epoxydiane oligomers in the presence of polyfunctional amines and other curing agents (see, *e.g.*, Refs 11 and 47 – 52), almost all of them can be described by the scheme of the initial stage of polymer network formation (see above).

Analysis of the effect of constant and alternating force fields on the starting epoxy – amine system revealed[53] that pretreatment of the reaction system with weak magnetic fields leads to acceleration of curing and a decrease in its activation energy, which was attributed ordering of the associate structure of liquid. The effect of sonication manifests itself in a more complex manner. Initially, sonication destroys the available associate structure and hence decreases the curing rate. However, repeated and prolonged sonication leads to independence of the kinetic characteristics of curing on the ultrasonic field frequency and intensity and the physicomechanical parameters of the cured product are improved. Similar results obtained in studies[54 – 56] on the effect of preliminary sonication and vibration on the changes in the rate of subsequent curing of epoxy oligomers and liquid rubbers were also explained by the changes in the supramolecular structure of liquid.

A critical review of these, related and authors' works was reported in a monograph by Khozin.[42] The author unambiguously admitted the concept of aggregate structure of oligomers and used it to provide reasonable explanation for many unusual and in some cases coontradictory experimental results.[42,57 – 59]

Experimental data obtained in studies of the effect of the phase state of the starting system on the kinetics of the initial stage of matrix polymerisation of oligomers are in excellent agreement with the concept of the aggregate structure of oligomeric systems.

The initial curing rates ($W_0$) of tetramethylene α,ω-dimethacrylate and trioxyethylene α,ω-dimethacrylate in the SKI-3 *cis*-polyisoprene rubber matrix at different concentrations of oligoester acrylates $\varphi_1$ (single-phase systems) are listed in Table 1. The concentration dependence of $W_0$ for a tetramethylene α,ω-dimethacrylate – *cis*-polyisoprene blend in a wide range of compositions and the phase diagram of this system are shown in Fig. 2.

Analysis of the experimental data mentioned above revealed (i) a dramatic change in the $W_0$ value in the phase transition region, (ii) virtual independence of the parameter $W_0$ of $\varphi_1$ in the single-phase systems and (iii) much higher (five- to tenfold) curing rate in the oligomer-enriched phase (phase II) compared to the polymer-enriched phase (phase I), The rate of bulk polymerisation (homopolymerisation of oligoester acrylate in the absence of the second component) is higher than in phase I but lower than in phase II. The reasons for different rates of polymerisation in phases I and II and its difference from $W_0$ in the case of bulk polymerisation are non-trivial,

**Table 1**. Initial polymerisation rates $W_0$ ($min^{-1}$) at different oligomer concentrations in single-phase systems *cis*-polyisoprene – oligoester acrylate.

| System | $W_0$ at oligomer concentration (vol. fraction) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0.05 | 0.10 | 0.15 | 0.20 | 0.30 | 0.99 | 0.995 | 1.0 |
| SKI-3 – tetramethylene α,ω-dimethacrylate [a] | 0.09 | 0.12 | – | 0.14 | 0.16 | 0.97 | 1.05 | 0.32 |
| SKI-3 – tetramethylene α,ω-dimethacrylate [b] | – | 0.16 | – | 0.18 | 0.16 | 1.74 | – | 0.64 |
| SKI-3 – trioxyethylene α,ω-dimethacrylate [b] | – | 0.10 | 0.13 | – | – | – | 1.58 | 0.88 |

[a] Curing temperature 100 °C. [b] Curing temperature 107 °C.

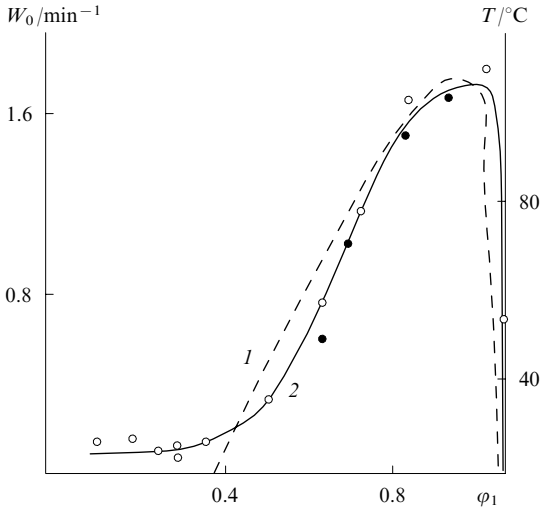



**Figure 2.** Phase diagram (*1*) and $W_0$-*vs.*-$\varphi_1$ plot for the *cis*-polyisoprene – tetramethylene α,ω-dimethacrylate system at a curing temperature of 107 °C and an initiator [azobis(isobutyronitrile)] concentration of 0.5 mass % (*2*).
Open circles denote experimental data and filled circles denote the results of calculations in the additive approximation.

being related to the effect of the medium viscosity on the parameters of the supramolecular structure of each phase.

As mentioned above, addition of relatively low concentrations of the thickening agent can lead to an increase in the number, size and lifetimes of kinetically favourable supramolecular aggregates, which in turn should cause $W_0$ to increase. The viscosity of phase II increases 8 to 15 times upon dissolution of ~1% of the thickening agent;[9] correspondingly, the parameter $W_0$ increases. If the content of the thickening agent exceeds 50%, the structure of the system becomes disordered, the number of kinetically favourable aggregates decreases and so does the curing rate compared to bulk polymerisation.

In the initially heterogeneous systems, a change in the component ratio causes no changes in the concentrations of the coexisting phases; it only leads to a change in the volume ratio of the phases I and II. Transition from homogeneous to

heterogeneous state due to, *e.g.*, an increase in the oligomer content in the starting system [at $\varphi_1 > (\varphi_1)_b$,§] is followed by the appearance of phase II (polymer solution in oligomer; here the initial polymerisation rate is higher) in phase I (oligomer solution in polymer). As $\varphi_1$ increases, phase II is accumulated.

When curing heterogeneous systems, polymerisation in each phase obeys its specific laws and the experimentally detected gross function $W_0 = f(\varphi_1)$ characterises the changes in the volume ratio of the phases. A satisfactory additive approximation of this dependence was found for the *cis*-polyisoprene – tetramethylene α,ω-dimethacrylate system (see Fig. 2).

Nevertheless, we shall emphasise that the phase diagram shows certain regions corresponding to systems in which the concentration dependences of the curing rate do not obey additive laws; interrelations between the properties of such systems and the supramolecular and phase structures are much more complicated.

If a liquid system arrives at a metastable region or vicinity of the upper or lower critical point, the correlation radii of concentration fluctuations dramatically increase.[60–62] A study[63] on the thermodynamics of mixing of PVC with oligoester acrylates revealed that, although aggregation of oligomeric molecules in these systems begins far from the phase transition boundary, it is the metastable state and the vicinity of the critical point that show catastrophic changes in the thermodynamic parameters due to formation of stable supramolecular structures.

Figure 3 presents the concentration dependences of the initial curing rate for the PVC – trioxyethylene dimethacrylate system and the phase diagram of this system, which includes the binodal and spinodal curves. At a curing duration of 40 days before switching on the initiation mechanism, the $W_0 = f(c)$ curve exhibits at least two peaks; the polymerisation rate at the maxima increases by at least a factor of 10 – 20. The first polymerisation rate peak coincides with the transition of the system to the metastable state (temperature – concentration conditions correspond to a point between the binodal and spinodal curves). The second polymerisation rate peak appears when the system approaches the critical state (vicinity of the critical solution point). This is probably due to transition of the system to a higher level of self-organisation in these regions. Numerous experimental facts (see, *e.g.*, Refs 60 and 62) indicate that low-molecular-mass liquid systems differing in microscopic nature of interaction show in the critical and metastable states 'a variety of singular-type changes in the physical properties, ... and the decisive role in these phenomena is played by the interaction (correlations) between abnormally growing fluctuations'.[60]

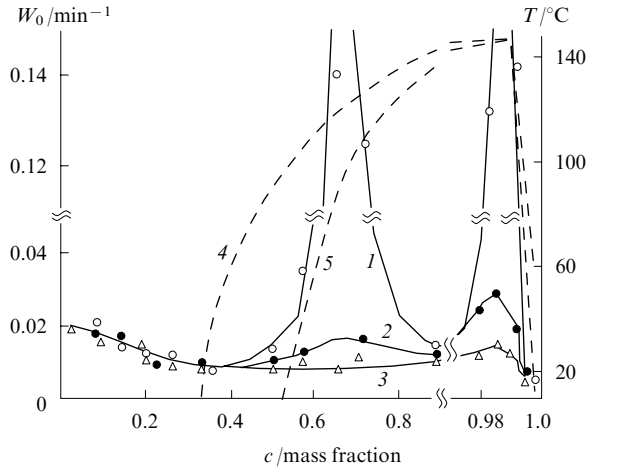



**Figure 3.** Concentration dependences of $W_0$ for the PVC – trioxyethylene dimethacrylate system at a curing temperature of 110 °C, initiator (dicumyl peroxide) concentration of 0.5% and curing duration of 40 (*1*), 5 (*2*) and 1 day (*3*). Phase diagram of this system: binodal (*4*) and spinodal (*5*).[63]

§ $(\varphi_1)_b$ is the concentration of oligomer at a point in the binodal curve.

Therefore, the hypothesis that abnormal increase in the oligomer polymerisation rate can be related to rearrangements of their supramolecular structures, which in this case obeys the laws characteristic of metastable and critical liquids, seems to be well substantiated.

The qualitative explanations for unusual experimental facts (see above) were theoretically substantiated by Arinshtein,[64,65] who described chemical processes in liquid condensed systems in the framework of the polychronous kinetics model (see Ref. 66). Arinstein introduced the notion 'spectrum of rate constants for elementary chemical reactions', which is due to different degree of mutual orientation of the reacting molecules.¶ The level of structural organisation is characterised by the orientation order parameter $\alpha$ (it should not be confused with the degree of conversion!), which can vary from 0 (isotropic system) to 1 (maximum anisotropy, all molecules are aligned).

Based on postulates, the kinetics of, *e.g.*, a bimolecular reaction is described by the following equation

$$\frac{dc(t)}{dt} = K_{ef}(\alpha)c^2(t), \tag{3}$$

where $c(t)$ is the running concentration of the reactant. In the linear approximation one has

$$K_{ef}(\alpha) = K_{ef}(0) + \frac{dK_{ef}(0)}{d\alpha}(1-\alpha) = k_1\alpha + k_2(1-\alpha), \tag{4}$$

where $k_1$ and $k_2$ are rate constants for chemical reactions in the ordered and disordered subsystems, respectively.

The evolution of the order parameter is described by the equation

$$\frac{d\alpha}{dt} = W_t(\alpha) + W_{ch}(c,\alpha). \tag{5}$$

The functions $W_t(\alpha)$ and $W_{ch}(c,\alpha)$ determine the changes in the order in the system in the absence of a chemical reaction and in the course of chemical transformations, respectively. As to the problem in question, it is first of all interesting to analyse the $W_t(\alpha)$ dependence, which has the form:[65]

$$W_t(\alpha) = -(\alpha - \alpha_t)f_t(\alpha) = -k_3(\alpha - \alpha_t), \tag{6}$$

¶ The studies in question use only one important approximation, according to which the spectrum of rate constants for a chemical reaction is represented by a distribution function of the orientation order parameter of the reacting molecules rather than an averaging expression, as in the classical gas-phase kinetics. This is due to long structural relaxation time in condensed media.

where $\alpha_t$ is the order parameter corresponding to the thermodynamic equilibrium of the system.

The last equality in expression (6) corresponds to $f_t(\alpha_t) = \text{const}$. Generally, both self-organisation ($\alpha_t \to 1$) and disordering ($\alpha_t \to 0$) processes can occur in the system that reached the equilibrium state.

Thus, from our analysis of studies [64, 65] it follows that the rate of a chemical reaction should naturally depend on the distribution function of the orientation order parameter of the reacting molecules both in the equilibrium and when the system moves along a trajectory to reach the equilibrium state. In our case this means that the initial rate of the chemical reaction should depend on the fraction of the reacting molecules that formed kinetically favourable supramolecular structures to the beginning of curing or, in other words, on the fraction of associates that had managed to relax to cybotaxes.

To date, the hypothesis of the aggregate nature of the kinetic anomalies has no direct experimental proofs, but its fruitfulness and predictive power in some cases are obvious.

If it is true, a general description of the curing of reactive oligomers can be done using a scheme proposed by Berlin [67] for the formation of a polymer network from oligoester acrylates.

It assumes that activation of functional groups is followed by chemical interaction between reactive centres that can begin both in cybotaxes and associates ('labile building blocks with kinetically favourable and unfavourable order', respectively, according to Ref. 40) and spontaneously in any other region of the system, *e.g.*, between non-organised molecules. Of course, since the local concentration of functional groups in aggregates is higher than the volume-average concentration (in cybotaxes, an additional orientation of molecules in the 'kinetically favourable order' is also possible), the initial rate of the chemical interaction in the organised structures is higher than in the non-organised ones. This is sufficient to formulate the proposition of kinetic microheterogeneity of the formation of a polymer network, namely, at the same instant of time polymerisation in different microscopic volume elements of aggregated oligomeric systems occurs at different rates. In turn, this means different degrees of polymerisation in different regions of the reaction volume at a specified instant of time. The system behaves as comprising a variety of microreactors in which the polymerisation occurs independently. Thus, kinetic heterogeneity gives rise to structural heterogeneity. These microscopic heterogeneities of the curing oligomeric system are 'nuclei' of subsequent morphological heterogeneity of the cured polymer.

According to this scheme, in the early stages of polymerisation an oligomer having two reactive centres mainly reacts with a similar molecule at only one functional group. Owing to chain propagation the formation of linear molecules is followed by the formation of branched ones bearing 'pendant' bonds [one end is chemically bonded to the growing chain while the other end(-s) is(are) potentially reactive]. Such reactive branched structures are called β-polymers. In the pre-gel state, linear molecules and β-polymer are dissolved in the reaction medium consisting of the molecules of the non-reacted oligomer.

**b. Interrelation between the curing kinetics and the duration of establishment of thermodynamic equilibrium in the starting system**

The dependence of the kinetic properties of oligomers and their mixtures on the time prehistory of the starting system has been reported repeatedly (see, *e.g.*, Refs 28 and 37). In particular, attainment of reproducibility of the kinetic curves for curing of reactive oligomeric systems in identical experiments (identical compositions, reaction conditions, *etc.*) requires not only meeting all conventional methodological criteria, but also performing a number of additional operations.[28] First of all the experimental sample should preliminarily (prior to switching on the initiation mechanism) be kept in rest for a particular (sometimes, rather long) time called the exposure time ($\tau_e$). For different oligomers and different reaction conditions the critical exposure time ($\tau_e^c$, at longer times the curing kinetics is independent of the time prehistory of the system) can be strongly different, from a few fractions of a second to several days and even months.[9]

The possibility of reliable detection of the lower limit of $\tau_e^c$ is determined by the experimental design and methodology and by the parameters of the instruments for conversion measurements. Generally, the dependence of the kinetic parameters of curing on $\tau_e$ can be due to variuos reasons. Some of them are related to structural features of the reactive systems, *e.g.*, the duration of the period needed to establish the equilibrium in the formation of elements of the 'kinetically favourable and unfavourable orders'. Other reasons are determined by the essentially kinetic effects, *e.g.*, diffusion-controlled processes of redistribution of the polymerisation initiator in the bulk of the system or changes in the concentration of inhibitors (or activators) in the sample during the exposure time. This can be quite important because storage of the sample can be accompanied by accumulation of peroxides or oxygen (uptake from the environment, *etc.*).

Undoubtedly, the commonly accepted kinetic considerations play an important and, in some cases, decisive role for explanation of certain features of oligomer curing. However, in the framework of this approach many other experimental observations made in studies of the curing kinetics of oligomeric systems remain unclear.

An illustrative example is as follows: it was found that as $\tau_e$ increases the parameter $W_0$ increases for one and decreases for the other group of systems (Figs 4*a* and 4*b*, respectively).[28] The classical kinetics provides no explanation for these observations. Indeed, if we assume that the increase in $W_0$ with an increase in $\tau_e$ observed for the polyisoprene rubber – oligoester acrylate system is due to a decrease in the inhibitor concentration during the exposure time, the reasons for the decrease in $W_0$ observed in similar experiments with butadiene-nitrile rubber – oligoester acrylate mixtures (see Fig. 4*b*) remain unclear. It is impossible to agree with the other 'kinetic' version, according to which the effect in question arises from gradual accumulation of peroxides in the isoprene samples during their storage (this cannot be ruled out in this experimental procedure), because the shape of the curve for the samples containing nitrile rubbers contradicts this version. No fundamental distinctions between the oxygen uptake by isoprene and nitrile rubbers and between the mechanisms of their oxidation, which could lead to different-type dependences $W_0 = f(\tau_e)$ for the curing of oligoester acrylates in the isoprene and nitrile rubber matrices, were determined.[68] Other explanations for these results, based on the classical principles of analysis of the kinetic effects, also appeared to be contradictory.[1, 69–71]

Special experiments [28] showed that the procedure for introduction of initiator into the system (mechanical mixing, swelling or use of combined solutions) and the order of mixing with other components (oligomer, rubber, with mixture) had no effect on the character of the kinetic curves of curing of both systems and on the $\tau_e^c$ values. The results of analysis showed than both systems were thoroughly cleaned from inhibitors and no chemical transformations in them were detected in the storage period. This gave grounds to assume that the most

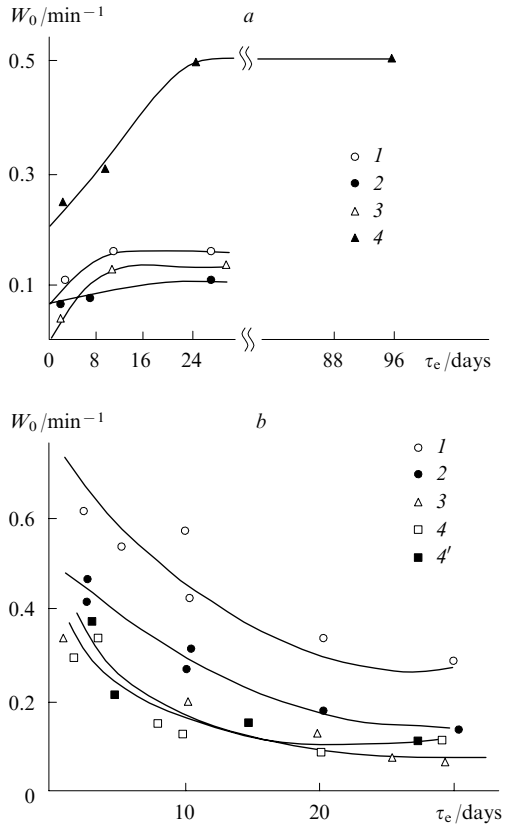



**Figure 4.** Initial curing rate $W_0$ of tetramethylene dimethacrylate in polyisoprene (*a*) and butadiene-nitrile rubber (*b*) matrices plotted *vs.* curing duration $\tau_e$ at different content of oligoester acrylate and different sample preparation procedures.[28]
Curing temperature is 80 °C, concentration of initiator (dicumyl peroxide) is 0.5%. Oligomer content (%): (*a*) 10 (*1*), 26 (*2*), 36 (*3*) and 50 (*4*); (*b*) 70 (*1*), 60 (*2*), 50 (*3*) and 30 (*4*). Preparation procedure: from combined solutions (samples *1*–*3*), from solution (sample *4*) and swelling (sample *4′*).

probable reason for the dependence of the curing kinetics on the time prehistory of the system consists in changes in its structural organisation at $0 < \tau_e < \tau_e^c$. Distinctions between the $W_0(\tau_e)$ plots for the nitrile and isoprene systems (see above) seem to be due to opposite trends in changes in the parameters of the corresponding supramolecular structures.

Before we go on to discuss these experiments, we will dwell on some generalisations of the laws of formation of thermodynamically equilibrium structures in oligomeric systems.[8,9,72,73] These structures are formed in a step-by-step manner; the process involves averaging of component concentrations, averaging of the associate-cybotaxis compositon (aggregates size and orientation order) and averaging of morphological parameters.

In the framework of the associate-cybotaxis model, the rate of relaxation of the oligomeric system to a thermodynamically equilibrium structure depends on the ratio of the rate constant for addition to supramolecular aggregates to the rate constant for elimination of particular (single) oligomer molecules from the aggregates; the equilibrium distribution functions with respect to the number and size of elements of the supramolecular structure are determined by the state parameters and by the nature of the medium in which the relaxation occurs.[8–10,72,73]

Analysis of the effect of the time prehistory of oligomeric systems on the curing kinetics including the description of molecular transformations (*e.g.*, determination of concentration dependences of the initial rates of addition polymerisation and polycondensation in single-phase systems at different $\tau_e$) can be performed using the methodology and formalism of classical kinetics.[70,71] However, the understanding of some unusual experimental observations requires a description with allowance for the effect of the duration of the evolution of the supramolecular and phase structures of the starting system.

As applied to the experiments considered above, this implies the following. If the systems under study do have the aggregate nature, the re-organisation of the supramolecular structure occurring at $0 < \tau_e < \tau_e^c$ and preset state parameters eventually leads to the equilibrium number, size and lifetime distribution functions of associates and cybotaxes. Depending on the medium polarity (compatibility of components), the attainment of equilibrium can be accompanied by either ordering or disordering of the system. For instance, butadiene-nitrile rubber films swollen in tetramethylene dimethacrylate possess better thermodynamic compatibility of components (Flory–Huggins parameter $\chi = 0.012$) compared to *cis*-polyisoprene films swollen in the same oligomer ($\chi = 0.136$); as $\tau_e$ increases, the initial polymerisation rate decreases in the former and increases in the latter case. This is due to the fact that different systems are characterised by different aggregate distribution functions that take the final form upon complete mixing in swelling (quasi-equilibrium, see a monograph[72]). Moreover, on the way towards thermodynamic equilibrium the evolution of the systems during the exposure time may have different trends (to segregation and to dispersion). Segregation of same-type molecules (aggregation) dominates in the case of poor compatibility of the different-type components; otherwise, molecular dispersion (disintegration of aggregates) is predominant. In other words, dissolution of polar oligoester acrylate in polar nitrile rubber leads to manifestation of the trend to molecular dispersion; as a consequence, the supramolecular aggregates formed in the mixing stage partially break down, *i.e.*, for this system the level of structural self-organisation eventually decreases. Disordering of supramolecular structures (decrease in the number of aggregates and anisotropy of cybotaxes or a decrease in the number or size of cybotaxes, which is equivalent to the decrease in the number of anisotropic molecules in the unit cybotaxis, *etc.*) should lead to a decrease in $W_0$.[28,74–76] That is why the dependence of $W_0$ on $\tau_e$ for this system decreases. Contrary to this, mixtures of oligoester acrylate with non-polar *cis*-polyisoprene rubber are characterised by increased segregation of oligomeric molecules (increase in aggregate size and anisotropy) during the exposure time and, as a consequence, by an increase in $W_0$ with time at $0 < \tau_e < \tau_e^c$.

It was theoretically shown[65] that as the system goes to thermodynamic equilibrium, the order parameter $\alpha_t$ can tend either to 1 or 0 depending on external conditions (medium, temperature), *i.e.*, the evolution of the system can be accompanied either by enhancement of self-organisation or by disordering.

Considering the parameter $\tau_e^c$ as a criterion for establishment of equilibrium in oligomeric systems, the following methodological limitations should be kept in mind.

1. The times $\tau_e^c$ measured by different methods can differ appreciably. For instance, experimental investigations of the viscous properties of oligoester acrylates[77,78] led to $\tau_e^c \approx 30$ min; however, the estimates obtained from pulsed NMR relaxation measurements[79,80] and polymerisation

kinetics studies [28, 29] carried out under identical conditions much exceed this value, being of the order of a few hours or even days. The most probable reason for this inconsistency is that the reactivity and transport properties of oligomers are controlled by different parameters of the supramolecular structure and the attainment of equilibrium values of these parameters takes different time. If the internal architecture of a structural inhomogeneity region seems to be insignificant for rheological studies (here, the number of aggregates and their size, strength of chemical bonds between them, *etc*., are important), in the case of kinetic experiments on oligomer curing an important role is also played by the orientation of molecules within the supramolecular aggregate.[9, 40] The fact that the relaxation rearrangement within the volume element of the supramolecular structure (aggregate) is still in progress has no effect on the measured viscosity value.

This was confirmed both experimentally and theoretically. It was shown [74] that incorporation of a non-reactive analogue into the structure of oligoester acrylate cybotaxis causes the initial polymerisation rate ($W_0$) to decrease, but has no effect on the rheological characteristics of the cybotaxis. This can manifest itself in the experiments only if the rate constants for polymerisation 'sense' the internal structure of the supramolecular formation while the rheological constants are neutral to it.

A consequence of the kinetic model for formation of the supramolecular structure of oligomers [81] is as follows: transition of oligomeric systems to the equilibrium state with respect to different characteristics can occur in different manner. For instance, a system can reach an equilibrium state with respect to certain characteristics that depend on the concentration of aggregates in a shorter time compared to the time interval taken to attain equilibrium with respect to the characteristics that mainly depend on the structure of the supramolecular aggregate.

Thus, criteria for establishment of equilibrium in oligomeric supramolecular structures determined by different experimental methods can differ from one another. This is quite understandable, because they can characterise the 'motion' of the system to thermodynamic equilibrium on different levels of structural organisation.

2. At preset state parameters of the system, the critical exposure time undoubtedly characterises the attainment of the equilibrium state. But the $\tau_e^c$ value can depend on the energy prehistory of the oligomeric system. According to the activation model for the formation of the supramolecular structure of oligomers,[72] the system consists of aggregates and 'non-organised' molecules. A sample prepared in some way including mixing, heating, cooling, deformation, *etc*. is characterised by a certain ratio of the 'organised' and 'non-organised' structures and by a random aggregate number and size distribution function determined by the prehistory of the system. When external factors are no longer in action, the system at rest spontaneously goes to equilibrium. Single molecules add to aggregates, thus changing their sizes and disturbing internal structure. As the time $\tau_e^c$ passes, one gets the equilibrium aggregate distribution function.

It should be noted that not all single molecules can add to aggregates; this is only possible for the activated molecules that overcame the energy barrier. Here, chemical activation is left out of consideration. The case in point are those single molecules whose kinetic energy became sufficiently high as a result of the action of thermal, mechanical and other factors in the course of sample preparation. Since conditions for preparation of identical samples can be different (experimental goals can also be different, *e.g*., isothermal tests, tests under linear or stepwise heating, *etc*.), the $\tau_e^c$ values obtained in different experiments may differ from one another. This holds for any measured characteristic.

3. A change in the state parameters of an equilibrium oligomeric system (*e.g*., raising the temperature from $T_1$ to $T_2$) causes changes in the supramolecular structure of the system and a corresponding change in $\tau_e^c$. An attempt to return the system to the initial equilibrium state by lowering the temperature from $T_2$ to $T_1$ may change the $\tau_e^c$ value in different manner. In this context the $\tau_e^c$ value can be either 'reversible' or 'irreversible'. For instance, a curing study [29] of polymer–oligomer films prepared by equilibrium swelling of rubber in oligoester acrylate at room temperature and exposed to air or an inert medium at the same temperature showed that $\tau_e^c = 10$ days. However, when the non-cured samples characterised by $\tau_e^c = 10$ days were again placed in contact with oligoester acrylate, they 'forgot' their kinetic stability and returned to the initial state. In this case reproducible $W_0$ values could be obtained after a new 10-day exposition. If the temperature or other exposure parameters were changed, both $\tau_e^c$ and $W_0$ values also changed. For the new exposure conditions these values were found to be 'reversible'.

At the same time experiments [82, 83] with stepwise change in the temperature of oligomeric samples provided that $\tau_e \geqslant \tau_e^c$ showed that the values of the characteristics measured under direct and reverse temperature variation (heating and cooling, respectively) are different. Methodological difference between these stages consists in the following. Let measurements be performed at the same temperature. Cooling implies that the sample was pre-heated to a higher temperature compared to the temperature of the experiment and then cooled to this temperature, whereas in the case of heating the sample was not pre-heated to temperatures higher than the temperature of the experiment. It is believed [76, 77] that each subsequent temperature increment in the case of stepwise heating provides activation of a new group of elements of the system, which are involved in the onset of a new level of structural organisation characterised by its own preset equilibrium level corresponding to the higher temperature. This was quantitatively confirmed in the analysis [72, 73, 84] of the known experimental data [76, 77, 82, 83, 85] in the framework of the activation and relaxation models for the formation of the supramolecular structure of oligomeric systems.

The system can be activated by applying not only thermal, but also mechanical, magnetic, electric and other force fields.[53–56, 74] Experimental data indicating both reversible and irreversible effects of force fields on the formation of the aggregate structure of oligomeric systems were considered in a monograph.[42] Seemingly, there are certain limiting (in some cases, 'beyond-the-limit') magnitudes of the forces acting on the system, which can lead either to creation of prerequisites for the onset of a higher level of structural organisation of the system during the time $\tau_e^c$ or to complete breakdown of the supramolecular structure of oligomers, which cannot be recovered in reasonable observation time.

In spite of these limitations, the allowance for $\tau_e^c$ when carrying out studies on oligomer curing kinetics in the early stages of the process may appear to be quite important. In support of the aforesaid we will return to Fig. 3, which shows the dependence of the initial rate, $W_0$, of polymerisation of trioxyethylene dimethacrylate in PVC matrix on the component ratio. As mentioned above, in the metastable state region and near the critical point the parameter $W_0$ increases by at least ten to twenty times. But the case in point is that the

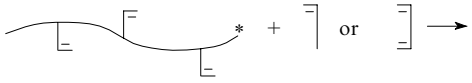
resulting $W_0$ value depends on both the component ratio and the time required for structural rearrangement to the thermodynamically allowed level. Unfortunately, experiments with allowance for this feature were scarce. At the same time the inclusion of (more exactly, ignoring) the kinetics of relaxation to the equilibrium state can change not only the numerical values of the measured characteristic, but also the character of the dependences. Indeed, maxima in the curve $W_0 = f(c)$ can be detected only if the condition $\tau_e \geqslant \tau_e^c$ is met, *i.e.*, taking into account the kinetics of attainment of thermodynamic equilibrium. At $\tau_e = 1$ day (curve *3*), the experimental curve shows almost no extrema, which are also slightly noticeable at $\tau_e = 5$ days. Only at $\tau_e = 40$ days, which is equal to or greater than $\tau_e^c$ and corresponds to the equilibrium state, the system exhibits its actual properties.

## III. The cyclisation reaction

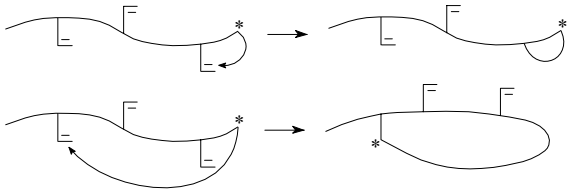
All computational methods assume a tree-like topological structure of network polymers. Clearly, ignoring the cyclisation reaction introduces a large error into the numerical values of the structural parameters. Erroneous character of this approach is particularly pronounced when considering three-dimensional radical polymerisation,[11, 15, 40] namely, it is cyclisation in the early stage of macroradical chain propagation that is responsible for the microheterogeneous mechanism of the process.

A simplified but clear scheme of three-dimensional radical polymerisation of oligomers containing two and more double bonds proposed by Matsumoto [86] is as follows:

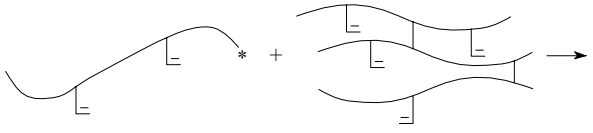
1. Growth of linear chains bearing pendant double bonds



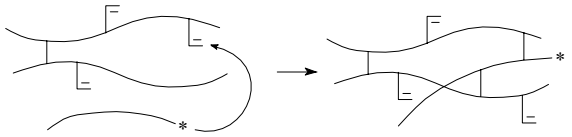

2. Primary intramolecular cyclisation



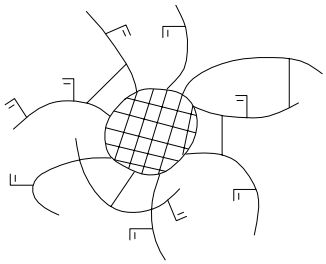
3. Intermolecular cross-linking



4. Intramolecular cross-linking (secondary cyclisation) in branched macromolecules, microgel particles and macrogel



The last two reactions can result in the formation of microgel particles



Now we will dwell on the second reaction, which leads to primary cyclic structures and is responsible for the shift of the gel point from the value calculated using the Flory – Stockmayer theory † towards higher conversions.

All versions of cyclisation probability calculations are based on the Jackobson – Stockmayer model,[92] which includes an equilibrium ring closure reaction at the ends of a freely joined chain consisting of $n$ segments; the equilibrium constant for this reaction is given by

$$K_{cycl}(n) \sim n^{-5/2}.$$

Clearly, this relationship is valid for large $n$. The case of small $n$ requires a detailed coonsideration of the conformational properties of the polymer chain [93, 94] and the thermodynamics of the polymer – environment interaction, which affects the size of the macromolecular coil.[11, 95]

Despite the variety of physicochemical mechanisms of polymerisation all of them have a common feature, namely, the system in the early stages of polymerisation is treated as a dilute solution of a polymer in a monomer (oligomer) and the volume distribution of the repeating units and pendant functional groups (in the case of three-dimensional polymerisation) is highly non-uniform. It is the relatively high local concentration of these fragments in the volume of the growing macromolecular coil that determines an increased cyclisation (intrachain cross-linking) probability in the initial stage of three-dimensional polymerisation.

The kinetic behaviour in the next reaction stages depends on the physicochemical features of the process, namely, (i) initial chain length determined by the ratio of the rates of the initiation, chain propagation and chain termination reactions, (ii) ratio of the reactivity of pendant functional groups to the reactivity of functional groups in the starting oligomer, (iii) polymer solubility in the medium, *etc*. It is these factors that are responsible for the specific features of three-dimensional radical polymerisation. In this case the formation of a polymer chain takes about a second, which corresponds to a conversion of few fractions of a per cent. Therefore, in the initial stage of polymerisation the system consists of a dilute solution of the polymer in oligomer. As a consequence, an active centre will more probably react with pendant functional groups of its 'own' chain rather than with similar groups from 'alien' chains. In other words, intramolecular cyclisation will predominate over intermolecular cross-linking.

Indeed, the coil volume of a growing macromolecular chain (degree of polymerisation is $P$) is to a first approximation proportional to $P^{3/2}$. The mean concentration of pendant

† At present, the applicability of this theory to critical conversion calculations in the case of three-dimensional polymerisation casts some doubt.[87–91]

functional groups (here, double bonds) is proportional to $P^{-1/2}$ and the intrachain cross-linking probability (at least one group reacts with the terminal radical) is proportional to $P^{1/2}$. Further evolution of the system is well-defined self-accelerating in character,[11,96] namely, the larger the number of intrachain cross-link points the smaller the coil and the higher the concentration of pendant groups and the cyclisation probability. Chain elongation also means a decrease in the concentration of chains and, correspondingly, a decrease in the interchain cross-linking probability. At the same time interchain cross-linking resulting in the formation of branched macromolecules also makes cyclisation more probable, because the higher the degree of branching the more compact the macromolecule.[97]

A strong proof of cyclisation is provided by the estimate of the degree of conversion with respect to pendant groups based on conversion with respect to bifunctional oligomer (concentration ratio of the oligomer reacted at both functional groups to the oligomer reacted at least one group).[98] Figure 5 presents this dependence for polymerisation of 1,4-divinylbenzene in toluene solution.[99] The curves do not approach zero upon extrapolation to zero conversion with respect to monomer; rather, the higher the dilution of the system the larger the intercept. But cyclisation in bulk in the case of copolymerisation of mono- and bifunctional monomers is also possible even at relatively low monomer concentration.[100]

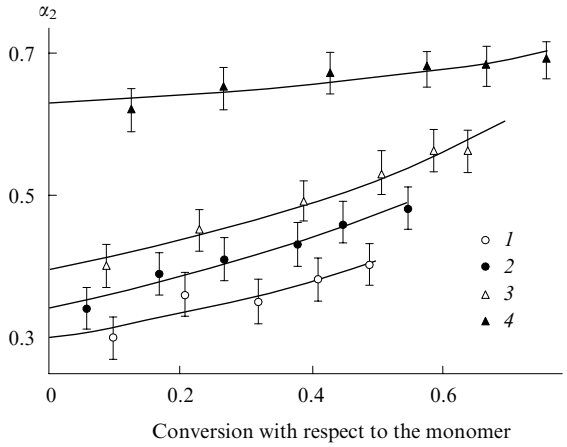



**Figure 5.** Degree of conversion of pendant functional groups ($\alpha_2$) plotted *vs.* conversion of the monomer at an initial concentration of 1,4-divinylbenzene of 5 (*1*), 2 (*2*), 1 (*3*) and 0.5 g per 100 mL of solution (*4*).[99]

Cyclisation was detected by different methods in studies of the initial steps of polymerisation of various systems. For instance, at least 80% pendant double bonds are involved in the cyclisation reaction in the course of copolymerisation of ethylene glycol dimethacrylate and styrene,[101] 1,4-divinylbenzene and styrene[102] and *N*,*N*′-methylenebis(acrylamide) and acrylamide.[103] Studies of other systems led to similar results.

Almost no cyclisation was observed during anionic polymerisation of 1,4-divinylbenzene in the bulk, whereas on dilution the lower the monomer concentration the more intense the cyclisation reaction (Fig. 6).[104]

Seemingly, this is due to the 'living' character of the process, *i.e.*, a relatively high concentration of chains, for which the growth time is commensurable with the overall duration of the polymerisation process. One can assume that there are no grounds for preferred development of the cyclisation reaction under conditions of 'living' radical polymerisation. However, the results of computer simulation of iniferter-assisted‡ three-dimensional radical polymerisation showed[105] that cyclisation does occur, being even more intense than in the case of conventional initiation. It is noteworthy that the last-mentioned type of initiation makes the process similar to 'living' polymerisation.[106]

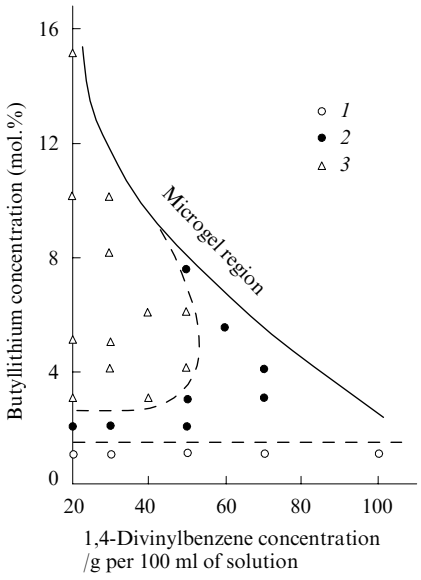



**Figure 6.** Polymer structure as a function of the concentrations of n-butyllithium and 1,4-divinylbenzene in tetrahydrofuran.[104] Linear polymer (*1*), branched polymer (*2*) and microgel (*3*).

$$R^1R^2 \xrightarrow{k_i} R^1 + R^2 \text{ (initiation)},$$
$$R^1 + M \xrightarrow{k'_p} P_1,$$
$$P_i + M \xrightarrow{k_p} P_{i+1} \text{ (chain propagation)},$$
$$P_i + R^2 \xrightarrow{k_t} P_iR^2 \text{ (reversible chain termination)},$$
$$P_iR^2 \xrightarrow{k_d} P_i + R^2 \text{ (destruction)},$$

where $R^1$ and $R^2$ denote different types of radicals; M is monomer; $P_i$ denotes the polymer chain and the number of repeating units (subscript); and $k_i$, $k'_p$, $k_t$ and $k_d$ are the rate constants for corresponding processes.

If $k_tR^2 \gg k_d$ ($R^2$ is the concentration of the radicals $R^2$), the polymerisation will be continuous in character even in the presence of of quadratic chain termination.

Thus, the qualitative picture of cyclisation in the course of polymerisation processes is now understandable. Quantitative results were obtained by computer simulation.[107–112] In particular, it was shown[112] that intrachain cross-linking already occurs at a chain length of 3–5 repeating units; this rejects the hypothesis[6] of formation of long β-polymer chains containing $10^3$–$10^4$ repeating units, each of them having a pendant double bond.

A variety of methods from simple probabilistic approaches[113–117] to strategies based on statistical physics,[118]

‡ Iniferter is a disulfide-type initiator; one of radicals formed upon its dissociation ($R^1$) induces chain propagation reaction while the other radical ($R^2$) only participates in the reversible chain termination reaction.

namely, the diagram technique [119] (idea of applying it to polymer physics was coined by Edwards [120]) were proposed for calculating the equilibrium cyclic structures formed in three-dimensional polycondensation. All of them were comprehensively treated by Kuchanov *et al.*[121]

Unlike addition polymerisation, chain growth in polycondensation occurs gradually, being accompanied by a decrease in the chain concentration; this creates severe conditions for cyclisation in the early stages of the process. Usually, polycondensation is a nonequilibrium process. As a consequence, rings are also nonequilibrium. This means that the topological structure of the polymer bears a 'fingerprint' of the kinetic features of the reaction.

However, one should keep in mind that gelation occurs at rather high conversions and therefore the possibility of intrachain cross-linking in the pre-gel state cannot be ruled out.[11, 122] According to Flory, [123] this reaction is insignificant up to the gel point. Indeed, this is confirmed (see references cited in monograph [11]) by coincidence of experimental and theoretical critical conversion values ($\alpha_c$). At the same time a considerable body of experimental data on the shift of $\alpha_c$ towards higher conversions contradict this assumption.

The conclusion of formation of inefficient rings in the course of polycondensation of epoxy oligomers was drawn based on analysis of the elastic properties of the polymers in the rubbery state.[124, 125] The cyclisation probability is related to the flexibility of reactants, that is, an aromatic diamine compared to aliphatic diamine as curing agents for diglycidyl bisphenol A ether (see Ref. 124) or diglycidyl bisphenol A ether compared to diglycidyl ethylene glycol ether in curing of ethylenediamine lead to much lower yield of cyclic structures. In some cases cyclic molecules were detected at $\alpha < \alpha_c$ in polycondensation of oligomeric chlorosilanes [126] and in the synthesis of polyurethanes.[45, 126–130] An important factor facilitating the cyclisation reaction is dilution of the system. It was shown [127, 128] that as the molecular mass of oligomer increases (and thus the concentration of reactive groups decreases) the proportion of cyclisation in the polyurethane, polydimethylsiloxane and polyester formation reactions considerably increases and reaches 10%–12% at the gel point. The shift of the gel point relative to the calculated value varied from 0.03 to 0.12. However, the authors noted that rings are mainly formed near the gel point owing to rapid increase in the number of functional groups in each macromolecule.[128]

Theoretical analysis of the kinetics of linear polycondensation (reaction of the AA + BB type) showed [131, 132] that accumulation of cyclic products begins at the very early stage of the reaction, their yield reaches a limiting value determined by the rate constant for cyclisation, but at the instant of reaction completion the amount of cyclic products can be so large that eventually the polymer will consist of cyclic fragments (however, this takes inifinite time). The MMD of the cyclic products depends only slightly on the reaction kinetics and conditions. Under almost any conditions the minimum-size rings are mainly formed.

Essentially the same laws are characteristic of polycondensation of $AB_f$-type polyfunctional oligomers with the functionalities $f \geqslant 2$, resulting in the formation of branched polymers. In particular, polycondensation of 2,2′-bis(hydroxymethyl)propionic acid ($AB_2$-type oligomer) involves formation of ring-containing macromolecules as a result of intramolecular reaction between the acid and hydroxyl groups.[133] The mole fraction of the ring-containing macromolecules is virtually independent of the degree of polymerisation, but appreciably increases with conversion. It should be noted that cyclisation places a rather strong limitation on the average degree of polymerisation $\overline{P}_w$, so the parameter $\overline{P}_w$ takes a finite value even at 100% conversion with respect to the A groups. This was shown both experimentally [133] taking hyperbranched polymers based on the $AB_2$, $AB_4$ and $AB_6$ type siloxysilanes as examples and theoretically by kinetic calculations and computer simulation.[134, 135] A comprehensive study [135] of polycondensation of $AB_2$ and $AB_4$ type oligomers by the Monte Carlo (MC) method revealed that at the limiting conversion all macromolecules contained rings, of which more than 80% were the simplest rings. For these oligomers the average degree of polymerisation of rings was 1.65 and 1.39, respectively.

Owing to formation of cyclic products in polycondensation of oligomers capable of forming polymer networks the gel point is considerably shifted towards higher conversions. For instance, a kinetic MC simulation [135] of polycondensation of tetraethylsiloxane showed that the critical conversion reaches a value of 82% (*cf.* 33% as predicted by theory) and that cyclisation mainly leads to formation of the smallest rings. MC simulation of polycondensation of an equimolar mixture of $A_2$ and $B_3$ revealed a shifh of the gel point to 0.949 ($\alpha_c = 0.866$ according to calculations).[136] At the moment of reaction completion, a total of 28% of the $-A-A-$ bonds are included in cyclic structures. About 22% of macromolecules in the sol fraction contain cyclic structures, of which 5% include two simple rings. A characteristic feature of the gel fraction is a broad ring size distribution, which is described by a non-monotonic function with a minimum corresponding to the structure containing twenty-four $A_2$-type units.

Thus, the formation of inefficient rings and their presence in the polymer structure should not be ignored in studies of the formation of network polymers.

## IV. Gelation kinetics under addition polymerisation conditions

As shown above, the probability of cyclisation or intrachain cross-linking in the initial stage of three-dimensional polymerisation is high. The kinetic behaviour in further stages of the process depends on the physicochemical characteristics, namely, on the structure of oligomeric liquid, initial chain length determined by the ratio of the rates of initiation, chain propagation and chain termination reactions, the ratio of the reactivities of pendant functional groups and groups in the starting oligomer, solubility of the polymer in the medium, *etc.* A number of illustrative examples can be found in studies by Korolev who conducted comprehensive investigations of radical three-dimensional polymerisation of oligoester acrylates (see, *e.g.*, Refs 7, 40, 41, 137 and 138).

First of all, the case in point is the critical conversion, or the gel point. According to Flory [95] and Stockmayer,[139] it is determined by the second moments of the MMD. Their method of gel point calculations is based on statistical approach, which is inapplicable to polymerisation processes (this has recently been established [15, 85]). Direct kinetic calculations were carried out.[87–91]

The physical mechanism of gelation assumes that it is the number of functional groups (and active centres) that is responsible for the rate of chain propagation. Therefore, the determining factor is the distribution of macromolecules according to functionality. Analytical calculations of the second moments of the distribution are almost impossible even for the simplest kinetic scheme. As an example, Fig. 7 presents the results of numerical calculations. The curves of

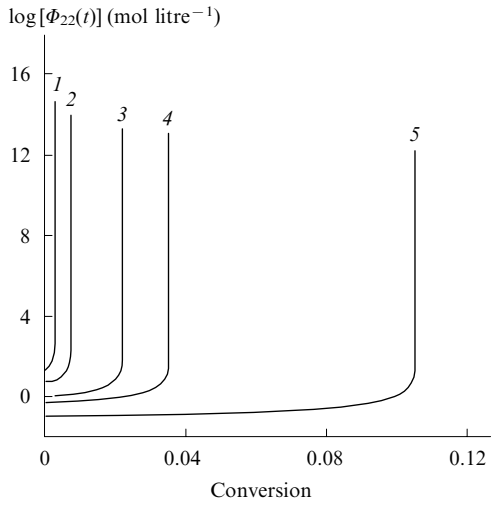



**Figure 7.** Kinetic curves of changes in the second moment of the functionality distribution $\Phi_{22}(t)$ under instantaneous initiation.[87]
Initiator concentration, $10^{-3}$ mol litre$^{-1}$: 20 (*1*), 5 (*4*), 1 (*3*), 0.5 (*4*), 0.1 (*5*).

changes in the second moment of the functionality distribution $\Phi_{22}(t)$ (see[§]) in the course of 'living' polymerisation under instantaneous initiation in the absence of chain transfer reactions have a specific shape,[87] namely, in a very narrow interval of conversion values the parameter $\Phi_{22}(t)$ increases by several orders of magnitude and tends to infinity. Because of this, without introducing a large error the critical conversion can be set to be equal to the intercept on the abscissa axis obtained by asymptotically extending the $\log[\Phi_{22}(t)]-\alpha$ curve. This value is much smaller than that determined from the number-average functionality.

This method was used in studies of various modifications of three-dimensional polymerisation including 'living' polymerisation under instantaneous and slow initiation, processes proceeding in the absence and presence of chain transfer reactions and reactions with quadratic or linear chain termination.[15,87–91]

According to calculations,[87] at a given concentration of active centres $R$ the $\alpha_c$ value is unambiguously given by the initial value $\Phi_{22}(0)$ and is independent of the initial concentration of functional groups

$$\frac{\alpha_c^2 \Phi_{22}(0)}{R} = 1. \qquad (7)$$

The physical meaning of the quadratic dependence with respect to the critical conversion is as follows. The formation of a cross-link point requires at least two consecutive reactions involving functional groups. The first reaction leads to incorporation of the polyfunctional oligomer into the polymer chain; therefore, pendant functional groups X should appear. The second reaction (interaction of groups X) results in the formation of the cross-link point Z. In the case of bifunctional oligomer $M_2$ one has

$$\frac{d\alpha}{dt} = k_p(1-\alpha)R,$$

$$\frac{dM_2}{dt} = -2k_p M_2 R,$$

$$\frac{dX}{dt} = 2k_p M_2 R - k_p X R,$$

$$\frac{dZ}{dt} = k_p X R,$$

$$\frac{dM_2}{d\alpha} = -2\frac{M_2}{1-\alpha},$$

$$\frac{dX}{d\alpha} = 2\frac{M_2}{1-\alpha} - \frac{X}{1-\alpha},$$

$$\frac{dZ}{d\alpha} = \frac{X}{1-\alpha},$$

$$Z = M_2\alpha^2.$$

The concentrations of functional groups, cross-link points and bifunctional oligomer are respectively denoted by $X$, $Z$ and $M_2$.

The more complex the mechanism the more complicated the dependences.[15,90,91] Nevertheless, in all cases the parameter $\Phi_{22}(0)$ plays the decisive role.

Usually, the calculated plots of $\alpha_c$ *vs.* kinetic parameters and $\Phi_{22}(0)$ exhibit two limiting portions corresponding to small and large $\Phi_{22}(0)$ values. The expressions for estimating the $\alpha_c$ values are listed in Table 2.

According to kinetic data,[11] the $\alpha_c$ value is rather small. Calculations[88] for a polyfunctional oligomer (slow initiation, termination by recombination) with the following kinetic parameters: $k_t = 10^5-10^7$ litre mol$^{-1}$ s$^{-1}$, $k_p = 10^2-10^3$ litre mol$^{-1}$ s$^{-1}$, $W_i = 10^{-4}$ mol litre$^{-1}$ s$^{-1}$, $\Phi_{22}(0) = 2M_0 = 20$ mol litre$^{-1}$ and $f = 2-4$ predict $\alpha_c \sim 10^{-4}-10^{-5}$.

Clearly, measuring so low conversions may introduce large errors. For ethylene glycol dimethacrylate,[140] the value $\alpha_c = 0.029$ lies beyond the error of determination and exceeds the theoretical estimate by two orders of magnitude.

The method that provides the shift of $\alpha_c$ towards higher conversions seems to be the best for comparing the calculated and experimental data. This can be done either by a decrease in the weight-average functionality $\Phi_{22}(0)$ by dilution of the system with a monofunctional co-monomer or by shortening the polymer chain length using sufficient amounts of chain transfer agents or highly efficient inhibitors of radical polymerisation.

The last-named technique was employed in a study of dimethacrylate triethylene glycol polymerisation initiated by dicyclohexyl percarbonate in the presence of a large amount of inhibitor (initiator : inhibitor mole ratio was equal to two).[88] Conversion was measured from contraction and the gel point was determined from the yield point. A comparison with the results obtained by other methods showed that the technique used gives quite correct critical conversion value.[141] For this type of experiments, the relation for the calculations of $\alpha_c$ is as follows:

$$\alpha_c = \frac{k_{tY} Y}{2k_p M_0}.$$

The results obtained are listed in Table 3. It follows that in the region of the longest growing polymer chains (at the lowest concentrations of inhibitor Y) the calculated and experimental

§ Strictly speaking, this is the difference between the second and first moments,
$\Phi_{22}(t) = \sum_n n^2 R(n) - \sum_n nR(n)$,
where $R(n)$ is the concentration of $n$-functional chains.

**Table 2**. Relations for critical conversion calculations.

| Process type | Small $\Phi_{22}$ | Large $\Phi_{22}$ | Criteria |
|---|---|---|---|
| 'Living' polymerisation, instantaneous initiation | $\frac{\alpha_c^2\Phi_{22}}{R}=1$ | $\frac{\alpha_c^2\Phi_{22}}{R}=1$ | $\frac{k_i}{k_p}>\sqrt{R\Phi_{22}}$ |
| The same + chain transfer | $\alpha_c=0.5\frac{k_X X_0}{k_p\Phi_{22}}$ | $\frac{\alpha_c^2\Phi_{22}}{R}=1$ | $\Phi_{22}><\frac{(k_X X_0)^2}{k_p^2 R}$ |
| 'Living' polymerisation, slow initiation | $\frac{\alpha_c^3 k_p\Phi_{22}^2}{W_i}=1$ | $\frac{\alpha_c^3 k_p\Phi_{22}^2}{W_i}=1$ | $\frac{k_i}{k_p}<\sqrt{R\Phi_{22}}$ |
| The same + chain transfer | $\alpha_c=0.5\frac{k_X X_0}{k_p\Phi_{22}}$ | $\frac{\alpha_c^3 k_p\Phi_{22}^2}{W_i}=1$ | $\Phi_{22}><\frac{(k_X X_0)^3}{k_p^2 k_i R}$ |
| Slow initiation, chain termination by recombination | $\alpha_c=0.33\frac{k_t R}{k_p\Phi_{22}}$ | $\frac{\alpha_c^3 k_p\Phi_{22}^2}{W_i}=1$ | $\Phi_{22}><\frac{\sqrt{k_t^3 W_i}}{k_p^2}$ |
| Slow initiation, linear chain termination | $\alpha_c=0.5\frac{k_{tY} Y}{k_p\Phi_{22}(0)}$ | – | – |
| Substitution effect, chain termination by disproportionation | $\alpha_c=\frac{\sqrt{k_t W_i}}{k_{p2} Z_{22}}$ | – | $\frac{k_{p1} Z_{22}}{\sqrt{k_t W_i}}<\frac{k_t}{k_{p2}}$ |

**Notations**: $\alpha_c$ is the critical conversion; $\Phi_{22}$ is the second moment of the functionality distribution (at $t=0$); $W_i$ is the initiation rate; $R$, $Y$ and $X_0$ are the concentrations of initiator, inhibitor and chain transfer agent, respectively; $k_i$, $k_p$, $k_t$, $k_{tY}$, and $k_X$ are the rate constants for initiation, chain propagation, quadratic and linear chain termination and chain transfer, respectively; $k_{p1}$ and $k_{p2}$ are the rate constants for propagation of free and pendant double bonds in those cases where the reactivities of the starting molecules containing two double bonds change upon a reaction involving one of them.

critical conversion values differ by more than an order of magnitude, but the differences decrease as the molecular mass increases (Y increases).

This unambiguously indicates that the main reason for the deviation of the experimental gel point from the calculated value is the cyclisation reaction.

Taking copolymerisation of styrene with various dimethacrylates as examples, Wesslau [142, 143] showed that the probability of cyclisation increases with conversion and reaches the limiting value at ~10%, being varied over a wide range from 0.11 to 0.63 depending on the molecular structure of the cross-linking agent.

Cross-linking of a microgel unavoidably leads to ν-syneresis, *i.e.*, displacement of low-molecular-mass components of the reaction system, oligomer and initiator from the microgel particle.[144–146] This process is self-accelerating in character, that is, as the local concentration of the oligomer in the microgel particle decreases, the probability of intrachain cross-linking increases and correspondingly microsyneresis enhances with an increase in the dentisy of cross-links. This is accompanied by the gel effect, namely, the mobility of macroradicals in the network dramatically decreases, their lifetimes increase and the length of the kinetic chain consisting of pendant functional groups also increases. Thus, even at low

**Table 3**. Experimental and calculated $\alpha_c$ values for inhibited polymerisation of dimethacrylate triethylene glycol.[88]

| Inhibitor concentration /mol litre$^{-1}$ | $\alpha_c$ | |
|---|---|---|
| | experiment | calculations |
| Inhibitor is trinitrotoluene, $k_{tY}\approx 10^2$ litre mol$^{-1}$ s$^{-1}$, $k_3=350$ litre mol$^{-1}$ s$^{-1}$, $M_0=4$ mol litre$^{-1}$ | | |
| 0.05 | ~0.01 | 0.0018 |
| 0.1 | 0.06 | 0.0036 |
| 0.2 | 0.08 | 0.0071 |
| 0.5 | 0.11 | 0.0179 |
| Inhibitor is benzoquinone, $k_{tY}\approx 2\times 10^3$ litre mol$^{-1}$ s$^{-1}$, $k_p\approx 350$ litre mol$^{-1}$ s$^{-1}$, $M_0\approx 4$ mol litre$^{-1}$ | | |
| 0.005 (4)[a] | 0.065 | 0.0036 |
| 0.005 (2)[a] | 0.055 | 0.0036 |
| 0.005 (1)[a] | 0.045 | 0.0036 |
| 0.01 | 0.085 | 0.0071 |
| 0.05 | 0.125 | 0.0357 |
| 0.1 | 0.135 | 0.0714 |

[a] The polymerisation kinetics were determined by precision calorimetry; figures in parentheses denote the initiation rates $W_i\times 10^7$ mol litre$^{-1}$ s$^{-1}$.

conversions the reaction system has a highly heterogeneous structure comprising microgel particles characterised by almost limiting conversions in the unreacted oligomer.

Manifestation of the gel effect is illustrated in Fig. 8, which presents the changes in the rate constants for bimolecular chain termination and propagation in the course of photochemically initiated polymerisation of diethylene glycol dimethacrylate at 40 °C.[147] The rate constant for chain termination decreases from the very beginning of the process, whereas the rate

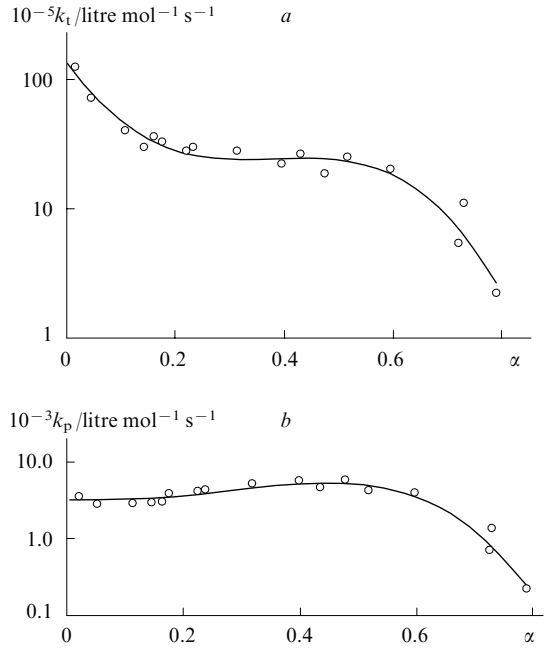



**Figure 8.** Changes in kinetic rate constants for chain termination $k_t$ (*a*) and propagation $k_p$ (*b*) reactions in the course of photopolymerisation of diethylene glycol dimethacrylate.[147]

constant for chain propagation remains unchanged up to ~50% conversion; at later stages of the process, both constants decrease. Similar dependences were observed earlier by Korolev and co-workers.[40] who studied polymerisation in the presence of initiators.

Having attained the conversion [7]

$$\alpha_{c1} = \frac{1}{(f-1)\,\overline{P}_n}$$

($\overline{P}_n$ is the number-average degree of polymerisation), all active chains appeared react with the double bonds of microgel particles. In this case, no new particles are formed and the polymerisation occurs in the form of the the particle size enlargement. The conversion inside particles reaches the limiting value. In the deeper stages, the reaction mainly occurs in the interfacial region rather than in the bulk of the microgel. Indeed, a light scattering study [148] showed that, starting from some instant, the number of particles slightly decreases while the particle size considerably increased with conversion (Fig. 9). This reaction stage corresponds to a plateau in the plot of changes in the rate constant for chain termination (see Fig. 8 *a*).

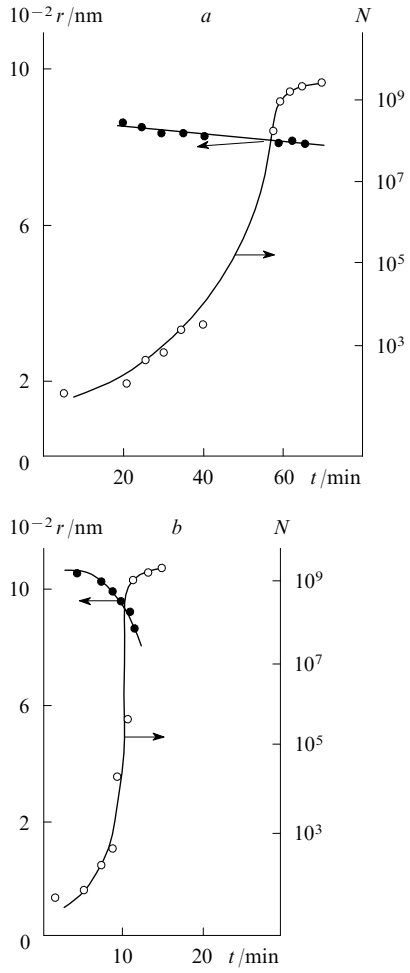



**Figure 9.** Changes in the number ($N$) and size ($r$) of microgel particles in the course of radical polymerisation of trioxyethylene glycol dimethacrylate (*a*) and bis(triethylene glycol)phthalate dimethacrylate (*b*).[148]

The radii of microgel particles can reach $10^2 - 10^3$ nm (macroscopic values compared to the size of macromolecules). In other words, the condition $\overline{M}_w \to \infty$ is met. This situation is typical of the post-gel region for all types of gelation processes. Namely, as an infinite cluster is formed, the process is reduced to an increase in its mass. Thus, the $\alpha_{c1}$ value can be treated as the gel point. From this point, almost the entire soluble fraction of the system consists of the starting oligomer or, in the case of copolymerisation, a monomer – oligomer mixture. In the early stages of the process, the sol fraction contains the β-polymer, that is, branched and often ring-containing macromolecules with deficiency in pendant double bonds.[149]

As the size of microgel particles increases, at a certain conversion the volume fraction of the gel reaches a value corresponding to the percolation threshold. For spherical particles, this corresponds to a volume fraction of the particles of 25%.[150] Indeed, experiments [40] with water uptake showed that interparticle contacts manifest themselves at a volume concentration of ~30%. However, the system of unconnected microgel particles undergoes deformations. The formation of macrogel through the reaction between particles is only possible provided a close packing of the particles in the reaction volume (packing density is ~52% for cubic lattice, 74% for hexagonal lattice and ~65% for random distribution, see Ref. 151); as a result, the system goes beyond the yield point. Then, the modulus of elasticity of the polymeric system increases exponentially (Fig. 10). The conversion corresponding to the yield point of the system is the second gel point ¶ ($\alpha_{c2}$); one has $\alpha_{c2} > \alpha_{c1} > \alpha_c$. Seemingly, it is this point that corresponds to the start of the decrease in the rate constants for chain propagation and termination (see Fig. 8).

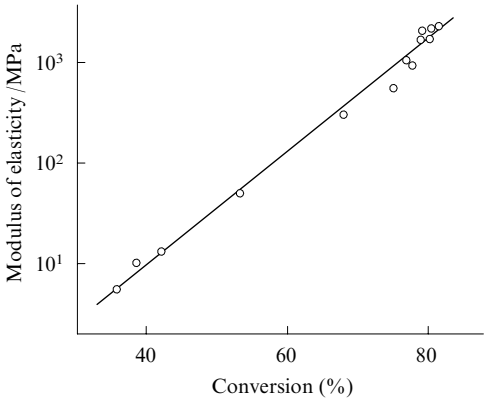



**Figure 10.** Changes in the modulus of elasticity in the course of radical polymerisation of trioxyethylene glycol dimethacrylate.[40]

Thus, radical polymerisation of oligoester acrylates results in polymers with heterogeneous supramolecular structures. But this mechanism is also typical of other processes,† *e.g.*, radical copolymerisation of mono- and polyfunctional oligomers.[7, 154 – 156] A characteristic feature of this mechanism is the

¶ The concept of two gel points was first introduced [152] to describe the curing of alkyd resins.

† Seemingly, the heterogeneous mechanism of three-dimensional polymerisation was first hypothesised [153] based on the results of light scattering studies of copolymerisation of unsaturated polyesters with methacrylate.

formation of a dilute solution of rather long chains in the initial stage.

As the chain length decreases in the initial stage (or the system is diluted with a monofunctional monomer),[149] the two-step process becomes a three-step one. For instance, a pulsed NMR study[157] of high-temperature (110 °C) inhibited (0.007 mass % of hydroquinone) polymerisation of trioxyethylene glycol dimethacrylate revealed the formation of linear or loosely cross-linked β-polymer in the very early stage (conversion $\leqslant 0.04$). This β-polymer is soluble or swellable in the starting oligomer, it is characterised by the transverse relaxation time $T_{2b}$, which is an order of magnitude shorter than the relaxation time $T_{2a}$ characterising the oligomer mobility restricted by the polymer formed. In turn, the time $T_{2a}$ is an order of magnitude shorter than the transverse relaxation time of the starting system $T_2^0$ (Fig. 11 *a*). Even less mobile elements, the phases c and c′ ($T_{2c}$ and $T'_{2c}$) corresponding to highly cross-linked structures, are formed almost simultaneously. Information on the phase ratio is presented in Fig. 11 *b*. The masses of the kinetic phases b and c increase with time, whereas the phase c′ is initially accumulated and then decreases until almost complete disappearance at $\alpha = 0.5$. Clearly, the last-mentioned phase consists of microgel particles.

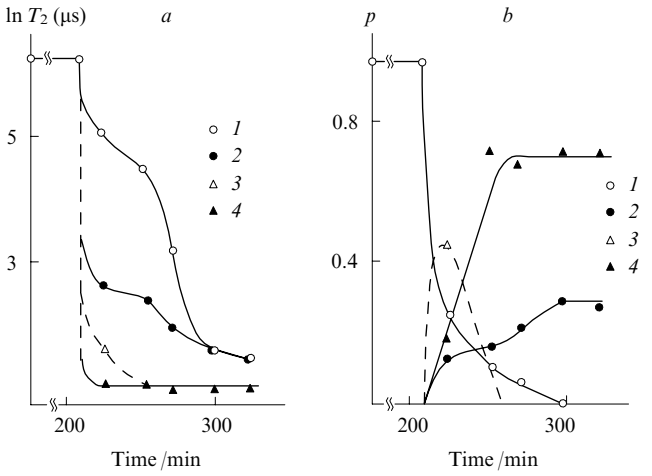



**Figure 11.** Changes in transverse relaxation times ($T_2$) of phases (*a*) and corresponding proton populations (*p*) (*b*) in the course of radical polymerisation of trioxyethylene glycol dimethacrylate.[157]
Phase: a (*1*), b (*2*), c′ (*3*) and c (*4*) (see text).

The microheterogeneous nature manifests itself in that the polymerisation kinetics in the conversion range from $\alpha_{c1}$ to $\alpha_{c2}$ are described by the Avrami equation.[158] The essence of analysis of phase transformations using the Avrami model is as follows. The microheterogeneous scheme (reaction volume consists of individual microreactors) assumes that the overall rate of the process is determined by the sum of the contributions of particular reactions occurring in the dispersion medium on the surface of particles and inside them

$$\alpha(t) = 1 - \exp\left(-\sum_i k_i t^{d_i}\right),$$

where $k_i$ is the specific polymerisation rate in the $i$th zone and $1 < d_i \leqslant 3$. If the reaction occurs in a homogeneous medium, than $d = 1$. For a heterogeneous reaction, one has $d \to 3$ (by analogy with crystallisation).‡ Variations of the parameter $d$ from 1 to 3 correspond to superposition of homogeneous (bulk) and heterogeneous (near the interface) components of the polymerisation process. The value $d = 0$ indicates reaction completion.

Polymerisation begins and for some time (until $\alpha = \alpha_{c1}$) occurs as a homogeneous process ($d = 1$, Fig. 12). At $\alpha \geqslant \alpha_{c1}$, an increase in the parameter $d$ is observed. In this stage, the $\alpha_{c1}$ values vary between 1% and 4%. Despite the fact that initiation occurs in the bulk, the reaction is localised within the near-surface layers of microgel particles owing to gel effect and microsyneresis. The larger the total volume of the near-surface layer (*i.e.*, the larger the surface area of the particles) the higher the overall reaction rate. Correspondingly, the $d$ value gradually increases and approaches a value of 3 and polymerisation develops as a frontal process and the reaction in this regime continues up to $\alpha = \alpha_{c2}$. Having attained the $\alpha_{c2}$ value, particles 'coagulate' by cross-linking and the integral surface and therefore the polymerisation rate decrease.

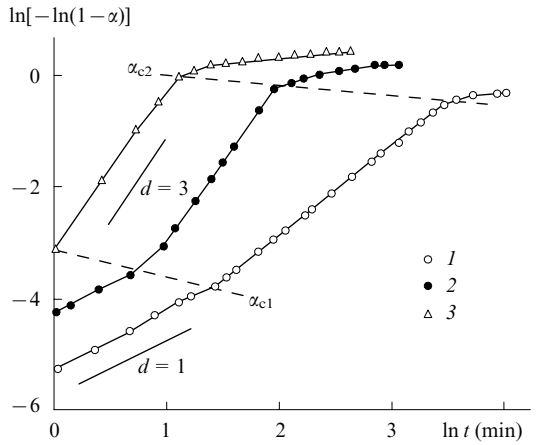



**Figure 12.** Kinetic curves for radical polymerisation of trioxyethylene glycol dimethacrylate in the Avrami equation coordinates.[159]

| | $T$/°C | $\alpha_{c1}$ | $\alpha_{c2}$ |
|---|---|---|---|
| *1* | 110 | 0.025 | 0.50 |
| *2* | 130 | 0.035 | 0.58 |
| *3* | 150 | 0.045 | 0.64 |

A scheme[40] of structural evolution in the course of curing of reactive oligomers in different stages of the process in the post-gel state is shown in Fig. 13. According to the scheme, the reaction volume gradually decreases due to an increase in the grain volume as follows

$$V = \frac{1-\alpha}{\alpha_{lim}},$$

where $\alpha_{lim}$ is the limiting conversion. In the course of reaction the grain surface area $S$ increases. Assuming a constant number of grains $N$, one has

$$S = (4\pi N)^{1/3}\left(\frac{3\alpha}{\alpha_{lim}}\right)^{2/3}.$$

‡ This relates the kinetics of three-dimensional radical polymerisation to the crystal growth kinetics; the Avrami equation was derived to describe the latter case.

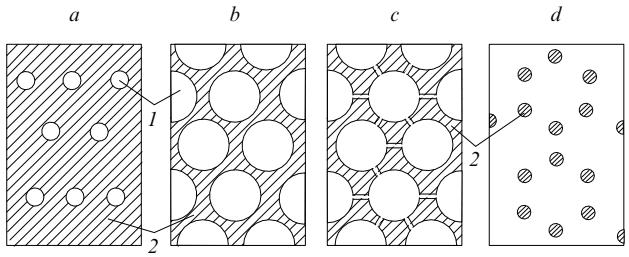



**Figure 13.** Evolution of the structure of reactive oligomers in different stages of curing in the post-gel state.[40]
Nucleation (*a*), grain growth (*b*), cross-linking (*c*), phase inversion (*d*); polymer grains (*1*) and intergrain space (*2*).

As the grain surface area increases, the rate of the reaction in the near-surface layer should increase, because the rate is proportional to the grain surface area. The integral reaction rate is determined by the contributions of the rates of the reactions occurring in the intergrain space ($W_1$) and in the near-surface regions ($W_2$),

$$W = W_1\left(L - \frac{\alpha}{\alpha_{\lim}}\right) + W_2(4\pi N)^{1/3}L\left(\frac{3\alpha}{\alpha_{\lim}}\right)^{2/3},$$

where $L$ is the thickness of the near-surface layer.

Since the rates $W_1$ and $W_2$ increase, the overall polymerisation rate also increases, *i.e.*, even after virtual completion of polymer network formation in grains the curing develops as a self-accelerating process.

However, grain growth leads to the appearance of intergrain contacts and coagulation. As a natural consequence, the polymer grain surface area accessible to free oligomer decreases. The $W_2$ value decreases. The character of the changes in $W_1$ depends on many factors. In particular, for radical polymerisation the reaction rate in the intergrain space at $\alpha > \alpha_{c2}$ first of all depends on the mobility of radicals, which in turn depends on the chemical nature of oligomeric blocks responsible for flexibility of the radicals, on the oligomer functionality, on plasticisers, *etc*. Generally, the contribution of the decrease in $W_2$ to the integral polymerisation rate predominates over the contribution of the changes in $W_1$; therefore, the parameter $W$ decreases and self-accelerating curing turns into a self-retarding process.

The parameter $\alpha_{c2}$ is related to the limiting degree of polymerisation as follows:

$$\alpha_{c2} = \gamma\alpha_{\lim},$$

where $\gamma$ is the grain volume fraction at the start of coagulation. The $\gamma$ estimate obtained assuming spherical grains of the same size is 0.65.[40] The final expression for the polymerisation rate has the form

$$W = W_2(4\pi N)^{1/3}L\left(1 - \frac{\alpha}{\alpha_{\lim}}\right)^{2/3}.$$

The results obtained with allowance for the volume-to-surface-area ratio for spherical particles and for the change in the particle radius $r$ in the course of polymerisation are as follows.

Assume that the sites of a cubic lattice (lattice constant is $2r_0$) are occupied by spherical grains. At $r < r_0$, they grow independently from one another; the conversion and the rate of chain propagation being proportional to the volume and the surface area of spheres, respectively. If

$$x = \frac{r}{r_0} > 1,$$

the volume $V$ and the surface area $S$ grow only towards 'free' space, *i.e.*, the volume and surface area of hypothetical spheres decrease respectively by

$$\Delta V = \pi h^2\left(r - \frac{h}{3}\right),$$

and

$$\Delta S = 2\pi rh,$$

where $h = r - r_0$ is the height of a spherical segment.

At $x < 1$ (assuming $\alpha_{\lim} = 1$), one gets

$$\alpha = \frac{\pi}{6}x^3, \quad W = x^2.$$

At $1 \leqslant x \leqslant 1.5$, one gets

$$\alpha = \frac{\pi}{12}\left(-3 + 9x^2 - 4x^3\right), \quad W = x(3 - 2x).$$

The $W(\alpha)$ plot shown in Fig. 14 is in agreement with the experimental data.[40]

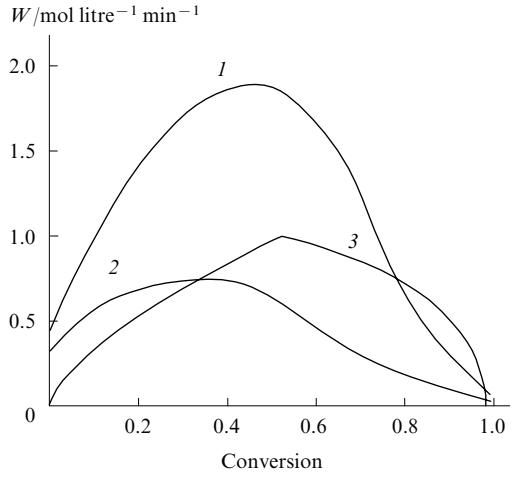



**Figure 14.** Kinetic curves for radical polymerisation of diethylene glycol dimethacrylate (*1*) and butanediol dimethacrylate (*2*)[40] and results of calculations (*3* in arb. units).

Clearly, the polymerisation rate depends on the mobility of the reacting components, which in turn depends on the oligomer functionality, flexibility of oligomeric blocks, presence of plasticiser in the reaction volume (it enhances the rotational and translational mobilities of the interacting molecules). This is of particular importance and should be taken into account when analysing the curing in the intergrain space.

Numerous experimental kinetic curves for curing of oligoester acrylates with different length and flexibility of oligomeric blocks were reported in a monograph.[40] Analysis of these curves showed that the longer the block and the larger the number of swinging atoms in the block the more flexible the

block and the higher the oligomer reactivity in late stages of curing. This manifests itself, in particular, in an increase in the integral values $\alpha_{c2}$ and $\alpha_{lim}$ with elongation of the oligomer block in various homologous series of oligoester acrylates.

EPR studies [41, 160, 161] of polymerisation of oligoester acrylates revealed inhomogeneity of the intergrain space. It consists of several microscopic volume elements where the process occurs locally. The structures thus formed are characterised by different degrees of cross-linking, cyclisation and connectivity of cross-link points. Correspondingly, each microscopic volume element owing to different mobility of elements of its own structure is characterised by a local glass transition temperature $T_{gi}$. 'Freezing' of mobility due to glass transition is yet another important factor determining the polymerisation kinetics in deep stages of the process and the final structure and, therefore, the properties of the polymer networks.

The properties of styrene – trioxyethylene glycol dimethacrylate copolymers (1 : 1 molar ratio) prepared by conventional procedure and by 'living' polymerisation (initiators: benzoyl peroxide, 0.03 mol litre$^{-1}$ and 2,2,6,6-tetramethylpiperidin-1-oxyl, 0.036 mol litre$^{-1}$) were compared.[162] The polymers prepared by 'living' copolymerisation were characterised by much smaller grain size.

To understand the reasons for this fact, it is appropriate to consider the key features of the mechanism of radical 'living' polymerisation.[163 – 167]

Usually, the process is conducted in the presence of a reactant that can reversibly interact with radicals in such a manner that the steady-state concentration of radicals decreases by several orders of magnitude. As a consequence, the rate of quadratic chain termination becomes negligible.

According to calculations [164] (Fig. 15), the most part of the initiator manages to react during the time interval that is insufficiently long for conversion to reach one hundredth of a per cent. Correspondingly, the concentration of radicals (mainly 'dormant' ones) almost equals the initial concentration of the initiator (0.04 mol litre$^{-1}$ according to Ref. 167). For this low conversion, the chain is a few repeating units long. According to Korolev's estimate for conventional polymerisation,[7] the concentration of chains is $10^{-5}$ – $10^{-7}$ mol litre$^{-1}$ at a polymerisation degree of the order of $10^3$ – $10^4$ units. In addition, since the kinetics of 'living' polymerisation is not determined by quadratic chain termination, the gel effect is not observed.[140, 168] It is this distinction between the two regimes

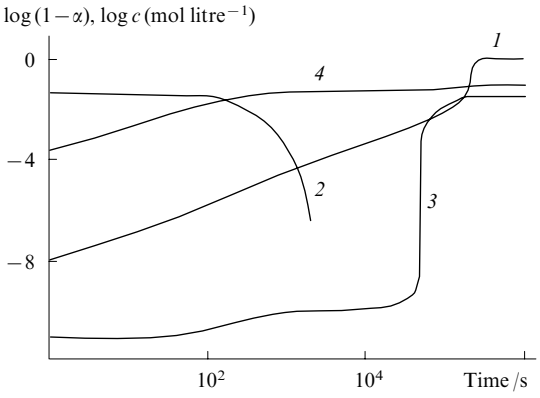



**Figure 15.** Changes in the component concentrations in the course of 'living' radical polymerisation.[164]
Conversion (*1*), initiator (*2*), active radicals (*3*) and 'dormant' radicals (*4*).

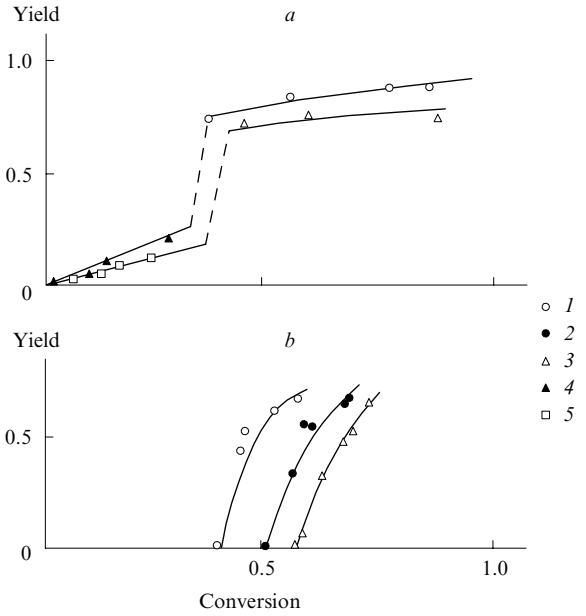



**Figure 16.** Yield of gel fraction in the case of conventional (*a*) and 'living' (*b*) copolymerisation of styrene with 4,4′-divinyldiphenyl.[141]
Concentration of 4,4′-divinyldiphenyl, mole fraction: 0.01 (*1*); 0.016 (*2*); 0.02 (*3*); microgel (*4*,*5*).

that is responsible for different pattern of formation of the polymer structures (Fig. 16). At the same time from the data listed in Table 4 it follows that cyclisation does occur, that is, the calculated critical conversion is lower than the experimentally determined one; the lower the concentration of the bifunctional co-monomer the larger the difference.

**Table 4**. Experimental and calculated $\alpha_c$ values for 'living' copolymerisation of styrene with divinylbenzene.[141]

| Initiator concentration [a] /mmol litre$^{-1}$ | Divinylbenzene concentration (mole fraction) | $\alpha_c$ | |
|---|---|---|---|
| | | experiment | calculations |
| 34 | 0.005 | 0.90 | 0.58 |
| | 0.0075 | 0.80 | 0.47 |
| | 0.009 | 0.65 | 0.43 |
| | 0.01 | 0.55 | 0.41 |
| | 0.015 | 0.48 | 0.33 |
| | 0.02 | 0.42 | 0.29 |
| | 0.025 | 0.375 | 0.26 |
| | 0.03 | 0.325 | 0.22 |
| | 0.04 | 0.26 | 0.20 |
| 23 | 0.01 | 0.41 | 0.34 |
| | 0.015 | 0.35 | 0.27 |
| 9.9 | 0.01 | 0.26 | 0.22 |
| | 0.015 | 0.23 | 0.18 |
| 6.1 | 0.01 | 0.175 | 0.17 |
| | 0.015 | 0.16 | 0.14 |

[a] PS-TMOPO, an adduct of low-molecular-mass polystyrene with a stable radical 2,2,6,6-tetramethylpiperidyl-1-oxyl.

Cyclisation in the case of ionic polymerisation is also possible.[169, 170] A study [171] of polymerisation of diglycidyl diphenylolpropane ether in the presence of dimethylbenzylamine (0.25 mol litre$^{-1}$) revealed a noticeable shift of the

experimentally determined gel point from the calculated value (Table 5). It is noteworthy that, first, the experimentally determined and calculated critical conversions differ by a factor of four to nine rather than a few orders of magnitude, as in the case of radical polymerisation and, second, the calculated values are reasonably large. This is due to intense chain termination. Therefore, the number-average degree of polymerisation in the initial stage of three-dimensional polymerisation [171] and in the case of linear analogue (phenylglycidyl ester) [172] is at most ten repeating units.

**Table 5**. Experimental and calculated $\alpha_c$ values for polymerisation of diglycidyl diphenylolpropane ether in the presence of dimethylbenzylamine.[171]

| $T$/°C | $\alpha_c$ | |
|---|---|---|
| | experiment | calculations |
| 40 | 0.38 | 0.10 |
| 50 | 0.43 | 0.09 |
| 60 | 0.47 | 0.09 |
| 70 | 0.61 | 0.07 |

A scheme of polymerisation is presented below:

appearance of active centre owing to protonation of catalyst A

$$A + H \rightleftharpoons R,$$

initiation

$$R_0 + M \longrightarrow R_1,$$

chain propagation

$$R_i + M \longrightarrow R_{i+1},$$

chain termination

$$R_i \longrightarrow P_i + A + H.$$

Despite a common pattern of the initial phase of polymerisation (cyclisation reaction), radical polymerisation and ionic polymerisation develop in different fashions. The kinetics of anionic polymerisation of diglycidyl diphenylolpropane ether in the presence of dimethylbenzylamine is satisfactorily described by the reaction scheme shown above up to the retardation stage caused the glass transition of the system (Fig. 17).[171] In this case cyclisation does not result in the formation of highly cross-linked microgel particles (no gel effect). The authors of a dielectric spectroscopy study [173] concluded that the reaction involves the stage of microgel formation. However, the onset of dipole conduction detected in that work is most probably due to the formation of a polyester (polymer with dipoles aligned to the backbone or, according to Stockmayer,[174] type A polymer with respect to dielectric properties) as final product of polymerisation.

Thus, the data listed above confirm that the gel effect is a necessary condition for the microgel mechanism of three-dimensional polymerisation. As to ionic polymerisation, the formation of microgel is only possible in highly dilute solutions (see Fig. 6).

Indeed, cyclisation is rather intense in the case of polymerisation of diallyl oligomers. However, no microgel formation in these processes was observed in the absence of the gel effect.[175, 176] Similar results were obtained in a study [177] of block polymerisation of neopentyl glycol dimethacrylate in the presence of large amount (up to 20%) of laurylmercaptan

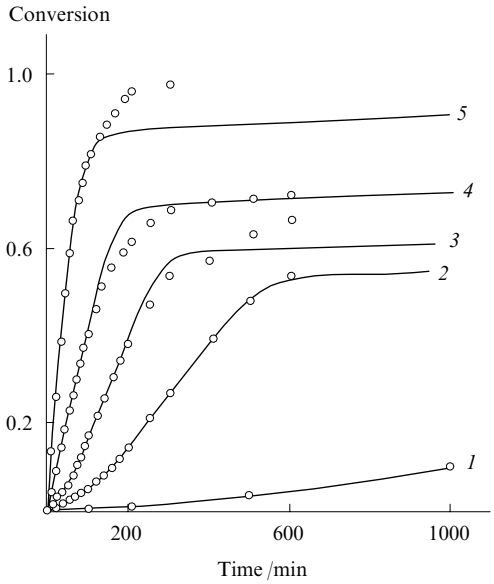



**Figure 17.** Kinetic curves for polymerisation of diglycidyl diphenylolpropane ether.[171]
Open circles denote the results of calculations and solid curves denote experimental data. $T$/°C: 20 (*1*), 40 (*2*), 50 (*3*), 70 (*4*) and 100 (*5*); with dimethylbenzylamine (0.25 mol litre$^{-1}$) as catalyst.

(chain transfer agent). The experimental and calculated values of the critical conversion differed by an order of magnitude, but owing to the low molecular mass ($\overline{P}_w$ varied from 47 to 142) the gel effect was not observed and no microgel formation was detected. A study [178] of copolymerisation of allyl methacrylate with alkyl methacrylates (methyl, butyl, lauryl and steryl methacrylate; 50 : 50 ratio) accompanied by intense intramolecular cross-linking (experimentally measured critical conversions exceeds the calculated values by two orders of magnitude) also revealed no gel effect and, correspondingly, no microgel formation.

The microgel character of the process in the absence of gel effect was found in studies of catalytic copolymerisation of octamethylcyclotetrasiloxane and 2,2′,4,4′,6,6′-hexamethyl-8,8′,10,10′-tetraphenylspiro(7,5)hexasiloxane.[179] However, in this case the phenomenon has another nature. Indeed, it was established that consumption of cyclosiloxane in the presence of spirosiloxane shows an induction period and that the higher the spirosiloxane concentration the longer the induction period. During the induction period the spirosiloxane is consumed almost completely and forms highly cross-linked particles owing to low concentration (1 mol % – 5 mol %). Then cyclosiloxane enters the reaction. Thus, the reason why the process proceeds by the microgel mechanism consists in dramatic difference between the copolymerisation constants.

## V. Gelation kinetics under polycondensation conditions

Unlike addition polymerisation, chain growth in polycondensation occurs gradually, being accompanied by a decrease in the chain concentration; this creates unfavourable conditions for cyclisation in the early stages of the process. However, at sufficiently high conversions gelation does occur and therefore the possibility of intrachain cross-linking in the pre-gel state is topical.[11, 122]

A trivial reason for the shift of the gel point towards higher conversions consists in deviation of the oligomer functionality from theoretical value,[5] because the critical conditions are determined by the weight-average functionality.

First, the purity of reactants used is usually less than 100%. For instance, a fraction of bifunctional epoxy oligomer molecules contain terminal hydroxyl groups (Tables 6 and 7). As can be seen, an increase in the molecular mass causes not only broadening of the MMD of the oligomers, but also a decrease in functionality with respect to epoxy groups and an increase in the proportion of hydroxyl-terminated branched molecules.

**Table 6**. Characteristics of selected epoxy oligomers.[5]

| Oligomer | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | Epoxy groups | | Hydroxy groups | |
|---|---|---|---|---|---|---|
| | | | $\bar{f}_n$ (see [a]) | number of groups | $\bar{f}_n$ (see [a]) | number of groups |
| DER-322 | 340 | 1.00 | 1.96 | 1–2 | 0.03 | 0–2 |
| ED-22 | 380 | 1.05 | 1.92 | 1–2 | 0.25 | 0–3 |
| EPO-128 | 380 | 1.05 | 1.96 | 0–2 | 0.27 | 0–3 |
| ED-20 | 410 | 1.08 | 1.92 | 0–2 | 0.36 | 0–4 |
| ED-5 | 410 | 1.09 | 1.85 | 0–2 | 0.65 | 0–5 |
| ED-16 | 600 | 1.25 | 1.90 | 0–2 | 1.02 | 0–6 |
| ED-8 | 1000 | 1.33 | 1.90 | 0–2 | 1.20 | 0–10 |

[a] Number-averaged functionality.

**Table 7**. Fractional composition of selected epoxy oligomers.[180]

| Oligomer | $\bar{M}_n$ | Mass percentage of fractions with $n$ [a] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 1 | 2–3 | 4 | 4–6 | 7–10 | 11 |
| DER-322 | 340 | 1.000 | < 0.01 | – | – | – | – | – |
| ED-24 | 380 | 0.914 | 0.076 | – | – | – | – | – |
| ED-16 | 472 | 0.492 | 0.300 | 0.179 | 0.029 | – | – | – |
| ED-8 | 877 | 0.151 | 0.160 | 0.295 | – | 0.192 | 0.138 | 0.064 |

[a] General formula

$$H_2C\!-\!CHCH_2O[A_n][C_6H_4CMe_2]C_6H_4OCH_2CH\!-\!CH_2,$$

(the epoxy rings are at the two terminal positions)

A = $[C_6H_4CMe_2C_6H_4OCH_2CH(OH)CH_2O]$.

Second, the equivalent ratio of functional groups may change during the preparation of reaction mixtures.

The critical conversion also depends on the reactivity of functional groups including the substitution effect. Note that reactions with substitution effect can fundamentally change their kinetic type. For instance, polycondensation for a number of aromatic polyamides, polyesters and polyethers with the substitution effect can occur as a polymerisation process in which the growing terminal functional group becomes the most reactive owing to the resonance or inductive effect of other groups.[181] This can also be achieved by selective transfer of catalyst to the terminal functional group and by controlled monomer transfer from the solid to liquid phase in which the reaction occurs.[181]

Taking the urethane formation reaction as an example, it was shown [182, 183] that $\alpha_c$ depends on the temperature and concentration of catalyst (parameters that immediately affect the system of donor-acceptor equilibria and the rate constants). As the concentration, $c_{cat}$, of the catalyst (tin dibutyllaurate) increases, the critical conversion decreases and reaches a calculated value of $\alpha_c = 0.92$ at $c_{cat} \approx 3 \times 10^{-4}$ mol litre$^{-1}$ assuming equal reactivities of functional groups (Table 8). Noteworthy is that no gelation occurs in the absence of catalyst.

**Table 8**. Dependence of gelation conditions on catalyst concentration at 60 °C.[183]

| $10^4\, c_{cat}$ /mol litre$^{-1}$ | $\alpha_c$ | Gel yield |
|---|---|---|
| 0 | – | 0 |
| 0.34 | 0.97 | 0.52 |
| 0.56 | 0.95 | 0.68 |
| 0.72 | 0.94 | 0.79 |
| 1.13 | 0.93 | 0.81 |
| 2.61 | 0.92 | 0.85 |

The shift of $\alpha_c$ towards higher conversions can be due to an increase in the $k_2/k_1$ ratio at different initial reactivities of functional groups (Fig. 18) or negative substitution effect (Fig. 19).

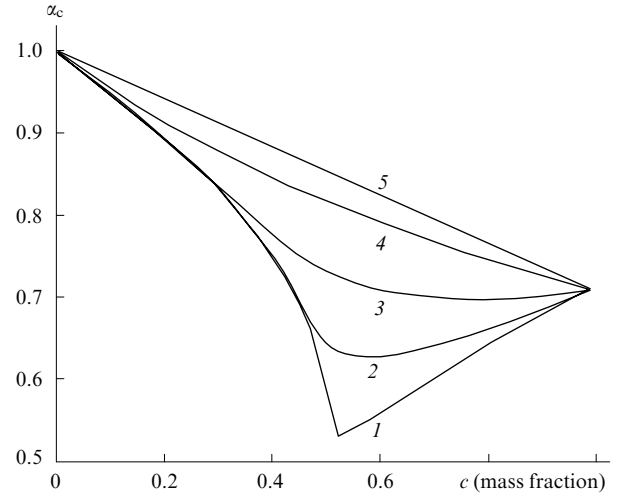



**Figure 18.** Gel point magnitude *vs.* concentration of trifunctional agent for stepwise polymerisation $A_2 + A_3 + B$ at different rate constants. $k_2/k_1 = 0.01$ (*1*), 0.1 (*2*), 0.3 (*3*), 1 (*4*), 10 (*5*).

In the former case the reaction scheme is as follows:

$$A_3 + B \xrightarrow{k_1} A_3B,$$
$$A_2 + B \xrightarrow{k_2} A_2B,$$

where $A_3$ is triol, $A_2$ is oligodiol and B is diisocyanate.

In the second case one has

$$A_3 + B \xrightarrow{k_1} A_3B,$$
$$A_3B + B \xrightarrow{k_2} A_3B_2,$$
$$A_3B_2 + B \xrightarrow{k_2} A_3B_3,$$
$$A_2 + B \xrightarrow{k_1} A_2B.$$

If the catalyst affects the system of donor-acceptor equilibria and(or) the rate constants, one should expect that

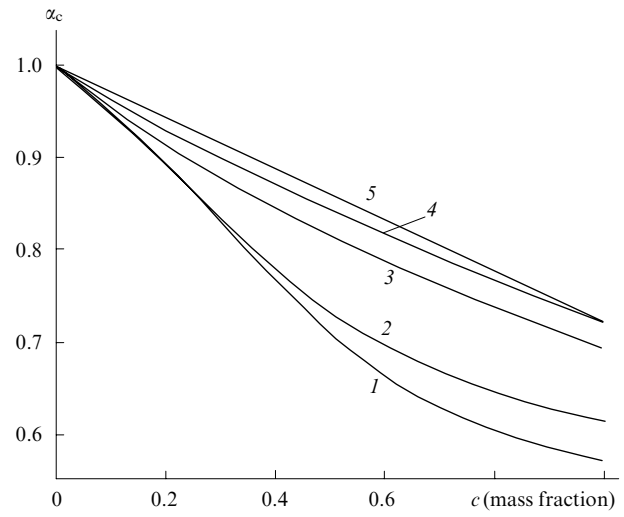



**Figure 19.** Gel point magnitude *vs.* concentration of trifunctional agent for stepwise polymerisation $A_2 + A_3 + B$ at negative substitution effect. $k_2/k_1 = 10$ (*1*), 5 (2), 1 (*3*), 0.5 (*4*), 0.1 (*5*).

temperature variations will have a similar effect. Indeed, the temperature dependence of $\alpha_c$ ($c_{cat} = 2.6 \times 10^{-4}$ mol litre$^{-1}$) is as follows:[183]

| $T$/°C | 30 | 40 | 50 | 60 | 70 | 80 |
|---|---|---|---|---|---|---|
| $\alpha_c$ | – | 0.95 | 0.93 | 0.92 | 0.91 | 0.90 |

As temperature decreases, the gel point shifts to the right on the conversion axis; otherwise, it shifts to the left, *i.e.*, gelation occurs at a lower conversion compared to the theoretical predictions made assuming equal reactivities of hydroxyl groups.

Thus, the effect observed seems to be quite understandable from the kinetic standpoint. The data on the shift of the gel point in polycondensation of epoxy oligomers can be interpreted in similar fashion. Namely, in curing of amines the substitution effect (ratio of the rate constants for the reactions of the secondary and primary amino groups, $k_2/k_1$, varies from 0.42 to 0.7, whereas for the shift $\Delta\alpha_c$ one has $\Delta\alpha_c \approx 0.1-0.2$; see Ref. 184).

Usually, gel point calculations are carried out using the probabilistic approach [11] that dates back to Flory.[95] Kuchanov [85] was the first who pointed that this approach gives incorrect results when the substitution effect is included. There is also a universal computational method based on the bond block concept.[15, 185–192] The key features of this approach are as follows.

A bond block is a relatively small fragment of the entire topological structure of a given polymer. It is represented by a connected graph $G$ whose edges and vertices correspond to chemical bonds and units connected by these bonds.[12] A complete set of concentrations of all blocks $y(G)$ unambiguously characterises the composition and topological structure of the polymeric system. In this sense the parameter $y(G)$ is similar to the MMD of a linear polymer. It should be emphasised that the bonds formed in the course of polymer network formation are also taken into account. Correspondingly, the reacting polyfunctional oligomers play the role of cross-link points and bifunctional oligomers act as network chains. Owing to combination of the kinetic and probabilistic methods the approach based on the bond block concept offers the possibility of exact solution to the problem of polycondensation kinetics with the substitution effect (including structural analysis of polymer networks).

The kinetic equations describing the formation of bond blocks can be divided into closed groups, each corresponding to relatively small blocks. Because the systems are small, direct solution of differential equations is straightforward even with the substitution effect. Larger blocks and corresponding chains are assembled from smaller fragments obtained by the kinetic method using probabilistic calculations. This is possible if the reactions responsible for assembling occur with no substitution effect.

Let us illustrate this approach using a model example of the reaction of a bifunctional epoxy oligomer with a diamine. Following a known algorithm,[186, 191, 192] it is assumed that diamine units form cross-link points of the polymer network while the epoxy oligomer forms chain fragments connecting the cross-link points. The reaction of primary amino groups with epoxy groups results in secondary amino groups. But the reactivities of these amines are different.[184] The polymer network structure is determined by the concentration of cross-link points of different functionality $A_i$, where $i$ is the functionality. It is these structural elements that represent the bond blocks whose concentrations should in this case be calculated by solving the corresponding kinetic equations. The functionality of a cross-link point is characterised by the number of oligomeric fragments added to it; the relative concentration of cross-link points $a_i = A_i/A_0$ ($A_0$ is the initial concentration of amine) changes during the reaction. Since the reactivity of epoxy groups is assumed to be constant in the course of reaction, the structure of the polymer network can be calculated using the probabilistic approach and the cross-link point concentrations determined from kinetic calculations.

The critical conversion with respect to epoxy groups is defined [191, 192] as solution to the equation

$$\alpha \sum_i (i-1) n_{Ai} = 1, \qquad (8)$$

where $n_{Ai} = iA_i / \sum_i iA_i$ is the fraction of cross-link points $A_i$.

Formally, Eqn (8) has the same form as the critical condition in the case of $f$-functional polycondensation

$$\alpha_c(\bar{f}_w - 1) = 1$$

but the difference consists in that the weight-average functionality

$$\bar{f}_w = \sum_i i n_i$$

changes in the course of the process, being a function of conversion rather than the characteristic of the initial system.

The curves in Figs 18 and 19 were plotted using the approach considered above.

Numerous data indicating a shift of the gel point towards low conversions were reported by Andrianov and Emel'yanov,[122, 193] who studied polycondensation of tetrafunctional oligomeric ester acids with various alcohols and diamines (Table 9).

It is noteworthy that the smaller the molecular masses of the reactants the larger the shift of the gel point. At the same time most oligomers have symmetric structures and functional groups are sufficiently distant from one another; this excludes the possibility of a reaction or substitution effect. Thus, the

**Table 9**. Dependence of gelation conditions on the nature of reactants.[193]

| Reactants | $\alpha_c$ (calculations) | Reaction | $\alpha_c$ |
|---|---|---|---|
| $A_4 + B_2$ | 0.575 | I + $HO(CH_2)_2OH$ | 0.20 |
| | | I + $HO(CH_2)_4OH$ | 0.25 |
| | | I + $HO(CH_2CH_2O)_2OH$ | 0.27 |
| | | I + $HO(CH_2CH_2O)_3OH$ | 0.33 |
| | | I + $HO(CH_2CH_2O)_7OH$ | 0.35 |
| | | I + $HO(CH_2CH_2O)_xOH$ [a] | 0.44 |
| | | I + $HO(CH_2CH_2O)_xOH$ [b] | 0.54 |
| $A_4 + B_2$ | 0.575 | $C[CH_2OC(O)(CH_2)_2COOH]_4$ + II | 0.21 |
| | | $C[CH_2OC(O)(CH_2)_4COOH]_4$ + II | 0.40 |
| | | $C[CH_2OC(O)(CH_2)_8COOH]_4$ + II | 0.46 |
| | | $C[CH_2OC(O)(CH_2)_4COOH]_4$ + III | 0.40 |
| | | $C[CH_2OC(O)(CH_2)_8COOH]_4$ + III | 0.45 |
| $A_4 + B_3$ | 0.414 | $C[CH_2OC(O)(CH_2)_2COOH]_4$ + IV | 0.35 |
| | | $C[CH_2OC(O)(CH_2)_4COOH]_4$ + IV | 0.36 |
| | | $C[CH_2OC(O)(CH_2)_8COOH]_4$ + IV | 0.40 |
| | | $C[CH_2OC(O)(CH_2)_4COOH]_4$ + V | 0.21 |
| | | $C[CH_2OC(O)(CH_2)_8COOH]_4$ + V | 0.39 |
| $A_4 + B_4$ | 0.333 | $C[CH_2OC(O)(CH_2)_2COOH]_4$ + VI | 0.20 |
| | | $C[CH_2OC(O)(CH_2)_4COOH]_4$ + VI | 0.23 |
| | | $C[CH_2OC(O)(CH_2)_8COOH]_4$ + VI | 0.24 |

**Notations:** I is $C[CH_2OC(O)(CH_2)_4COOH]_4$, II is $O[SiMe_2CH_2OCH_2.CH_2OH]_2$, III is $O[SiMe_2CH_2NHPh]_2$, IV is $PhSi[OSiMe_2CH_2OCH_2.CH_2OH]_3$, V is $EtSi[OSiMe_2CH_2OCH_2CH_2OH]_3$, VI — $Si[OSiMe_2.CH_2OCH_2CH_2OH]_4$. [a] Molecular mass 600. [b] Molecular mass 1000.

observed behaviour seems to have a structural rather than kinetic nature.

As mentioned above, aggregates formed as a result of strong intermolecular interaction including those formed in epoxy oligomers do exist. The structural characteristics of a number of epoxy oligomers are listed in Table 10.

Similarly to the urethane formation reaction, the reactions of epoxy groups lead to formation of other (*e.g.*, hydroxyl) groups that assist strengthening of intermolecular interactions; as a result, a glass transition of the system can occur. Polymer coils and aggregates in the starting system are similar in size (see Table 10), which indicates their 'genetic' relation.

In his monograph Khozin reported [42] the dependences of the aggregate size and density of epoxy oligomer ED-20 on the sonication duration.

| Treatment duration /min | 0 | 15 | 30 | 45 | 60 |
|---|---|---|---|---|---|
| Aggregate size /μm | 0.05 | 0.15 | 0.98 | 0.62 | 0.01 |
| Density /kg $m^{-3}$ | 1163.1 | 1165.3 | 1169.9 | 1166.7 | 1162.8 |

Vibroacoustic treatment causes rearrangement of the aggregate structure in liquid oligomer. The pattern of structural changes is complicated. Initially, the effective aggregate size and density of molecular packing increase but then decrease upon attainment of a particular intensity of vibroacoustic treatment. The extremal character of the dependence was logically explained by structural ordering in the early stage (formation of regular aggregates is facilitated) and subsequent disintegration of aggregates and structural disordering under the action of excess energy upon attainment of a certain energy limit, which depends on the chemical structure, molecular mass of oligomer and the treatment temperature.

Comparison of these data obtained for the starting systems with the characteristics of the cured polymers reveals an excellent correlation, that is, the aggregate size and density of the starting systems change in parallel with the glass transition temperature, formation of sol fraction, compression strength and flexural strength of polyepoxides. Although this is an indirect proof, this is a strong argument in favour of fixation of ordered structural fragments formed in the liquid system under polycondensation conditions.

At the same time numerous data give reasonable doubt of the determining role of microgel mechanism under polycondensation conditions. Indeed, in most cases the kinetics of both urethane formation reaction [44, 182, 183] and polycondensation of epoxy oligomers [51, 52, 194–197] in the whole range of conversions obey the laws that follow from chemical considerations. Moreover, direct measurements of the content of polycondensation products of diglycidyl diphenylolpropane ether and 4,4′-diamino-3,3′-dichlorodiphenylmethane by gel permeation chromatography showed [50] that the changes in their concentrations are described by statistical laws up to the gel point (Fig. 20). Analysis of the kinetics of urethane formation using the Avrami equation [44, 45] showed that in all cases the exponent is almost equal to unity, *i.e.*, the microheterogeneous mechanism can be ruled out.

In this connection the method of kinetic analysis in terms of the Avrami equation deserves attention. It was proved [198] that for any self-accelerating process described in the coordinates of the Avrami equation the exponent will be greater than unity. Radical polymerisation is often accompanied by self-acceleration due to the gel effect; therefore, the fact that $d > 1$ does not necessarily indicate a microheterogeneous character of the process.

Dynamic light scattering [199] and broadband dielectric spectroscopy [200–203] studies revealed that curing of epoxy oligomers with amines is accompanied by formation of clusters that are similar to the theoretically predicted dynamic heterogeneous structures [204–207] observed in supercooled liquids (see Refs 208–211). Thus, there are no grounds to believe that 'microheterogeneity' in the case of radical polymerisation and in polycondensation has the same sense.

A glass transition of the system is a natural reason for the chemical reaction to cease. Figure 21 presents the relaxation state diagram (*TTT*-diagram, Temperature, Time of Reaction, Time of Relaxation) proposed by Gillham [212] and modified in more recent studies [195, 213] where the need of allowance for the

**Table 10**. Structural characteristics of epoxy oligomers obtained by light scattering (LS) and electron microscopy (EM).[42]

| Oligomer | Mean size of associate /nm | | Volume fraction of associates | | Number of molecules in associate | Mean size of globules /nm | Volume fraction of globules |
|---|---|---|---|---|---|---|---|
| | LS | EM | LS | EM | | | |
| ED-20 | 10 | 20 | 0.1 | 0.09 | $7.3 \times 10^3$ | 20 | 0.45 |
| ED-16 | 10 | – | 0.25 | – | $5.8 \times 10^3$ | – | – |
| ED-8 | – | 150 | – | 0.1 | $1.3 \times 10^6$ | 90 | 0.12 |
| ED-49 | – | 120 | – | 0.32 | $2.3 \times 10^5$ | 90 | 0.2 |

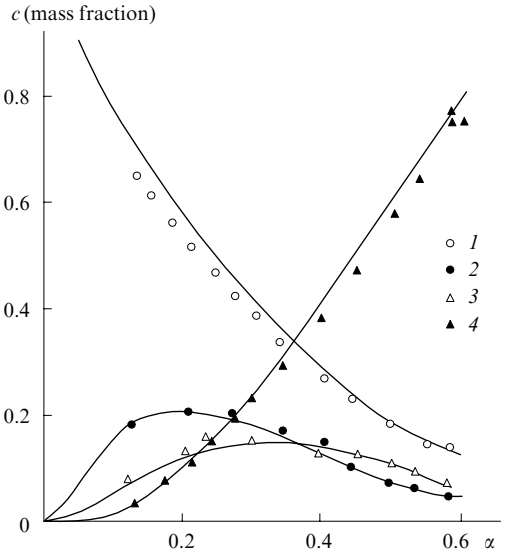



**Figure 20.** Changes in component concentrations in the course of curing of diglycidyl diphenylolpropane ether (E) with 4,4′-diamino-3,3′-dichlorodiphenylmethane (A).[50]
Points denote experimental data and solid curves denote the results of calculations. The components: E + A (*1*), EA (*2*), $E_2A + EA_2$ (*3*), $\sum_{i,j} E_i A_j$, $i + j > 3$ (*4*).

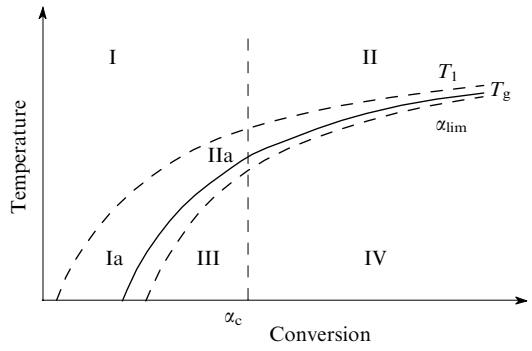



**Figure 21.** Relaxation state diagram.
Low-molecular-mass liquid (regions I + Ia), elastic network (regions II + IIa), low-molecular-mass glass (III) and glassy network (IV). The $T_g$ curve confiines the glassy state region. The $T_1$ curve confines the existence region (Ia and IIa) of a labile network of physical bonds; $\alpha_{lim}$ denotes the limiting conversion curve.

labile network of physical bonds (curve $T_1$, regions Ia and IIa) was pointed.

The glass transition temperature ($T_g$ curve) increases with conversion and, if the curing temperature is below the limiting value of $T_g$, conversion is limited to $\alpha_{lim}$. It is noteworthy that the $\alpha_{lim}$ value is somewhat higher than the conversion corresponding to the glass transition temperature.[214–216] There are two possible reasons. First, the glass transition is a relaxation process;[208] the reaction rate decreases as the system goes throughout the glass transition. Second, the glass transition temperature is an averaged characteristic; real systems are characterised by more or less broad distributions over structural fragments and, correspondingly, over local $T_g$ values. An additional conversion can be attained due to occurrence of the reaction in the regions characterised by lower $T_g$, where the reactant mobilities remain sufficiently high. In principle, the aforesaid can be applied not only to stepwise, but also addition polymerisation; the difference is that in the latter case one should consider the local rather than overall conversion.

## VI. Conclusion

The fundamentals of the kinetics of formation of network polymers from reactive oligomers were laid more than three decades ago. Soviet researchers including Andrianov, Baturin, Al Berlin, A Berlin, Enikolopov, Korolev, Kuchanov, Lipatov, Lipatova, Rosenberg, Khozin, Entelis and other contributed largely to the development in this field and since then research has been incessant. Although the state of the art in chemical physics of oligomeric systems is, unfortunately, far from being suitable for making reliable, highly predictive quantitative calculations of all relationships between the molecular, supramolecular, topological and phase structures of oligomers and various dynamic and static characteristics in the uncured and cured states, a number of approaches were proposed to formulation of the problems that are, according to Lipatov, 'still unsolved and still not being solved'.[217]

One of these approaches involves investigations of the supramolecular structure of oligomeric liquids and their effect on the kinetics of formation and on the structure of polymer networks. Despite some advances in the field (we dwelled on them in this review) no direct proofs of the kinetic role of oligomeric aggregates have been reported so far. In addition, versatility of microheterogeneous character of polymer network formation is still debatable. We believe that we succeeded in revealing the reactions and systems in which these processes are possible and impossible.

A number of problems related to design of composite materials[218] were solved using the assumptions that liquid oligomeric systems consist of isotropic and anisotropic aggregates in the medium of 'non-organised' molecules[8–10] and that the supramolecular structure of oligomers can be 'inherited' in the course of curing.[42] Moreover, these assumptions are now used in studies of biologically active oligomeric systems,[219–221] which allows one to hope that the problems in this field will soon change their status from 'still not being solved' to 'still unsolved'.

## References

1. N M Emmanuel', D G Knorre *Kurs Khimicheskoi Kinetiki* (Course of Chemical Kinetics) (Moscow: Vysshaya Shkola, 1984)
2. V V Korshak *Raznozvennost' Polimerov* (Heterounit Structure of Polymers) (Moscow: Nauka, 1977)
3. A A Askadskii, V I Kondrashchenko *Komp'yuternoe Materialovedenie Polimerov* (Computer Materials Science of Polymers) (Moscow: Nauchnyi Mir, 1999)
4. D W Van Krevelen *Properties of Polymers: Correlation with Chemical Structure* (Amsterdam: Elsevier, 1972)
5. S G Entelis, V V Evreinov, A I Kuzaev *Reaktsionnosposobnye Oligomery* (Reactive Oligomers) (Moscow: Khimiya, 1985)
6. A A Berlin *Vysokomol. Soedin., Ser. A* **20** 483 (1978) [a]
7. G V Korolev, M M Mogilevich, I V Golikov *Setchatye Poliakrilaty. Mikrogeterogennye Struktury, Fizicheskie Setki, Deformatsionno-Prochnostnye Svoistva* (Cross-Linked Polyacrylates Microheterogeneous Structures, Physical Networks, Deformation and Mechanical Properties) (Moscow: Nauka, 1995)
8. S M Mezhikovskii, A E Arinshtein, R Ya Deberdeev *Oligomernoe Sostoyanie Veshchestva* (Oligomeric State of Substance) (Moscow: Nauka, 2005)

9. S M Mezhikovskii *Fizikokhimiya Reaktsionnosposobnykh Oligomerov. Termodinamika. Kinetika. Struktura* (Physical Chemistry of Reactive Oligomers. Thermodynamics. Kinetics. Structure) (Moscow: Nauka, 1998)
10. S M Mezhikovskii, in *Materialy III Mezhdunarodnoi Shkoly po Khimii i Fizikokhimii Oligomerov* (Proceedings of the IIIth International School on Chemistry and Physicochemistry of Oligomers) (Moscow: Institute of Chemical Physics, Russian Academy of Sciences, 2007) p. 28
11. V I Irzhak, B A Rozenberg, N S Enikolopyan *Setchatye Polimery. Sintez, Struktura, Svoistva* (Network Polymers. Synthesis, Structure, Properties) (Moscow: Nauka, 1979)
12. O Ore *Theory of Graphs* (Providence, RI: American Mathematical Society, 1963)
13. Yu S Lipatov *Fiziko-Khimicheskie Osnovy Napolneniya Polimerov* (Physicochemical Foundations of Filling of Polymers) (Moscow: Khimiya, 1991)
14. B A Rozenberg, V I Irzhak *Macromol. Symp.* **93** 227 (1995)
15. V I Irzhak *Usp. Khim.* **73** 275 (2004) [*Russ. Chem. Rev.* **73** 251 (2004)]
16. V V Kireev *Vysokomolekulyarnye Soedineniya* (High-Molecular-Mass Compounds) (Moscow: Vysshaya Shkola, 1992)
17. W Carothers *Trans. Faraday Soc.* **32** 44 (1936)
18. M Szwarc *Carbanions, Living Polymers and Electron Transfer Processes* (New York: Wiley, 1968)
19. W G Stewart *Phys. Rev.* **31** 174 (1929)
20. Ya I Frenkel' *Sbornik Nauchnykh Trudov. Kineticheskaya Teoriya Zhidkosti* (Collection of Scientific Works. Kinetic Theory of Liquid) (Moscow; Leningrad: Academy of Sciences of the USSR, 1959) Vol. 3
21. B A Baum *Metallicheskie Zhidkosti* (Metallic Liquids) (Moscow: Nauka, 1979)
22. S M Mezhikovskii *Kinetika i Termodinamika Protsessov Samoorganizatsii v Oligomernykh Smesevykh Sistemakh* (Kinetics and Thermodynamics of Self-Organisation Processes in Oligomeric Blend Systems) (Moscow: Institute of Chemical Physics, Academy of Sciences of the USSR, 1994)
23. A A Berlin, N N Tvorogov, G V Korolev *Dokl. Akad. Nauk SSSR* **170** 1073 (1966) [b]
24. Al Al Berlin, B R Smirnov *Zh. Teor. Eksp. Khim.* **3** 93 (1967) [c]
25. I A Gusakovskaya, Candidate Thesis in Chemical Sciences, Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka, 1969
26. G V Korolev *Mikrogeterogennyi Mekhanizm Trekhmernoi Radikal'no-initsiirovannoi Polimerizatsii* (Microheterogeneous Mechanism of Three-dimensional Radical-initiated Polymerisation) (Chernogolovka: Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, 1986)
27. N N Semenov *Khim. Tekhnol. Polim.* (7–8) 196 (1960)
28. L A Zhil'tsova, S M Mezhikovskii, A E Chalykh *Vysokomol. Soedin., Ser. A* **27** 587 (1985) [a]
29. S M Mezhikovskii, A E Chalykh, L A Zhil'tsova *Vysokomol. Soedin., Ser. B* **28** 53 (1986) [a]
30. G V Korolev, E O Perepelitsina *Dokl. Akad. Nauk* **371** 488 (2000) [b]
31. G V Korolev, A A Il'in, M M Mogilevich, V P Grachev, E O Perepelitsina, E S Evplonova *Vysokomol. Soedin., Ser. A* **45** 883 (2003) [a]
32. G V Korolev, E O Perepelitsina *Vysokomol. Soedin., Ser. A* **39** 338 (1997) [a]
33. E O Perepelitsina, Candidate Thesis in Chemical Sciences, Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 2006
34. G V Korolev, E O Perepelitsina *Vysokomol. Soedin., Ser. A* **43** 774 (2001) [a]
35. A E Arinshtein, S M Mezhikovskii *Khim. Fiz.* **16** 122 (1997) [d]
36. V V Shilov, Yu S Lipatov, in *Fizikokhimiya Mnogokomponentnykh Polimernykh Sistem* (Physical Chemistry of Multicomponent Polymeric Systems) (Kiev: Naukova Dumka, 1986) Vol. 2, p. 25
37. S M Mezhikovskii, Doctoral Thesis in Technical Sciences, Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow, 1983
38. G V Korolev, A A Il'in, M E Solov'ev, M M Mogilevich, E S Evplonova *Vysokomol. Soedin., Ser. A* **43** 1822 (2001) [a]
39. G V Korolev, A A Il'in, M E Solov'ev, A V Srybnyi, M M Mogilevich, E S Evplonova *Vysokomol. Soedin., Ser. A* **44** 1947 (2002) [a]
40. A A Berlin, G V Korolev, T Ya Kefeli, Yu M Sivergin *Akrilovye Oligomery i Materialy na Ikh Osnove* (Acrylic Oligomers and Materials Based on Them) (Moscow: Khimiya, 1983)
41. G V Korolev, M M Mogilevich *Trekhmernaya Radikal'naya Polimerizatsiya. Setchatye i Giperrazvetvlennye Polimery* (Three-dimensional Radical Polymerisation. Cross-Linked and Hyperbranched Polymers) (St Petersburg: Khimiya, 2006)
42. V G Khozin *Usilenie Epoksidnykh Polimerov* (Strengthening of Epoxy Polymers) (Kazan: PIK 'Dom Pechati', 2004)
43. T E Lipatova, in *Doklady I Vsesoyuznoi Konferentsii po Khimii i Fizikokhimii Oligomerov* (Reports of the First All-Union Conference on Chemistry and Physical Chemistry of Oligomers) (Chernogolovka: Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, 1977) Vol. 3, p. 230
44. T E Lipatova *Kataliticheskaya Polimerizatsiya Oligomerov i Formirovanie Polimernykh Setok* (Catalytic Polymerisation of Oligomers and Formation of Polymer Networks) (Kiev: Naukova Dumka, 1974)
45. T E Lipatova *Vysokomol. Soedin., Ser. A* **15** 327 (1973) [a]
46. Yu S Lipatov, T E Lipatova, in *TezisyDokladov V Konferentsii po Khimii i Fizikokhimii Oligomerov* (Abstracts of Reports of the Vth Conference on the Chemistry and Physical Chemistry of Oligomers) (Chernogolovka: Institute of Chemical Physics, Russian Academy of Sciences, 1994) p. 15
47. N S Enikolopov, in *Doklady I Vsesoyuznoi Konferentsii po Khimii i Fizikokhimii Oligomerov* (Reports of the First All-Union Conference on Chemistry and Physical Chemistry of Oligomers) (Chernogolovka: Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, 1977) Vol. 1, p. 87
48. O Mitsukazu, Y Yoshukazu *J. Adhes. Soc. Jpn.* **23** 89 (1987)
49. B A Rozenberg *Problemy Fazoobrazovaniya v Oligomer–Oligomernykh Sistemakh* (The Problems of Phase Formation in Oligomer–Oligomer Systems) (Chernogolovka: Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, 1986)
50. V M Lantsov, M K Pakter, V I Irzhak, L A Abdrakhmanova, L M Kuznetsova, G V Borisenko, Yu S Zaitsev *Vysokomol. Soedin., Ser. A* **29** 2292 (1987) [a]
51. B A Rozenberg *Makromol. Chem., Makromol. Symp.* **41** 165 (1991)
52. V I Irzhak, B A Rozenberg *Vysokomol. Soedin., Ser. A* **27** 1795 (1985) [a]
53. T Ya Kol'tsova, M S Akutin, in *TezisyDdokladov II Konferentsii po Khimii i Fizikokhimii Oligomerov* (Abstracts of Reports of the IInd Conference on the Chemistry and Physical Chemistry of Oligomers) (Chernogolovka: Institute of Chemical Physics, Academy of Sciences of the USSR, 1979) p. 42
54. A A Karimov, V G Khozin, A V Murafa, in *Tezisy Dokladov III Konferentsii po Khimii i Fizikokhimii Oligomerov* (Abstracts of Reports of the IIIrd Conference on the Chemistry and Physical Chemistry of Oligomers) (Chernogolovka: Institute of Chemical Physics, Academy of Sciences of the USSR, 1986) p. 88
55. E V Moskalev, M S Trizno, in *TezisyDokladov III Konferentsii po Khimii i Fizikokhimii Oligomerov* (Abstracts of Reports of the IIIrd Conference on the Chemistry and Physical Chemistry of Oligomers) (Chernogolovka: Institute of Chemical Physics, Academy of Sciences of the USSR, 1986) p. 127
56. S A Lyubartovich, O B Tret'yakov, V I Korotkov, in *Kauchuk-89. Problemy Razvitiya Nauki i Proizvodstva* (Caoutchouc-89. Problems of Development of Science and Industry) (Moscow: TsNIITEneftekhim, 1990) Pt. 1, p. 87
57. V G Khozin *Vibroakusticheskaya Modifikatsiya Epoksidnykh Oligomerov* (Vibroacoustic Modification of Epoxy Oligomers) (Kiev: Naukova Dumka, 1990)
58. V G Khozin, A A Karimov, I N Dement'eva, S Ya Frenkel' *Vysokomol. Soedin., Ser. B* **25** 819 (1983) [a]

59. V G Khozin, A V Murafa, A M Cherevatskii *Mekhan. Kompozit. Mater.* (1) 130 (1987) [e]
60. M A Anisimov *Kriticheskie Yavleniya v Zhidkostyakh i Kristallakh* (Critical Phenomena in Liquids and Crystals) (Moscow: Nauka, 1987)
61. L D Landau, E M Lifshits *Statisticheskaya Fizika* (Statistical Physics) (Moscow: Nauka, 1964)
62. V P Skripov *Metastabil'naya Zhidkost'* (Metastable Liquid) (Moscow: Nauka, 1972)
63. A V Kotova, Candidate Thesis in Chemical Sciences, Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow, 1988
64. A E Arinshtein *Khim. Fiz.* **12** 73 (1993) [d]
65. A E Arinshtein, Doctoral Thesis in Physical and Chemical Sciences, Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 1995
66. O N Karpukhin *Usp. Khim.* **47** 1119 (1978) [*Russ. Chem. Rev.* **47** 587 (1987)]
67. A A Berlin *Vysokomol. Soedin., Ser. A* **12** 2313 (1970) [a]
68. N M Emanuel', A L Buchachenko *Khimicheskaya Fizika Molekulyarnogo Razrusheniya i Stabilizatsii Polimerov* (Chemical Physics of Molecular Destruction and Stabilisation of Polymers) (Moscow: Nauka, 1988)
69. E T Denisov *Kinetika Gomogennykh Khimicheskikh Reaktsii* (Kinetics of Homogeneous Chemical Reactions) (Moscow: Vysshaya Shkola, 1988)
70. Kh S Bagdasar'yan *Teoriya Radikal'noi Polimerizatsii* (Theory of Radical Polymerisation) (Moscow: Nauka, 1966)
71. Al Al Berlin, S A Vol'fson, N S Enikolopyan *Kinetika Polimerizatsionnykh Protsessov* (Kinetics of Polymerisation Processes) (Moscow: Khimiya, 1978)
72. A E Arinshtein, S M Mezhikovskii *Modeli Formirovaniya Nadmolekulyarnoi Struktury Oligomernykh Zhidkostei. Teoriya i Eksperiment* (Models of Formation of Supramolecular Structure of Oligomeric Liquids. Theory and Experiment) (Chernogolovka: Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1997)
73. A E Arinstein, S M Mezhikovskii *Int. J. Polym. Mater.* **47** 249 (2000)
74. S M Mezhikovskii *Vysokomol. Soedin., Ser. A* **29** 1571 (1987) [a]
75. S M Mezhikovskii *Inzh.-Fiz. Zh.* **76** 39 (2003) [f]
76. S M Mezhikovskii, in *Polimery-2003* (Polymers-2003) (Moscow: Institute of Chemical Physics, Russian Academy of Sciences, 2003) p. 152
77. S M Mezhikovskii, E I Vasil'chenko *Dokl. Akad. Nauk* **339** 627 (1994) [b]
78. S M Mezhikovskii, E I Vasil'chenko, T B Repina *Vysokomol. Soedin., Ser. B* **37** 887 (1995) [a]
79. A V Kotova, L A Abdrakhmanova, V M Lantsov, S M Mezhikovskii *Vysokomol. Soedin., Ser. A* **29** 1768 (1987) [a]
80. S M Mezhikovskii, V M Lantsov, L A Abdrakhmanova *Dokl. Akad. Nauk SSSR* **302** 878 (1988) [b]
81. T F Irzhak, S M Mezhikovskii, V I Irzhak *Dokl. Akad. Nauk* **379** 628 (2001) [b]
82. E I Vasil'chenko, T B Repina, S M Mezhikovskii, in *Tezisy Plenarnykh i Stendovykh Dokladov V Konferentsii po Khimii i Fizikokhimii Oligomerov* (Abstracts of Plenary Reports and Posters of the Vth Conference on Physical Chemistry of Oligomers) (Chernogolovka: Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1994) p. 62
83. S M Mezhikovskii, E I Vasil'chenko, in *Nauchnaya Konferentsiya IKhF RAN* (Scientific Conference of Institute of Chemical Physics, Russian Academy of Sciences) (Moscow: Institute of Chemical Physics, Russian Academy of Sciences, 1995) p. 42
84. A E Arinshtein, S M Mezhikovskii *Dokl. Akad. Nauk* **354** 457 (1997) [b]
85. S M Mezhikovskii, in *Problemy Reologii Polimernykh i Biomeditsinskikh Sistem* (The Problems of Rheology of Polymeric and Biomedical Systems) (Saratov: Saratov State University, 2001) p. 33
86. A Matsumoto *Adv. Polym. Sci.* **123** 41 (1995)
87. G V Korolev, T F Irzhak, V I Irzhak *Vysokomol. Soedin., Ser. A* **43** 970 (2001) [a]
88. G V Korolev, T F Irzhak, V I Irzhak *Vysokomol. Soedin., Ser. A* **43** 2106 (2001) [a]
89. G V Korolev, T F Irzhak, V I Irzhak *Vysokomol. Soedin., Ser. A* **44** 5 (2002) [a]
90. G V Korolev, T F Irzhak, V I Irzhak *Khim. Fiz.* **21** 58 (2002) [d]
91. V I Irzhak, T F Irzhak, G V Korolev *Macromol. Symp.* **171** 11 (2001)
92. H Jacobson, W H Stockmayer *J. Chem. Phys.* **18** 1600 (1950)
93. A Yu Grosberg, A R Khokhlov *Statisticheskaya Fizika Polimerov* (Statistical Physics of Polymers) (Moscow: Nauka, 1989)
94. G M Bartenev, S Ya Frenkel' *Fizika Polimerov* (The Physics of Polymers) (Leningrad: Khimiya, 1990)
95. P J Flory *Principles of Polymer Chemistry* (Ithaka: Cornell University Press, 1953)
96. N K Bonetskaya, V I Irzhak, A M El'yashevich, N S Enikolopyan *Dokl. Akad. Nauk SSSR* **222** 140 (1975) [b]
97. V I Irzhak *Usp. Khim.* **75** 1018 (2006) [*Russ. Chem. Rev.* **75** 919 (2006)]
98. W Funke1, O Okay, B Joos-Müller *Adv. Polym. Sci.* **136** 141 (1998)
99. O Okay, M Kurz, K Lutz, W Funke *Macromolecules* **28** 2728 (1995)
100. D T Landin, C W Macosko *Macromolecules* **21** 846 (1988)
101. J Malinsky, J Klaban, K Dušek *J. Macromol. Sci., Part A: Pure Appl. Chem.* **5** 1071 (1971)
102. H Galina, K Rupicz *Polym. Bull.* **3** 473 (1980)
103. H Tobita, A E Hamielec *Polymer* **31** 1546 (1990)
104. J C Hiller, W Funke *Angew. Makromol. Chem.* **76–77** 161 (1979)
105. J H Ward, N A Peppas *Macromolecules* **33** 5137 (2000)
106. T Otsu, A Matsumoto *Adv. Polym. Sci.* **136** 75 (1998)
107. H J Herrmann, D Stauffer, D P Landau *J. Phys., A* **16** 1221 (1983)
108. R Bansil, H J Herrmann, D Stauffer *Macromolecules* **17** 998 (1984)
109. J G Kloosterboer *Adv. Polym. Sci.* **84** 1 (1988)
110. I I Romantsova, O V Pavlova, S M Kireeva, Yu M Sivergin *Dokl. Akad. Nauk SSSR* **289** 422 (1986) [b]
111. F R Gaisin, Yu M Sivergin, R R Ismailov, S M Usmanov *Plast. Massy* (6) 31 (2006)
112. Yu M Sivergin, R R Ismailov, F R Gaisin, S M Usmanov *Vysokomol. Soedin., Ser. A* **49** (2007) [a]
113. F S Harris *J. Chem. Phys.* **23** 1518 (1955)
114. C A J Hoeve *J. Polym. Sci.* **21** 11 (1956)
115. R W Kilb *J. Phys. Chem.* **62** 969 (1958)
116. Z Ahmad, R T F Stepto *Colloid Polym. Sci.* **258** 663 (1980)
117. H Rolfes, R T F Stepto *Makromol. Chem., Macromol. Symp.* **76** 1 (1993)
118. S I Kuchanov, S V Korolev, M G Slin'ko *Dokl. Akad. Nauk SSSR* **267** 122 (1982) [b]
119. A A Abrikosov, L P Gor'kov, I E Dzyaloshinskii *Metody Kvantovoi Teorii Polya v Statisticheskoi Fizike* (Methods of Quantum Field Theory in Statistical Physics) (Moscow: Fizmatgiz, 1970)
120. S F Edwards *Proc. Phys. Soc.* **88** 265 (1968)
121. S Kuchanov, H Slot, A Stroeks *Prog. Polym. Sci.* **29** 563 (2004)
122. K A Andrianov, V N Emel'yanov *Usp. Khim.* **45** 1817 (1976) [*Russ. Chem. Rev.* **45** 931 (1976)]
123. P Flory *Faraday Discuss. Chem. Soc.* **57** 7 (1974)
124. D H Kaelble *J. Appl. Polym. Sci.* **9** 1213 (1965)
125. N Hata, J Kumanotani *J. Appl. Polym. Sci.* **15** 2371 (1971)
126. F P Price, S G Martin, J P Bianchi *J. Polym. Sci.* **22** 41 (1956)
127. R F T Stepto *Faraday Discuss. Chem. Soc.* **57** 69 (1974)
128. J I Cail, R F T Stepto, D J R Taylor *Macromol. Symp.* **171** 19 (2001)
129. I I Nazarova, Yu A Ol'khov, V B Nazarov, S M Baturin, S G Entelis *Vysokomol. Soedin., Ser. A* **17** 78 (1975) [a]
130. Yu A Ol'khov, S M Baturin, S G Entelis *Vysokomol. Soedin., Ser. A* **18** 150 (1976) [a]

131. T F Irzhak, N I Peregudov, V I Irzhak, B A Rozenberg *Vysokomol. Soedin., Ser. B* **35** 905 (1993) [a]
132. T F Irzhak, N I Peregudov, V I Irzhak, B A Rozenberg *Vysokomol. Soedin., Ser. B* **35** 1545 (1993) [a]
133. K Dušek, J Šomvársky, M Smrčková, W J Simonsick, L Wilczek *Polym. Bull.* **42** 489 (1999)
134. C Cameron, A H Fawcett, C R Hetherington, R A W Mee, F V McBride *Macromolecules* **33** 6551 (2000)
135. S E Rankin, L J Kasehagen, A V McCormick, C W Macosko *Macromolecules* **33** 7639 (2000)
136. D H Armitage, C Cameron, A H Fawcett, C R Hetherington, F V McBride, R A W Mee *Macromolecules* **33** 6569 (2000)
137. G V Korolev *Usp. Khim.* **72** 222 (2003) [*Russ. Chem. Rev.* **72** 197 (2003)
138. G V Korolev, M L Bubnova *e-Polymers* 030 (2002)
139. W H Stockmayer *J. Chem. Phys.* **11** 45 (1943)
140. W Funke, O Okay, B Yoos-Müller *Adv. Polym. Sci.* **136** 139 (1998)
141. N Ide, T Fukuda *Macromolecules* **32** 95 (1999)
142. H Wesslau *Makromol. Chem.* **93** 55 (1966)
143. H Wesslau *Angew. Makromol. Chem.* **1** 56 (1967)
144. K Dušek *J. Polym. Sci., Part B: Polym. Lett.* **3** 209 (1965)
145. K Dušek *J. Polym. Sci., Part C: Polym. Symp.* **16** 104 (1967)
146. B V Ozerkovskii, V D Plotnikov, V P Roshchupkin *Vysokomol. Soedin., Ser. A* **25** 1816 (1983) [a]
147. E Andrzejewska *Macromol. Symp.* **171** 243 (2001)
148. V P Roshchupkin, B V Ozerkovskii, Yu B Kalmykov, G V Korolev *Vysokomol. Soedin., Ser. A* **19** 699 (1977) [a]
149. L Ya Tsarik, Doctoral Thesis in Chemical Sciences, Irkutsk State University, Irkutsk, 1990
150. D Stauffer *Introduction to Percolation Theory* (London: Taylor and Francis, 1985)
151. G S Zhdanov *Fizika Tverdogo Tela* (Physics of Solid) (Moscow: Moscow State University, 1962)
152. E Bobalek, E Moore, S Levy, C Lee *J. Appl. Polym. Sci.* **8** 625 (1964)
153. L Gallacher, F A Bettelheim *J. Polym. Sci.* **58** 697 (1964)
154. V P Roshchupkin, S V Kurmaz *Usp. Khim.* **73** 247 (2004) [*Russ. Chem. Rev.* **73** 225 (2004)]
155. S Mallam, F Horkey, A M Hecht, E Geissler *Macromolecules* **22** 3356 (1989)
156. M Shibayama, T Norisuye, S Nomura *Macromolecules* **29** 8746 (1996)
157. A V Kotova, V M Lantsov, L A Abdrakhmanova, S M Mezhikovskii *Vysokomol. Soedin., Ser. A* **29** 1761 (1987) [a]
158. V P Roshchupkin, B V Ozerkovskii, Z A Karapetyan *Vysokomol. Soedin., Ser. A* **19** 2239 (1977) [a]
159. A V Kotova, S M Mezhikovskii *Int. J. Polym. Mater.* **47** 271 (2000)
160. G V Korolev, M P Berezin *Kineticheskie Proyavleniya Assotsiativnoi Struktury Zhidkikh Oligomerov v Protsessakh Polimerizatsii i Sopolimerizatsii. Mekhanizmy Assotsiativnykh Protsessov i Metodika Issledovaniya ikh s Pomoshch'yu Spin-zonda* (Kinetic Manifestations of Associative Structure of Liquid Oligomers in Polymerisation and Co-polymerisation. Mechanism of Associative Processes and Spin-Probe Investigation Procedure) (Chernogolovka: Branch of the Institute of Chemical Physics, Russian Academy of Sciences, 1994)
161. G V Korolev, M P Berezin *Mikrogeterogennyi Mekhanizm Trekhmernoi Radikal'noi Polimerizatsii* (Microheterogeneous Mechanism of Three-dimensional Radical Polymerisation) (Chernogolovka: Institute of Problems of Chemical Physics, Russian Academy of Sciences, 2002)
162. G V Korolev, I S Kochneva, G M Bakova, M P Berezin, L I Makhonina *Vysokomol. Soedin., Ser. A* **44** 1484 (2002) [a]
163. G V Korolev, A P Marchenko *Usp. Khim.* **69** 447 (2000) [*Russ. Chem. Rev.* **69** 409 (2000)]
164. T F Irzhak, V I Irzhak *Vysokomol. Soedin., Ser. A* **42** 2137 (2000) [a]
165. M Souaille, H Fischer *Macromolecules* **33** 7378 (2000)
166. A Goto, T Fukuda *Prog. Polym. Sci.* **29** 329 (2004)
167. H Fischer *Macromolecules* **30** 5666 (1997)
168. G V Korolev, I S Kochneva, G M Bakova, M P Berezin *Vysokomol. Soedin., Ser. A* **43** 784 (2001) [a]
169. R F Bates, G J Howard *J. Polym. Sci., Part C: Polym. Symp.* **16** 921 (1967)
170. D J Worsfold *Macromolecules* **3** 514 (1970)
171. E A Dzhavadyan, L M Bogdanova, V I Irzhak, B A Rozenberg *Vysokomol. Soedin., Ser. A* **39** 591 (1997) [a]
172. P P Kushch, B A Komarov, B A Rozenberg *Vysokomol. Soedin., Ser. A* **24** 312 (1982) [a]
173. G F Novikov, T L Elizarova, A V Chukalin, L M Bogdanova, E A Dzhavadyan, B A Rozenberg *Vysokomol. Soedin., Ser. A* **42** 1288 (2000) [a]
174. W H Stockmayer *Pure Appl. Chem.* **15** 539 (1967)
175. A Matsumoto, S Yokoyama, T Khono, M Oiwa *J. Polym. Sci., Polym. Phys. Ed.* **15** 127 (1977)
176. A Matsumoto, H Inoue, T Matsumoto, M Oiwa *J. Macromol. Sci., Part A: Pure Appl. Chem.* **26** 1279 (1989)
177. A Matsumoto, D Mitomi, H Aota, J Ikeda *Polymer* **41** 1321 (2000)
178. A Matsumoto, S Asai, S Shimizu, H Aota *Eur. Polym. J.* **38** 863 (2002)
179. A B Zachernyuk, E A Burlova, A A Zhdanov *Vysokomol. Soedin., Ser. A* **29** 1548 (1987) [a]
180. V M Lantsov, M K Pakter, V I Irzhak, L A Abdrakhmanova, E I Abramova, I N Zakirov, G I Vasil'ev, Yu S Zaitsev *Vysokomol. Soedin., Ser. A* **29** 2297 (1987) [a]
181. A Yokoyama, T Yokozawa *Macromolecules* **40** 4093 (2007)
182. Yu A Ol'khov, A I Ivanov, V V Lugovoi, S M Baturin, S G Entelis *Vysokomol. Soedin., Ser. A* **12** 1694 (1970) [a]
183. Yu A Ol'khov, S M Baturin, S G Entelis *Vysokomol. Soedin., Ser. A* **15** 2058 (1973) [a]
184. E Girard-Reyder, C C Riccardi, H Sautereau, J-P Pascault *Macromolecules* **28** 7599 (1995)
185. T F Irzhak, N I Peregudov, M L Tai, V I Irzhak *Vysokomol. Soedin., Ser. A* **36** 914 (1994) [a]
186. V I Irzhak, M L Tai, N I Peregudov, T F Irzhak *Colloid Polym. Sci.* **272** 523 (1994)
187. T F Irzhak, N I Peregudov, M L Tai, V I Irzhak *Vysokomol. Soedin., Ser. A* **37** 653 (1995) [a]
188. T F Irzhak, N I Peregudov, M L Tai, V I Irzhak *Vysokomol. Soedin., Ser. A* **37** 2071 (1995) [a]
189. T F Irzhak, N I Peregudov, M L Tai, V I Irzhak *Vysokomol. Soedin., Ser. B* **38** 1921 (1996) [a]
190. T F Irzhak, N I Peregudov, M L Tai, V I Irzhak *Prog. Colloid Polym. Sci.* **102** 42 (1996)
191. T R Deberdeev, R M Garipov, T F Irzhak, R Ya Deberdeev, V I Irzhak *Dokl. Akad. Nauk* **393** 209 (2003) [b]
192. T R Deberdeev, R M Garipov, T F Irzhak, R Ya Deberdeev, V I Irzhak *Vysokomol. Soedin., Ser. A* **46** 412 (2004) [a]
193. K A Andrianov, V N Emel'yanov *Vysokomol. Soedin., Ser. A* **9** 1005 (1967) [a]
194. Yu A Ol'khov, S M Baturin, S G Entelis *Vysokomol. soedineniya. Ser. A* **21** 861 (1979) [a]
195. E A Dzhavadyan, V I Irzhak, B A Rozenberg *Vysokomol. Soedin., Ser. A* **41** 624 (1999) [a]
196. E A Dzhavadyan, T I Ponomareva, V I Irzhak, V A Kozhina, Yu P Chernov, A Ya Malkin, B A Rozenberg *Mekhan. Kompozit. Mater.* 771 (1990) [c]
197. J-E Ehlers, N G Rondan, L K Huynh, H Pham, M Marks, T N Truong *Macromolecules* **40** 4370 (2007)
198. T F Irzhak, S M Mezhikovskii, V I Irzhak *Vysokomol. Soedin.* 2008 (in the press) [a]
199. S Corezzi, D Fioretto, J M Kenny *Phys. Rev. Lett.* **94** 065702 (2005)
200. B Fitz, S Andjelić, J Mijović *Macromolecules* **30** 5227 (1997)
201. S Andjelić, B Fitz, J Mijović *Macromolecules* **30** 5239 (1997)
202. B D Fitz, J Mijović *Macromolecules* **32** 4134 (1999)
203. R Volponi, S Corezzi, D Fioretto *Macromolecules* **40** 3450 (2007)
204. E W Fischer, C Becker, J-U Hagenah, G Meier *Prog. Colloid Polym. Sci.* **80** 198 (1989)

205. E W Fischer *Physica A* **201** 183 (1993)
206. A S Bokii *Fiz. Nizk. Temp.* **22** 956 (1996) [g]
207. A S Bokii *Fiz. Nizk. Temp.* **24** 27 (1998) [g]
208. V G Rostiashvili, V I Irzhak, B A Rozenberg *Steklovanie Polimerov* (Vitrifying of Polymers) (Leningrad: Khimiya, 1986)
209. P N Pusey, W van Megen *Nature (London)* **320** 340 (1986)
210. B V R Tata, P S Mohanty, M C Valsakumar *Phys. Rev. Lett.* **88** 018302 (2002)
211. J Dudowicz, K F Freed, J F Douglas *J. Chem. Phys.* **124** 064901 (2006)
212. M T Aronchime, J K Gillham *Adv. Polym. Sci.* **78** 83 (1986)
213. B A Rozenberg, E A Dzhavadyan, V I Irzhak, in *Networks: Formation and Control of Properties* Vol. 2 (London: Wiley, 1999) p. 131
214. I A Chernov, T R Deberdeev, G F Novikov, R M Garipov, V I Irzhak *Plast. Massy* (8) 5 (2003)
215. R M Garipov, S Yu Sof'ina, E N Mochalova, T R Deberdeev, A A Efremova, V I Irzhak *Plast. Massy* (12) 16 (2004)
216. R M Garipov, V V Mikheev, T R Deberdeev, V I Irzhak, Al Al Berlin *Dokl. Akad. Nauk* **392** 649 (2003) [b]
217. Yu S Lipatov *Oligomery — Nereshennye Problemy i Eshche ne Reshaemye* (Oligomers. Unsolved and Not Being Solved Problems) (Chernogolovka: Institute of Problems of Chemical Physics, Russian Academy of Sciences, 2002)
218. A A Kul'kov, in *Materialy VIII Mezhdunarodnoi Konferentsii po Khimii i Fizikokhimii Oligomerov* (Proceedings of VIIIth International Conference on Chemistry and Physical Chemistry of Oligomers) (Chernogolovka: Institute of Problems of Chemical Physics, Russian Academy of Sciences, 2002) p. 13
219. V G Artyukhov *Oligomernye Belki: Strukturno-funktsional'nye Modifikatsii i Rol' Sub'edinichnykh Kontaktov* (Oligomeric Proteins: Structural and Functional Modification and Function of Subunit Contacts) (Voronezh: Voronezh State University, 1997)
220. L P Smirnov, N N Nemova, in *Materialy III Mezhdunarodnoi Shkoly po Khimii i Fizikokhimii Oligomerov* (Proceedings of IIIrd International School on Chemistry and Physical Chemistry of Oligomers) (Moscow: Institute of Chemical Physics, Russian Academy of Sciences, 2007) p. 49
221. A L Rabinovich, in *Materialy III Mezhdunarodnoi Shkoly po Khimii i Fizikokhimii Oligomerov* (Proceedings of IIIrd International School on Chemistry and Physical Chemistry of Oligomers) (Moscow: Institute of Chemical Physics, Russian Academy of Sciences, 2007) p. 72

[a] — *Polym. Sci. (Engl. Transl.)*
[b] — *Dokl. Phys. Chem. (Engl. Transl.)*
[c] — *J. Theor. Exp. Chem. (Engl. Transl.)*
[d] — *Chem. Phys. Rep. (Engl. Transl.)*
[e] — *Mechan. Compos. Mater. (Engl. Transl.)*
[f] — *J. Eng. Phys. Thermophys. (Engl. Transl.)*
[g] — *Low Temp. Phys. (Engl. Transl.)*