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Current trends in investigations into the microheterogeneous mechanism of three-dimensional radical polymerisation

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Abstract. Data on the kinetics and mechanism of the three-dimensional radical polymerisation of multifunctional vinyl monomers (oligomers) containing two (or more) double bonds are generalised and analysed. The history of this field of research is briefly outlined. The characteristic feature of the mechanism of three-dimensional radical polymerisation, *i.e.*, microheterogeneity, is considered. Special attention is focused on recent advances (last decade) in studies of three-dimensional radical polymerisation associated with the development of new techniques (fiber-optic techniques, information technologies, *etc.*). Consideration is given to methodological aspects of kinetic experiments in highly cross-linked reaction media in which three-dimensional radical polymerisation proceeds. The bibliography includes 223 references.

I. Introduction

In 1977, rigorous proof of the specific mechanism of radical polymerisation of multifunctional monomers (oligomers) was reported for the first time.[1] In the last 25 years, this mechanism found considerable supporting evidence. Presently, this mechanism is called microheterogeneous. The hypothesis about the microheterogeneous character of the formation of highly cross-linked polymer networks (three-dimensional polymerisation) was advanced long before 1977 and was rather clearly formulated by Howink as early as 1934.[2] Later on, this idea was developed by Kozlov,[3,4] Galacher and Bertelheim,[5] Korolev *et al.*,[6,7] Notley,[8] Bobalec *et al.*,[9] and Dušek.[10]

First attempts to refine the model of microheterogeneous radical polymerisation were undertaken using the three-dimensional radical polymerisation (TRP) of phenol – formaldehyde resins as an example.[3,4] In 1962, the knowledge of the mechanism of radical polymerisation was substantially improved due to the application of light scattering to the investigation of the nucleation and evolution of microheterogeneity (microgel particles) in the course of the polymerisation of unsaturated esters.[5] In the same year, an hypothesis was proposed about the formation of discrete microgel particles, which serve as autonomous microreactors in the course of the polymerisation of multifunctional methacrylic esters.[6] In such autonomous microreactors, polymerisation proceeds much more rapidly than in the remaining bulk of the reaction system due to the local gel effect. In addition, important details of the TRP mechanism were revealed.[8] In 1964, the microheterogeneous mechanism was postulated also for three-dimensional polyesterification of non-radical three-dimensional polymerisation processes.[9] In 1970, the mechanism of TRP involving microheterogeneity was formulated on the basis of new experimental data.[7] In 1971, microsyneresis was observed[10] in the course of formation of highly cross-linked macromolecular structures.

However, only long-term studies of model objects, *viz.*, oligoester acrylates (OEA) belonging to a new class of unsaturated oligomers whose chemical structures were varied in a desired mode,† with the use of original procedures‡ culminated in 1977 with experimental evidence for the microheterogeneous mechanism of radical polymerisation. Hence, the above hypothesis not only became a proven concept but also was detailed. This provided a model suitable for quantitative calculations. The results of these calculations were reported in the study.[11]

The present review surveys the most important stages of investigation into three-dimensional radical polymerisation of multifunctional oligomers, which is one of the most important fields of polymer science. Considerable progress made in this field recently in response to the requirements of modern technology is associated mainly with advances made due to the discovery of microheterogeneity as the main characteristic feature of the mechanism of TRP. Prospects of further progress are based on the possibilities of modern computer modelling and the discovery of new phenomena in the kinetics of radical polymerisation (living chains, kinetically active associates).

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† The compounds were synthesised by A A Berlin and co-workers in the N N Semenov Institute of Chemical Physics of the Russian Academy of Sciences.

‡ Procedures specially designed for kinetic, structural and physical measurements during TRP were developed by G V Korolev and co-workers in the N N Semenov Institute of Chemical Physics of the Russian Academy of Sciences.

II. Characteristic features of three-dimensional radical polymerisation

Three-dimensional radical polymerisation can involve many practically important classes of unsaturated multifunctional compounds, *viz*., oligoester acrylates and maleates (for example, maleate–styrene resins), compositions based on allylic compounds, divinylbenzene and its derivatives. Oligoester acrylates are used as construction materials in the aircraft industry (as fiber glasses), paint-and-varnish materials and hermetics, stomatological materials (fillings, protection varnishes, materials for prosthetics) and modern liquid-crystalline systems. Since maleate–styrene resins contain a volatile toxic component (styrene), these polymers are of limited utility. Other classes of polyunsaturated compounds are of even more limited use. For example, divinylbenzene is used primarily in the synthesis of polymeric substrates for ion-exchange resins.

The TRP polymers are infusible and insoluble. These valuable properties are common to all polymers formed by any type of three-dimensional polymerisation, including non-radical polymers (for example, polycondensation of epoxide or phenol–formaldehyde resins). The advantages of TRP are both high polymerisation rates at rather low temperatures and the fact that various specific (associated with the chain nature of the process) highly efficient methods are avaliable, which allow one to influence the TRP rate just in the course of radical polymerisation. These methods are: (1) the use of initiators (organic peroxides, azodinitriles, *etc*. at concentrations of 10^{-3}–10^{-2} mol litre^{-1}), which enable one to reach very high TRP rates (10^{-2}–10^{-3} mol litre^{-1} s^{-1}) at moderate temperatures (300–350 K); (2) the use of inhibitors (stable free radicals, quinones, haloids, nitro compounds, *etc*. at concentrations of 10^{-4}–10^{-2} mol litre^{-1}), which allow one to suppress TRP within a predetermined period of time τ (induction period) in order to prevent premature spontaneous polymerisation, particularly, in the course of technological processes; (3) the use of external sources of initiation (light or radiation), which enables one to start or terminate the TRP process at any temperatures (including below room temperature) at any instant of time and to control the TRP rate within any limits by decreasing or increasing the irradiation intensity. In the last-mentioned case, it is possible to reach high rates such that highly reactive monomers (for example, oligoester acrylates) are virtually instantaneously cured into thin films, which is of considerable importance, for instance, in solving the problem of freezing of liquid-crystalline structures.

Three-dimensional radical polymerisation can involve only unsaturated compounds (monomers, oligomers) whose molecules contain two or more double bonds. Only in this case does polymerisation afford linear chain structures (primary carbon chains) bearing one (if the starting monomer contains two multiple bonds per molecule) or more (if the number of multiple bonds is larger than two) double bonds that remain intact per unit (pendant vinyl groups), which serve as centres of branching and cross-linking of carbon chains to form a network. Further polymerisation of these vinyl groups gives rise to secondary structures (first branched structures and then three-dimensional networks) in which carbon chains are cross-linked to each other by cross-bonds, the starting molecules located between the vinyl groups (oligomeric blocks) serving as such cross-links. Generally, the latter are heteroatomic chains consisting of two or more carbon atoms and two or more heteroatoms (oxygen, nitrogen, sulfur, phosphorus, *etc*.).

Figure 1 shows successive stages of TRP exemplified by monomers containing two vinyl groups each. Apparently, the final structure is a macromolecular three-dimensional network. Hence, polymerisation of such polyfunctional compounds is called three-dimensional polymerisation. Network junctions are of the utmost importance as characteristics of highly cross-linked macromolecular structures, because it is the junction mobility that controls the relaxation properties of polymeric materials, which,

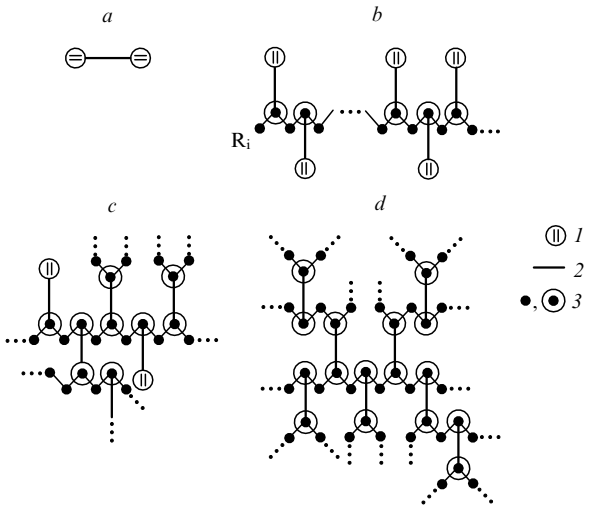


Figure 1. Successive stages of TRP of monomers containing two vinyl groups each; (*a*) the initial state, (*b*) primary (non-branched) polymer chain containing pendant double bonds, (*c*) fragment of the network with an incomplete structure (conversion <1), (*d*) fragment of the final network (conversion is ~ 1); (*1*) vinyl groups, (*2*) oligomeric blocks, (*3*) secondary or tertiary carbon atoms containing substituents H or R, R_i is the radical of the initiator.

in turn, determine their main physical–mechanical characteristics. It can be seen that TRP gives rise to trifunctional junctions. Two or three interjunction chains per junction are very short rigid carbon chains $-CH_2-$, whereas the third heterochain (best suited for constructing a cross-linked structure) is longer and more flexible due to the presence of heteroatoms (in particular, oxygen). In the worst situation, this chain is also rigid, for example, in monomers of divinylbenzene, whose molecule contains the rigid aromatic $-C_6H_4-$ fragment and is devoid of heteroatoms.

The above-described topological feature is typical of polymer networks formed in TRP. Other types of polymerisation, for example, non-radical three-dimensional polymerisation (polycondensation) of compounds devoid of double bonds, afford products in which two short carbon chains are absent, because the latter can be generated only through the radical-initiated cleavage of multiple bonds. Catalytic hardening of diepoxides gives rise not to $-CH_2-$ but to $-OCH_2-$ heterochains, which, being also short, are much more flexible. Hence, macromolecular networks formed in the course of TRP, all other factors being the same, should be characterised by rigid structures and low relaxation ability. In certain cases, this is an advantage, whereas in other cases this is a drawback. Networks can be rather easily modified by copolymerisation with the use of comonomers, which contain only one double bond per molecule and are able to alternate under given conditions (copolymerisation constants for the monomers r_1 and r_2 are lower than unity). In this case, short interjunction carbon chains are elongated, but the volume concentration of the network junctions simultaneously decreases.

Three-dimensional radical polymerisation is a specific process. Thus, a homogeneous reaction system is transformed into a microheterogeneous system (microgel, nanodispersion) consisting of cross-linked polymer particles, which are rather weakly linked to each other by crossing chains, virtually from the very beginning of the polymerisation. These particles serve as autonomous microreactors in which further polymerisation proceeds. The particles remain discrete upon the completion of the polymerisation process. This is responsible for the specific morphology of TRP products as a nanodispersion of highly cross-linked particles (grains) separated by interlayers of a poorly cross-linked (defect) polymer (Fig. 2).

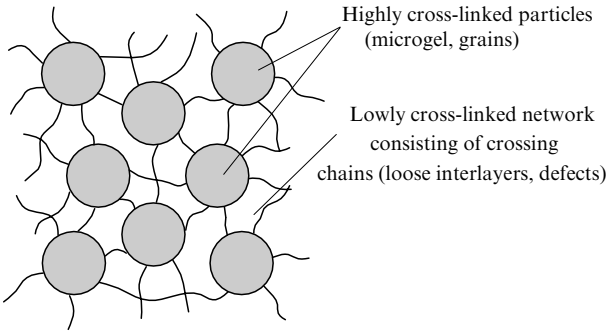


Figure 2. Morphology of TRP products as highly cross-linked particles separated by interlayers of a lowly cross-linked polymer.

The above-mentioned features complicate the TRP process. Therefore, the elucidation of the mechanism of TRP called for the development of a special methodology and new theoretical research in the field of radical polymerisation. As a result, TRP was classified as a special case of radical polymerisation, which could not be interpreted within the framework of the commonly accepted notions.

The basic research into the TRP mechanism was completed in 1977,[1] when the microheterogeneous model was proposed. These new concepts were experimentally supported by a series of systematic studies of the kinetics and mechanism of curing of oligoester acrylates. The latter proved to be very convenient model compounds for such studies, because the procedure for their synthesis enables one to vary the chemical composition and the length of oligomeric blocks over wide ranges in a desired fashion, while the terminal groups (methacryl or acryl), which are able to undergo polymerisation, remain intact.

Below are given the chemical formulae of several types of oligoester acrylates, which served as the basic compounds for revealing the fundamental features and mechanism of TRP.

Oligoesters containing unsaturated terminal groups, which are able to undergo TRP, can be described by the general formula

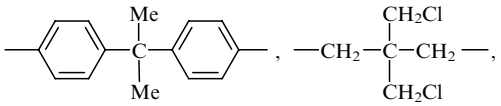
$$R^3C(O)OR^2[OC(O)R^1C(O)OR^2]_nC(O)OR^3,$$

1

where the substituents R^1, R^2 and R^3 correspond to saturated dicarboxylic acids, polyols and unsaturated monocarboxylic acids, respectively; $n = 0, 1, 2, \ldots$ (preferentially, $n \leqslant 2$). For oligomers of the first type, $R^2(OH)_2$ is generally a diol $[(CH_2)_m(OH)_2, m = 1, \ldots, 10]$ and R^3CO_2H is generally acrylic or methacrylic acid. Phthalic, adipic, sebacic, thiodivaleric and carbonic (used as $COCl_2$) acids can serve as $R^1(CO_2H)_2$. In the case of carbonic acid, the oligoester fragment of molecule **1** includes not only ester groups $[-C(O)O-]$ but also carbonate groups $[-OC(O)O-]$ possessing specific properties. Hence, oligoester acrylates of this type are considered as a special class and are called oligocarbonate (meth)acrylates.[12] For this type of oligoester acrylates, the functionality in the TRP process (f) determined by the number of terminal groups (multiple bonds) in the molecule, which can be involved in polymerisation, is equal to two.

Oligoester acrylates of the second type described by formula **1** contain polyol $R^{2\prime}(OH)_m$, where $m > 2$ (generally, glycerol with $m = 3$ or pentaerythritol, xylitol with $m > 3$) instead of diol $R^2(OH)_2$. For such oligoester acrylates, the functionality in TRP is 3 (or larger). Correspondingly, the volume-averaged concentration of the macromolecular network junctions in the polymer increases (compared to oligoester acrylates of the first type).

Different reactions resulting in the introduction of various fragments, such as



the urethane groups, the symmetrical triazine ring, phosphorus-containing groups and metals, into compounds **1**,[11] give rise to oligoester acrylates of the third type.

III. Methodological basis of three-dimensional radical polymerisation

Beginning in 1960, systematic studies on the synthesis of various oligoester acrylates with variable structures were carried out by researchers under the supervision of A A Berlin. The results of these studies not only stimulated fundamental investigation but also gave impetus to the development of new (and also to the improvement of known) experimental techniques for studying the kinetics and mechanism of TRP (including structure–physical studies of polymerisates). The necessity of developing such techniques was dictated by the fact that conventional methods (gravimetry, dilatometry, molecular-mass distribution measurements, *etc.*) are inefficient in studies of TRP due to cross-linking of the reaction system in the early stages of polymerisation and the insolubility of the polymer formed.

Calorimetry,[13–25] spectroscopy,[13,23,26–34] densitometry [13] and other kinetic methods [13,24,35–57] proved to be most efficient in studies of the kinetics and mechanism of TRP as well as of the structure–physical features of highly cross-linked polymers.

1. Calorimetry

High-precision isothermal microcalorimetry using Calvet calorimeters finds wide application. Studies with the use of DSC non-isothermal calorimeters followed by complex mathematical treatment of experimental data give less reliable results. High heats of polymerisation ($\Delta H = 42-92$ kJ mol^{-1}) are virtually independent of the conversion. Hence, only the velocity of heat evolution dQ/dt in the course of polymerisation can be continuously recorded with high accuracy by identifying this velocity with the polymerisation rate

$$W = -\frac{d[M]}{dt} \equiv \frac{dQ}{dt}.$$

The difference between the initial and running concentrations of the monomer $[M_0] - [M_t]$ is equal to the instantaneous quantity of liberated heat Q divided by ΔH of the monomer. In the case of copolymerisation, when

$$[M] = \sum_i M_i$$

and

$$\Delta H = \sum_i H_i,$$

the application of calorimetry to kinetic measurements is limited to azeotropic systems characterised by constant compositions of the monomer mixture and copolymer in the course of copolymerisation. For example, copolymerisation of the compound M_1 containing reactive styrene groups with the compound M_2 containing the methacryl groups in a molar ratio $[M_1]:[M_2] \simeq 1$ afforded a copolymer consisting of alternating units (because the copolymerisation constants correspond to the condition $r_1 \simeq r_2 < 1$), whose composition is independent of the conversion. In this case, the molar heat of copolymerisation can be calculated by averaging the heats of homopolymerisation of both monomers

$$\Delta H = 0.5(\Delta H_1 + \Delta H_2).$$

Then

$$[M] = [M_1] + [M_2] = \frac{2Q}{\Delta H_1 + \Delta H_2}$$

and

$$[M_1] = [M_2].$$

Most data on the TRP kinetics published in 1960 – 2003 were obtained by calorimetric methods.

Considerable progress has been made in the calorimetry of TRP, particularly in studies of photochemically initiated fast processes. The use of high-precision quick-response photocalorimeters, for example, a DSC-7 differential scanning calorimeter, Perkin-Elmer, Norwalk and CT,[15] photocalorimeters[15] equipped with a monochromatic photoaccessory, allows one to perform measurements in a second-scale range and, consequently, to record the kinetics of very fast TRP processes not only in the steady-state mode (during photoinitiation) but also in the post-effect mode (after termination of photoinitiation) at any stage of polymerisation (especially, at high conversions). Such a combination of steady- and non-steady-state kinetic measurements is necessary for estimating the rate constants of elementary stages of chain propagation and termination (k_p and k_t, respectively) as functions of the conversion (C). The results of such calculations are used as components of the database for macromolecular design.

It should be noted that the parameters $k_p = f(C)$ and $k_t = \varphi(C)$ for TRP (for oligoester acrylates) were experimentally measured for the first time in the 1960s.[13, 24, 25]

2. IR spectroscopy

For kinetic studies of TRP, second in importance to calorimetry is the IR spectroscopic method of the determination of the instantaneous concentration of double bonds. In the Real-Time Infrared (RTIR) version, this method (1430, Perkin-Elmer, Norwalk and CR spectrometers) proved to be even faster than the photocalorimetric method. It enables one to solve the same problems of the stationary and non-stationary kinetics in an even shorter time. For example, the instantaneous concentrations of double bonds in acrylates were measured very rapidly (20 spectra per second)§ from the peak at 811 cm^{-1}.[26] The main source of errors in IR spectroscopy as applied to TRP is associated with the distortion of the spectral shape, which increases as the conversion increases due to cross-linking of the matrix. The latter is tantamount to a change in the calibration in the course of transformation. Generally, this problem can be solved to a greater or lesser extent on the basis of choosing spectral lines which show the least changes with increasing conversion.

3. Densitometry

Densitometric methods of kinetic measurements, particularly those on the basis of flotation and titration, proved to be convenient under the conditions of TRP. Densitometric methods are based on an increase in the density of polymerisation systems (from the density of the monomer up to that of the polymer) with increasing conversion. The difference between these values is 10% – 20% of the density of the starting system. The density increases linearly with conversion. The deviations from linearity may appear only at high conversions in the case of very dense networks and high rates of TRP. Under these conditions, physical processes of structural relaxation may lag compared to the chemical addition reaction accompanying the contraction. Evidently, this complication is also inherent in dilatometry, which is based on measurements of the contraction of a polymerisation system in the course of TRP.[24]

§ In the plenary paper (*Photopolymerisation of functionalised oligomers*) presented at the International Conference on Chemistry and Physical Chemistry of Oligomers (September 9 – 14, 2002, Moscow – Chernogolovka), C Decker reported that this number could be increased to 50 spectra per second.

4. Other methods of kinetic measurements

Such methods as gravimetry, chemical analysis (determination of the concentration of double bonds),[35] dilatometry and some other techniques are employed with advantage and give excellent results in studies of radical polymerisation. However, substantial modifications of these methods were required to use them in the investigation of TRP. The first two methods deal with monomers isolated from reaction systems, and it is necessary to modify procedures for isolation, because conventional precipitation of the polymer cannot be performed due to cross-linking, while extraction may appear to be incomplete due to the presence of pendant double bonds. Hence, isolation should be preceded by the stage of de-cross-linking[36] (a very cumbersome and insufficiently selective process of destroying interchain cross-links, for example, by hydrolysis if cross-links contain ester or other bonds subjected to destruction by hydrolysis). The classical version of dilatometry is unsuitable for studies of TRP, because the system loses flowability in the early stages of polymerisation (at a conversion of less than 1%). Specially designed dilatometers are used, among which are long thin glass tubes (2 – 3 mm in diameter and 500 – 1000 mm in height), elastic dilatometers, *etc*. A very complicated differential dilatometric apparatus[24] equipped with two elastic cells and a high-precision detector of displacements proved to be most successful. This apparatus was used for performing the first non-stationary kinetic measurements of TRP processes and determining the dependences $k_p = f(C)$ and $k_t = \varphi(C)$.[13, 25]

In recent years, specific methods in which the TRP process was monitored by indirect evidence associated with an increase in the viscosity, freezing of the molecular mobility of components of the reaction system, for example, of the unconsumed monomer (NMR spectroscopy[37, 38]) or the addition of compounds, which are specially introduced as a molecular probe (fluorescence methods[40 – 43]), have also gained acceptance. Compounds, which can undergo isomerisation in a TRP system, are also used as molecular probes.[44] If the activation volume in polymerisation is rather large, the isomerisation rate can serve as a measure of the free volume in the isomerisation system and, consequently, as an indirect characteristic of the conversion.

The use of isomerisable compounds, such as azobenzene and stilbene, as photochromic probes made it possible not only to observe an increase in the conversion in the course of TRP but also to judge the character of the free volume distribution in the system as well as to identify the microheterogeneous structure of the polymer network formed.[44]

Methods based on light scattering are of particular importance in studies of the mechanism of TRP, because they allow one to observe the evolution of the structural microheterogeneity in the course of TRP.[11, 45 – 53] The sizes of strongly branched macromolecules and microgels in the pre-gel state can be estimated with static and dynamic light scattering.[20, 22, 54]

5. ESR method

Since free radicals $R^{\bullet}$ in cross-linked reaction media have long lifetimes (τ_R), the concentrations of $R^{\bullet}$ can be directly measured by ESR.[11 – 13, 45, 50, 57 – 70] The use of ESR proved to be particularly efficient in the following fields of investigation: studies of the kinetics of accumulation[11, 13, 45, 61, 62] and decay[11 – 13, 45, 63] of free radicals and structure – physical studies.[11, 45, 50, 65 – 70]

a. Studies of the kinetics of accumulation of free radicals in a non-stationary mode

In the case of the thermal decomposition of initiators (organic peroxides) in partially cured oligoester acrylates (30% – 70% conversion), the temperatures of the process can be chosen in such a way that the kinetics of accumulation of $R^{\bullet}$ can be recorded by ESR over 10 – 20 min. For a non-stationary mode, this kinetics can be described by the following classical formula:

$$[R^{\bullet}] = \sqrt{\frac{W_i}{k_t}}\ \mathrm{th}(\sqrt{W_i k_t}\, t).$$

At short times

$$t \leqslant \frac{0.3}{\sqrt{W_i k_t}}$$

this formula is approximated by the equation

$$[R^\bullet] \simeq W_i t,$$

at long times

$$t > \frac{1}{\sqrt{W_i k_t}}$$

this formula is approximated by the equation

$$[R^\bullet] \simeq \sqrt{\frac{W_i}{k_t}},$$

which allows one to calculate W_i and k_t from the experimental data. The initiator and temperature can be chosen in such a way that once the stationary value of $[R^\bullet]$ is attained, $[R^\bullet]$ begins to slowly (at long times) decrease due to consumption of the initiator. Then, knowing the kinetics of this decrease, the rate constant of thermal decomposition of the initiator k_d can also be calculated. In this case, the efficiency of initiation can be estimated as

$$f = \frac{k_i}{k_d} = \frac{W_i}{[I]k_d},$$

where [I] is the concentration of the initiator and k_i is the rate constant of initiation determined by the equation

$$W_i = k_i[I].$$

Therefore, this method enables one to determine k_i, k_d, k_t and f for TRP at high conversions and, correspondingly, to estimate the influence of cross-linking on chain initiation and termination. In the case of organic peroxides, k_t and f for oligoester acrylates decrease by factors of 10^6-10^7 and 25–50, respectively, as the conversion increases from 0% to 70%–90%. In the case of azonitriles as initiators, these values decrease by factors of 250–500.[11, 13, 45, 61, 62]

b. Study of the kinetics of termination of accumulated free radicals

In studies of the kinetics of termination of accumulated (trapped) free radicals, photochemical or radiation initiation is used to prevent the undesirable thermal generation of $R^\bullet$ in the course of ESR measurements. Studies by ESR revealed important characteristic features. First, it was found that the kinetics of $R^\bullet$ death is described by the following complex equation:

$$[R^\bullet] = f(t),$$

whose curve has bends at points $t_1, t_2, \ldots, t_i$ ($i = 2-4$). In intervals between the bends, the kinetics are adequately described by the classical equation

$$-\frac{d[R^\bullet]}{dt} = (k_t)_i[R^\bullet]^2,$$

where $k_{t1} > k_{t2} > \ldots > k_{ti}$. Second, the numerical value of k_{t1} correlates with the conversion and depends on the nature of the starting cross-linking monomer (oligomer). The factors controlling the flexibility of oligomeric blocks are of primary importance in these correlations. In a macromolecular network, the oligomeric blocks serve as interjunction chains, which link long carbon chains (*i.e.*, serve as interchain cross-links). The most important factors are the length of the oligomeric block and the presence of interatomic bonds characterised by low rotational barriers (for example, the replacement of the C–C groups by C–O–C leads to an increase in flexibility). Analysis of the termination kinetics of trapped $R^\bullet$ not only makes it possible to examine the mechanism of TRP but also enables one to obtain structure–physical information. Thus, bends in the $[R^\bullet] = f(t)$ curves are indicative of the microheterogeneity of a highly cross-linked polymeric matrix. The numerical values of k_{t1} serve as a measure of relaxation of a cross-linked structure at the molecular level.[11–13, 45, 63]

c. Synchronic comparison of the $[R^\bullet] = f_1(t)$ and $W = f_2(t)$ kinetic curves measured continuously

The polymerisation rate

$$W = f_2(t)$$

can be measured by any continuous method (preferentially, by high-precision kinetic calorimetry). Since

$$W = k_p[R^\bullet][M],$$

the current concentration of free radicals serving as chain carriers in the reaction system can be calculated from the instantaneous rate of TRP and the instantaneous concentration of the [M] monomer according to the formula

$$[R^\bullet]_2 = \frac{W}{k_p[M]}.$$

The concentration $[R^\bullet]_2$ can be underestimated to any extent as compared to $[R^\bullet]_1$ determined by ESR, because $[R^\bullet]_2$ is the concentration of only those radicals, that are involved in chain propagation at a particular moment

$$R^\bullet + M \longrightarrow RM^\bullet.$$

If some radicals lose the ability to be involved in the reaction (for example, due to immobilisation in a highly cross-linked polymeric matrix), a synchronic comparison of the results of ESR measurements of $[R^\bullet]_1$ with the results of calculations using kinetic data on $[R^\bullet]_2$ makes it possible to determine the proportion of the radicals that lose activity

$$\gamma_R = \frac{[R^\bullet]_1 - [R^\bullet]_2}{[R^\bullet]_1},$$

in a broad range of conversions and, consequently, to reveal the characteristic features of the changes in γ_R in the course of TRP. In the case of dimethacrylates, γ_R increases sharply once a certain (critical) conversion is attained. At moderate temperatures (20–70 °C), depending on the flexibility of the methacrylate molecules, this value varies from 10% (for very rigid molecules) to 50% (for very flexible molecules). The critical conversion increases as the temperature is raised.[11, 13, 45]

d. Structure–physical studies by ESR

In studies of TRP products using paramagnetic probing with stable iminoxyl radicals externally introduced by vapour sorption,[65] two types of ESR spectra, *viz.*, narrow (2945.2–3024.8 A m^{-1}) and broad (5412.8–5651.6 A m^{-1}), are superimposed. This fact is interpreted as the manifestation of the microheterogeneity of TRP products. Thus, the narrow signal corresponds to defect microregions with a loose network (with a low concentration of junctions) and, correspondingly, with a high mobility of probe molecules (correlation time $\tau_c \ll 10^{-7}$ s), while the broad signal corresponds to microregions with low molecular mobility ($\tau_c \geqslant 10^{-7}$ s). When varying the temperature over a broad range (from −195 to +150 °C), the temperature range $\Delta T = T_2 - T_1$ (transition region) was found in which the intensity of the narrow signal increased at the expense of the intensity of the broad signal up to the complete disappearance of the latter at the upper limit ΔT (at T_2). Only the narrow signal was observed above T_2. By contrast, only the broad signal was observed below T_1. The state corresponding to the broad signal was interpreted as the glassy state, the state corresponding to the narrow signal was considered as the high-elasticity state, and ΔT was assigned to the α-transition region. Within the framework of this interpretation, the ratio between the intensities of the narrow (I_1) and broad (I_2) signals in the region of their superposition (ΔT)

characterises the ratio between the total microvolumes in the highly elastic and glassy states

$$\frac{I_1}{I_2} = \frac{\sum_{1}^{m} \Delta V_i}{\sum_{m}^{n} \Delta V_i},$$

where ΔV_i is the volume of the ith microregion, m, $(n-m)$ and n are the numbers of highly elastic and glassy microregions and their sum, respectively, and $\sum_{1}^{n} \Delta V_i$ is the total volume of the system.

Evidently, a smooth change in I_1/I_2 in a very broad range of ΔT (several tens degrees) can occur only if a microheterogeneous system consists of a large set of subsystems (microregions ΔV_i) including n different types of ΔV_i, each being characterised by its own (local) glass transition temperature T_{gi}, which successively changes in the series ΔV_1, ΔV_2, ..., ΔV_n. For example, $T_{g1} > T_{g2} > ... > T_{gn}$. If n is rather large, a change in I_1/I_2 is smooth (without jumps). Apparently, the value of ΔT corresponds to the difference $T_{g1} - T_{gn}$ and, consequently, characterises the degree of microheterogeneity of TRP products (n is the number of subsystems ΔV_i, which differ by T_{gi}; ΔV_i with higher degrees of cross-linking have higher local temperatures T_{gi}).

For oligoester acrylates,[65] ΔT values were estimated and their evolution in the course of TRP was traced. It was found that the degree of microheterogeneity characterised by the parameter ΔT increases with increasing conversion but only to a certain limit reached at $C \simeq 50\%$.

Other applications of ESR to structure–physical studies of TRP products, including radiation and diffusion probing, were described in the monographs [11,45] and original publications. [50,66–69]

A simple method was proposed for the identification of the structural heterogeneity of highly cross-linked methyl methacrylate–ethyleneglycol dimethacrylate (EGDMA) copolymers.[70] The radicals accumulated in the polymer network were used to study the permeation of oxygen molecules by ESR. It was found that the permeability coefficient is maximum at the EGDMA concentration of ~ 70 mass %, which indicates that the porosity of the network increases with increasing concentration and reaches a maximum at the above-mentioned concentration of EGDMA.

This method can be considered as diffusion probing with oxygen molecules, which enables one to identify very small microheterogeneities.

6. NMR method

Nuclear magnetic resonance has proved to be an efficient method for studying chemical structures, molecular mobility and intermolecular interactions in high-molecular-weight compounds. However, this method is of limited use for studying TRP products because of their insolubility and non-fusibility. Of the other NMR techniques that are available, pulse NMR, broad-line NMR, and high-resolution cross-polarisation magic-angle spinning ^{13}C NMR spectroscopic methods appeared to be the most efficient.[37,38,43,45,59,71–73]

Studies of oligoester acrylates by pulse NMR demonstrated [71] that the kinetics of the magnetisation decay includes at least two modes (fast and slow), whose contributions can be rather precisely separated due to a large difference in their relaxation times. Analysis of the kinetics of the magnetisation decay for a series of samples with different conversions led to the conclusion that a polymerisation system is microheterogeneous starting from low conversions up to completion of TRP.

Broad-line NMR spectroscopy is generally used for revealing the temperature dependence of the second moment of NMR lines in a broad temperature range. Analysis of this dependence allows one to judge the presence of relaxation transitions and to estimate the corresponding activation energies. Investigation of a model series of oligoester acrylates with specified variations in the structure revealed fundamental characteristic features.[45,72] High-resolution cross-polarisation magic-angle spinning ^{13}C NMR spectroscopic studies of an analogous series of oligoester acrylates provided data on the configurations of the units in a polymer network and on the structural microheterogeneity manifested in broadening of spectral lines.

7. Physical-mechanical and thermomechanical methods

Upon deformation (ε) of TRP products in the mode of uniaxial compression with low rates ($\dot{\varepsilon} = 10^{-4}-10^{-3}$ s^{-1}), profiles of deformation curves can be recorded in the range of $0 \leqslant \varepsilon \leqslant 0.5$ including the region of the transition from the Hook to the forced elastic deformation. Analysis of the profiles of deformation curves in this transition region allows one to draw justified conclusions about the structural features of highly cross-linked polymers, including their microheterogeneity. Thermomechanical curves $\varepsilon = f(T)$ in the region of the α transition are also suitable for an analogous analysis.

In the case of oligoester acrylates, physical-mechanical and thermomechanical measurements were carried out on a high-precision apparatus [74] specially designed for studying mini-samples (~ 0.1 g). These measurements were performed on a large number of various oligoester acrylates, including polymers, which can be synthesised only in small amounts and exclusively in laboratory conditions.

Physical-mechanical measurement in the dynamic mode have also been successfully employed in studies of the structures of TRP products. For this purpose, relaxation time spectra have been analysed. It was found that the degree of microheterogeneity of the structure correlates with the width of the spectra in a certain frequency region.[75]

8. Application of pulsed radiation in non-stationary kinetic studies of three-dimensional radical polymerisation

A new promising method for determining the rate constants of elementary steps of the polymer chain growth is based on the use of pulsed coherent radiation (laser as a source) for photoinduced polymerisation followed by the analysis of molecular-mass distribution of the polymer formed (gel chromatography).[76,77]

For TRP, this method can be used only in the early stages of polymerisation until the gel point is reached and the strongly branched polymer is still able to dissolve in chromatographic eluents.

Nevertheless, measurements of k_p even in this very limited conversion range ($C \leqslant 1\%$ in block polymerisation, $C \leqslant 10\%$ in solution) are of great importance, because they allow one to judge the effect of the degree of branching of growing polymer chains on their reactivity, which is one of the fundamental problems of TRP.

9. Complex techniques

Three-dimensional radical polymerisation involves a chemical transformation (radical polymerisation) and a series of competitive physical transformations (aggregation, microsyneresis, *etc.*), which actively influence the chemical process. Hence, it is best to study TRP using complex techniques, which enable one to perform both kinetic measurements and follow the structural evolution in the course of polymerisation or reveal the structural features of the final polymeric products.[11,15,20–23,34,35,39,43,45,48,50,53,54,66–69,78–86]

Advances in studies of the TRP mechanism and its main characteristic feature, *viz.*, microheterogeneity, are associated primarily with the development and use of a methodological complex, which involves more than ten kinetic and structure–physical methods.[11,45,53] For example, in order for the structure–physical and kinetic information to be obtained directly in the course of polymerisation, the following combined approaches were developed: spectroturbidimetry in combination with calorimetry, the use of calorimeter–dielcometer, molecular labels and

IR spectroscopic monitoring of the kinetics of three-dimensional copolymerisation.[48, 78–82] In some cases, not only known procedures were combined but also original techniques were developed. Among these methods are the detection of the local redistribution of an initiator using radiation probing in combination with diffusion probing with paramagnetic NO molecules.[11, 45, 50, 66–69]

Studies of TRP by complex methods are being extensively developed.[15, 20–23, 34, 35, 39, 43, 54, 83–86]

IV. Kinetic features of three-dimensional radical polymerisation

1. Characteristic features of polymerisation in a cross-linked polymerisation system at high conversion

All TRP processes follow the same scheme. The initial polymerisation rate W_0 is not constant even in a very narrow conversion range $0\% < C < 5\%$ and it increases virtually from the very beginning with increasing C. At a certain value of $C = C_{max}$, the rate reaches maximum W_{max} followed by sharp autoretardation of TRP up to complete termination at $C = C_{lim} < 100\%$. Apparently, both autoacceleration at the first stage of TRP at $0 < C \leqslant C_{max}$ and autoretardation at the second stage at $C_{max} < C \leqslant C_{lim}$ should be interperted within the framework of the diffusion kinetics. As the diffusion mobility of the reagents is frozen by the cross-linked structure formed in the reaction medium, first faster elementary steps (chain termination, k_t) and then slower elementary steps (propagation, k_p) become diffusion-controlled. Because of this, first autoacceleration takes place due to a decrease in effective k_t followed by autoretardation due to a decrease in effective k_p.

An analogy can be drawn with the well known gel effect, which takes place in usual linear bulk polymerisation of some monomers [for example, of methyl methacrylate (MMA)] and also gives rise to autoacceleration–autoretardation, because it has the same physical causes, *viz*., freezing of diffusion mobility of the reagents to the level at which the elementary steps become diffusion-controlled, and their effective rate constants decrease as the diffusion hindrance increases. The only difference is the mechanism of freezing of diffusion mobility, which leads to substantial quantitative differences for TRP, both processes being qualitatively analogous.

In linear polymerisation, double bonds remain only in the monomers up to the end of the polymerisation process. Hence, the diffusion control over the processes involving monomer molecules (chain propagation) takes place only at very deep stages of polymerisation, when the polymer–monomer mixture begins to transform into the glassy state. In TRP, the starting molecules contain two or more double bonds. The addition of one of these bonds to the growing cross-linked network gives rise to pendant double bonds with substantially limited mobility. Hence, not only chain termination but also chain growth in TRP becomes diffusion-controlled even at low conversions. As a result, autoacceleration slows down. A comparison of autoacceleration for MMA and dimethacrylates (DMA) shows that the W_{max}/W_0 ratio for MMA is 10–20 times larger than that for DMA, whereas dW/dC in the region characterised by the highest level of autoacceleration is 100–200 times larger than the corresponding value for DMA and dW/dC sharply increases with increasing conversion (for DMA, dW/dC is nearly constant throughout the autoacceleration region $0 < C < C_{max}$).

The specific mechanism of freezing of the diffusion mobility in TRP is manifested also in specific kinetic features related to the correlation between the reactivity of the initial molecules and their physical (conformational) properties (length of the molecule, rotational barriers of the atomic groups). These characteristic features were analysed for a large number of TRP objects involving oligoester acrylates, because the method for their synthesis allows one to vary the molecular structure over a very wide range. It should be noted that only one particular parameter (for example, the length) can be varied, all other parameters (the nature of the groups capable of undergoing polymerisation, the nature of the groups responsible for the internal rotation barriers and, finally, the flexibility) being unchanged. By contrast, the internal rotational barriers can be varied, all other parameters being constant. The reactivity of TRP monomers, which is characterised by the parameters W, W_{max}, C_{max}, and C_{lim} (where W is instantaneous polymerisation rate in the range $W_0 < W < W_{max}$) at $T = \text{const}$, was found to increase with increasing length of oligomer blocks of the starting molecules and increasing flexibility, which is characterised by barriers to internal rotation provided that the nature of reaction centers (double bonds) is unaltered. The dependence of the above-mentioned physical (conformational) properties of the initial molecules on the reactivity becomes sharper with increasing conversion, the parameters W_{max}, C_{max} and, particularly, C_{lim}, being most sensitive.

The kinetic features of TRP are illustrated in Figs 3–7. The reactivity is expressed in terms of the reduced rate $W/[M]$ {[M] is the instantaneous concentration of the monomer, which was measured using a specially designed high-speed kinetic calorimeter (Fig. 3) and a high-precision DAK-1-1 kinetic Calvet calorimeter (Figs 4–7)}. The parameters associated with the nature of the monomers (oligomers), *viz*., the length of the chain linking the terminal methacryl groups (oligomeric block) and internal rotation barriers of the atomic groups of the oligomeric block, control the mobility of cross-linking chains of macromolecular networks formed in the course of TRP. It is these oligomeric blocks that become one of three cross-linking chains with trifunctional junctions once both methacryl groups of dimethacrylate are involved in the reaction. Since two other cross-linking carbon chains are very short and rigid, it is the third chain that provides junction relaxation controlling the molecular mobility of a highly cross-linked reaction medium. Curves *1*, *2*, *4* and *5* in Fig. 3 correspond to analogous (with the same set of rotation barriers) DMA with successively increasing length of the oligomeric block. The reactivity sharply increases in the same order, particularly, at deep stages of transformation, so that the maximum conversion for DMA with the shortest oligomeric block $C_{lim} \to 40\%$ (curve *1*), whereas autoretardation in the case of DMA with rather long chains (curves *4* and *5*) virtually disappears and $C_{lim} \to 100\%$. Curves *3* and *4* correspond to DMA, which have

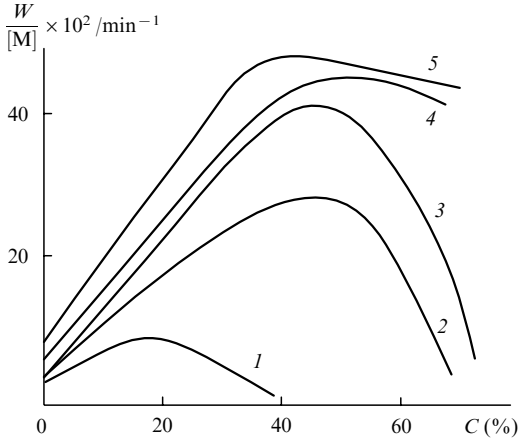


Figure 3. Kinetics of polymerisation of related molecules of different length (*1*, *2*, *4*, *5*) and internal rotational barriers of molecules of comparable length (*2*, *3*). $T = 70$ °C, benzoyl peroxide (1 mass %) as the initiator.

The following reagents were subjected to TRP: $M-(CH_2)_n-M$, $n = 4$ (BM; curve *1*), $n = 10$ (DM; curve *2*); $M(CH_2)_2O(CH_2)_2O(CH_2)_2M$ (TGM-3; curve *3*); $M[(CH_2)_2O(CH_2)_2O(O)C-Z-C(O)O]_n(CH_2)_2.O(CH_2)_2M$, $n = 1$ (decanediol dimethacrylate orthophthalate, DMP-1; curve *4*), $n = 2$ (DMP-2; curve *5*). Here and in Figs 4–7, M is the $CH_2 = C(CH_3)C(O)O$ group and Z is the fragment of orthophthalate.

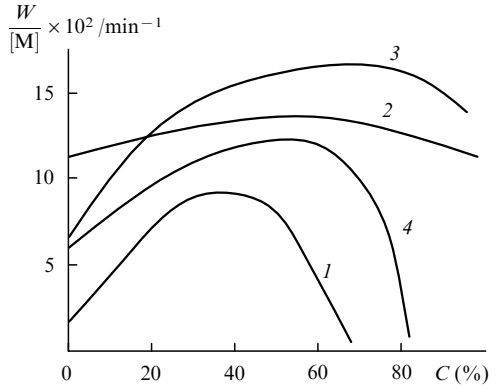


Figure 4. Kinetics of copolymerisation of the molecules of different types;
(*1*) homopolymerisation of TGM-3, (*2*) homopolymerisation of DMP-8, (*3*) copolymerisation of TGM-3 and DMP-8 in a mass ratio of 1 : 1; (*4*) homopolymerisation of GMP-9 $M(CH_2CH_2O)_3(O)C-Z-C(O).(OCH_2CH_2)_3M$ serving as a model of a copolymerisation system with respect to the number of double bonds. $T = 50$ °C, dicyclohexyl peroxydicarbonate (CPC) as the initiator, [CPC] = 1 mass %.

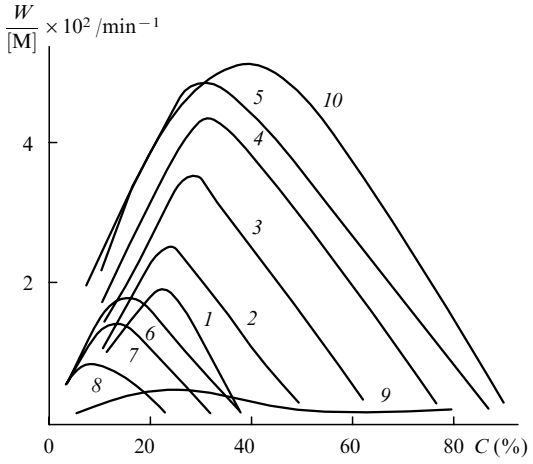


Figure 5. Effect of inert solvents on the kinetics of TRP using TGM-3 as an example.
The concentration of TGM-3 in a solution (vol.%): 100 (*1*), 80 (*2*), 60 (*3*), 50 (*4*), 40 (*5*), 90(*6*), 80 (*7*), 70 (*8*), 30 (*9*), 40 (*10*). $T = 40$ °C, [CPC] = 2.6×10^{-3} mol litre^{-1}; the solvent: (*2–5*) benzene, (*6–9*) heptane, (*10*) acetonitrile.

oligomeric blocks of similar lengths but differ by the set of internal rotational barriers. In decanediol dimethacrylate (DM, curve *2*), only two ester groups are rather weakly hindered. In triethyleneglycol dimethacrylate (TGM-3, curve *3*), not only rotations of the ester groups but also those of the ether bonds are weakly hindered and, as a result, the reactivity in the later stages of TRP increases.

Figure 4 shows the data on the dependence of TRP on nontrivial factors, which are also associated with the physical properties of the reaction medium. It appeared that the reactivities of binary systems of dimethacrylates of different length are not intermediate between the reactivities of each component but are higher than both of them (!) (*cf.* curves *1*, *2* and *3*). Curve *4* corresponds to dimethacrylate, which was specially chosen in such a way that the length of its oligomeric block was equal to the average length in the binary system (the nominal volume concentrations of the junctions of the macromolecular network, which were equal to the concentration of the double bonds in the starting mixture, were also equalised). As can be seen from curve *4*, in this case the reactivity has an intermediate value and the unusual effect typical of mixtures of molecules of different length disappears.

The influence of external factors, which are not associated with the nature of the starting oligomers, *viz.*, dilution of the reaction mixture with inert solvents, addition of inhibitors and surfactants, is illustrated in Figs 5–7. It can be seen that good solvents (from the viewpoint of thermodynamic affinity) enhance the reactivity, whereas bad solvents (heptane) decrease the reactivity. Apparently, it is associated with the fact that the chain growth is diffusion-controlled even in the early stages of polymerisation due to microheterogeneity. Hence, good solvents hinder microheterogenisation of the reaction mixture, whereas bad solvents facilitate chain aggregation and, consequently, increase microheterogenisation.

Figure 6*a* presents the kinetic dependences reflecting the influence of a rather strong inhibitor (X), *viz.*, benzoquinone, for which the rate constant of the linear chain termination is ~ 4 times as large as that of chain growth. Due to this difference in the rate constants, X is completely consumed in the early stages of TRP. The concentration of X was varied, the concentration of the initiator for each [X] being chosen so that the reactivity in the initial stages of TRP remained the same (see curves *1–3* at $C < 20\%$). A considerable increase in the difference in the reactivity as C increases cannot be explained without considering the microheterogeneous character of TRP. Actually, the microheterogenisation in the presence of X proceeds in such a way that the higher is the concentration of X, the larger is the number of

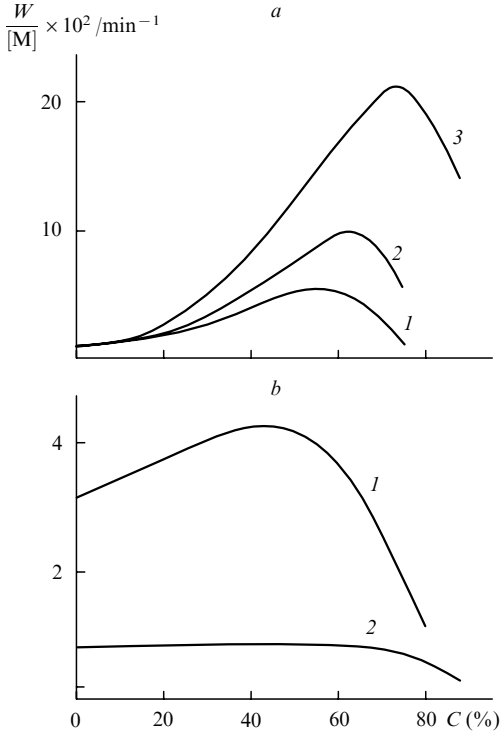


Figure 6. Effect of the structural defects, which are generated upon termination of growing polymer chains by inhibitors, on the kinetics of TRP.
(*a*) polymerisation of GMP-9 at a fixed molar ratio initiator (CPC)/inhibitor (benzoquinone) = 1 : 1; increasing absolute concentrations of the initiator and inhibitor (mass %): (*1*) 2, (*2*) 4, (*3*) 6; $T = 35$ °C;
(*b*) polymerisation of TGM-3 in the presence of inhibitors (trinitrotoluene, TNT), which act throughout the TRP process; $T = 60$ °C, dinitrile of azoisobutyric acid (AIBN) as the initiator, [AIBN] = 0.02 mol litre^{-1}; [TNT] = 5×10^{-3} (*1*), 3×10^{-2} mol litre^{-1} (*2*).

autonomous microreactors (N) simultaneously acting in the reaction system [11, 45]

$$N_{\lim} = \frac{(k_X[X])^2}{(f-1)k_p^2[M]_0}.$$

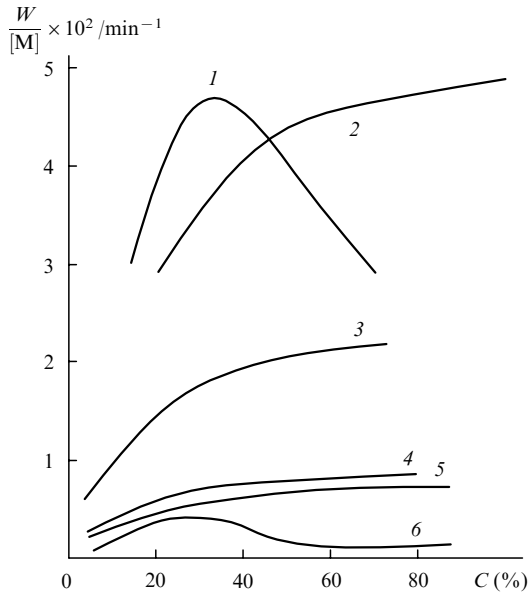


Figure 7. Kinetics of polymerisation of TGM-3 in a solution containing stabilising additives.
Additives: (*1–3*) acetonitrile, 40% TGM-3; (*4–6*) heptane, 30% TGM-3; $T = 40$ °C, [CPC] $= 2.6 \times 10^{-3}$ mol litre^{-1}. The additive and its concentration (mass %): (*1*, *6*) without an additive; (*2*) colloxylin, 0.1; (*3*) linoleic acid, 0.2; (*4*) polyisoprene, 0.4; (*5*) surfactant, 0.5.

This is consistent with the arrangement of curves *1–3*. Thus, the higher is the concentration [X], the higher is the reactivity.

The dependences shown in Fig. 6 *b* illustrate the influence of the inhibitors of another type with rather low constants k_X ($k_X < k_p$), which act throughout the process rather than only at the initial stages of TRP. In this case, quadratic chain termination R + R controlled by diffusion due to large sizes of R (macroradicals, some of which are already bound to the network) is changed for linear chain termination R + X involving small (mobile) molecules X, the latter process being diffusion-controlled to a much lesser extent. Hence, at a particular concentration of X (curve *2*), the kinetics typical of TRP (autoacceleration – maximum – autoretardation) are transformed in such a way that the stage of autoacceleration completely disappears and the stage of autoretardation is shifted to very high C.

The results of experiments on the suppression of microheterogenisation by adding surfactants are presented in Fig. 7. These compounds prevent aggregation, which is the initial stage of the formation of microheterogeneous (microgel) particles. Besides, within the framework of the microheterogeneous mechanism, autoretardation at deep stages of TRP is also interpreted as being a result of aggregation of microgel particles.[11,45] Three types of surfactants were used and the autoretardation stage was completely suppressed in all cases.

Therefore, the kinetic characteristic features at the later stages of TRP are determined by the conformational properties of the starting multifunctional monomers (oligomers), such as the length of the molecule and internal rotational barriers, and the reaction medium (diluents, surfactants, additives of inhibitors), which influence the aggregation of polymer chains and microgel particles as well as the length of primary polymer chains (inhibitors with $k_X > k_p$) and the character of chain termination (inhibitors with $k_X < k_p$). In the initial stages of TRP (initial rate W_0), the reactivity of the system at $C \to 0$ (non-cross-linked system) depends on other factors.

2. Early stages of three-dimensional radical polymerisation

At a very low conversion ($C < 5\%$), the reactivity of oligomers characterised by W_0 depends, generally, on the viscosity of the reaction system. The higher is the viscosity, the larger is W_0.[11,13,45,87,88] As in the case of the reactivity at a high conversion, the physical properties (those, which control the level of intermolecular interactions in the reaction system) of the starting oligomers rather than their conformational properties have a dominant role, *i.e.*, the presence of centres of strong intermolecular interactions, which can form hydrogen dipole–dipole and other labile bonds, is of importance. Cooperative hydrocarbon groups characterised by very weak dispersion interactions can also serve as such centres [for example, the methylene groups $-(CH_2)_n-$ at $n > 4$ are involved in intermolecular interactions with the energy $E > 17$ kJ mol^{-1} comparable to the energy of hydrogen bonds and the phenyl groups are involved in intermolecular interactions with $E = 29-33.5$ kJ mol^{-1}]. Generally, it is the ability of starting oligomers to form intermolecular interactions that controls the viscosity of the reaction system at low conversions. The viscosity exerts a trivial effect on W_0, *viz.*, chain termination in the TRP process is diffusion-controlled even at $C \to 0$, and the diffusion depends on the viscosity. The higher is the viscosity, the lower is the effective constant k_t and, consequently, the larger is W_0. A correlation between W_0 and the viscosity was found for a large number of compounds involved in TRP.

However, an anomalous reactivity was sometimes observed in the early stages of TRP.[11,45,89,90] In some cases, for example, the rate constant of chain growth (measured by a non-stationary kinetic method in the region of $C < 5\%$) sharply decreases in the presence of very small additives of inert compounds, including the polymer formed. In other cases, the viscosity has an anomalous effect on W_0, and W_0 increases rather than decreases as the viscosity decreases (for example, upon dilution with an inert solvent).[91] These anomalies provide evidence in favour of the existence of yet another specific feature of TRP processes associated with the involvement of polyfunctional molecules, which differ from usual monomers by a rather large size. These molecules are prone to the formation of associates. The lifetime (τ) of labile associates, particularly, if molecules contain centres of strong intermolecular interactions (generally, several centres, taking into account the large size of the molecules), often reaches $\tau_{ph} \simeq 3 \times 10^{-3}$ s, which is comparable to the characteristic time of the chain propagation ($\tau_{ch} \leqslant 10^{-4}$ s; the indices ph and ch denote 'physical' and 'chemical', respectively). Evidently, if $\tau_{ph} > \tau_{ch}$ and the degree of association of the starting oligomers is rather high, the chain growth takes place in an associated reaction medium. In this case, the packing (mutual orientation) of the molecules in the associate (if it is regular and characterised by the correlation time $\tau_0 > \tau_{ch}$) can be either favourable or unfavourable for growth

$$R(M)_nM^{\bullet} + M \longrightarrow R(M)_{n+1}M^{\bullet},$$

because all reactions of the addition of free radicals at the double bonds are sterically strictly controlled (as evidenced by very low steric factors $10^{-3}-10^{-5} \ll 1$). An anomalous change in W_0 is due to the presence of associates with either a favourable molecular packing (associate-plus) or an unfavourable molecular packing (W_0 increases with dilution; associate-minus). Recently, using polymerisation of specially chosen model compounds, which can form associates of both types (plus and minus), not only the existence of such associates and their effect on the kinetics of polymerisation processes have been proved but also the quantitative model of polymer chain growth in regular associates has been proposed.[92–102] The average length of sequences of molecules oriented in a like manner in the absence of perturbing agents (several tens of molecules can be involved in such a sequence) were calculated from the kinetic data on the influence of small additives of comonomers incorporated into the associate as agents interrupting the above sequence.

Recently, processes for the formation of associates in a medium containing groups capable of being involved in strong intermolecular interactions (acrylates and methacrylates) were examined by molecular mechanics and molecular dynamics.[101–104] These methods are based on the fundamental laws of

physics. Hence, the results of calculations by these methods are as convincing as the results of direct experiments and one can say about computer experiments. This is all the more important because the interpretation of the kinetic anomalies [92–95] was made possible based on the hypothesis of the existence of associates with a regular molecular packing (*i.e.*, molecules oriented in a particular way) in a medium of acrylates and methacrylates undergoing polymerisation. In other words, this hypothesis assumes the existence of associates with a pronounced long-range order. However, direct experimental methods for the detection of such associates, *i.e.*, methods necessary for verification of the correctness of this hypothesis, are lacking. In this case, the results of computer simulation (experiment) are evidently of great importance. Let us consider these results in more detail.

The kinetic anomalies,[89–106] which are presumably related to the formation of associates, are particularly pronounced in the polymerisation of higher alkyl acrylates (HAA) and higher alkyl methacrylates (HAM),[92–95, 100] which can be considered as models of monomers (oligomers) containing centres of strong intermolecular interactions. In the case of HAA, the kinetic anomalies are interpreted by postulating the formation of associates in which the mutual orientation of the molecules is favourable for chain growth (precursor). In the case of HAM, the formation of associates with the orientation of the molecules unfavourable for chain growth is postulated (anti-precursor). The correctness of these hypotheses was strongly supported by the results of experiments [93, 95, 100] on the influence of small additives (one molecule per 100 molecules of the main monomer) on the rate of polymerisation of comonomers possessing the same ability to undergo polymerisation *via* double bonds (the acryl group for HAA and the methacryl group for HAM) but containing alkyl substituents of different length. A very strong negative effect of such additives in the case of HAA was interpreted by assuming that the comonomer molecules are readily incorporated into the preassociate but simultaneously disturb the positional (or) orientational order due to the difference in the size of alkyl fragments. As a result, due to an unfavourable orientation of the double bonds, the molecules of additives terminate the polymer chain growth developed within the precursor. Based on these concepts, the computational apparatus was devised, which made it possible to evaluate the average number of molecules in the precursor (this number increases from 10 to 40 as n in the alkyl fragment $-(CH_2)_n-$ increases from 4 to 12) and the ratio between the rate constants of the chain growth within and outside the associate (from 50 to 200 in the same range of changes in n). The most probable reason for an increase in these parameters is the increase in the energy of intermolecular interactions in the homological series of HAA due to cooperation of weak dispersion interactions in alkyl fragments to form a centre of strong intermolecular interactions and, correspondingly, an enhancement of stability of the precursor.

The positive effect of very small additives of related comonomers observed in the case of HAM was interpreted as an effect of degradation (or a decrease in stability) of anti-precursors by molecules incorporated into the associates with a different positional or orientational packing.

The correctness of these hypotheses was confirmed by computer simulation,[101–104] as evidenced by the following results. It was demonstrated that higher alkyl acrylates and alkyl methacrylates, starting from butyl esters, can form regular associates, in which the ester molecules (or their hydrocarbon fragments, ester groups and double bonds) are mutually positionally and orientationally ordered (Fig. 8). These regular associates were related to kinetically active associates, whose existence was postulated in the interpretation of the kinetic anomalies occurring in HAA and HAM polymerisation.

The double bonds in the HAA and HAM molecules are ordered both within associates and with respect to the double bonds of the adjacent associates. The order of the double bonds within the associates is virtually identical to that in associates of

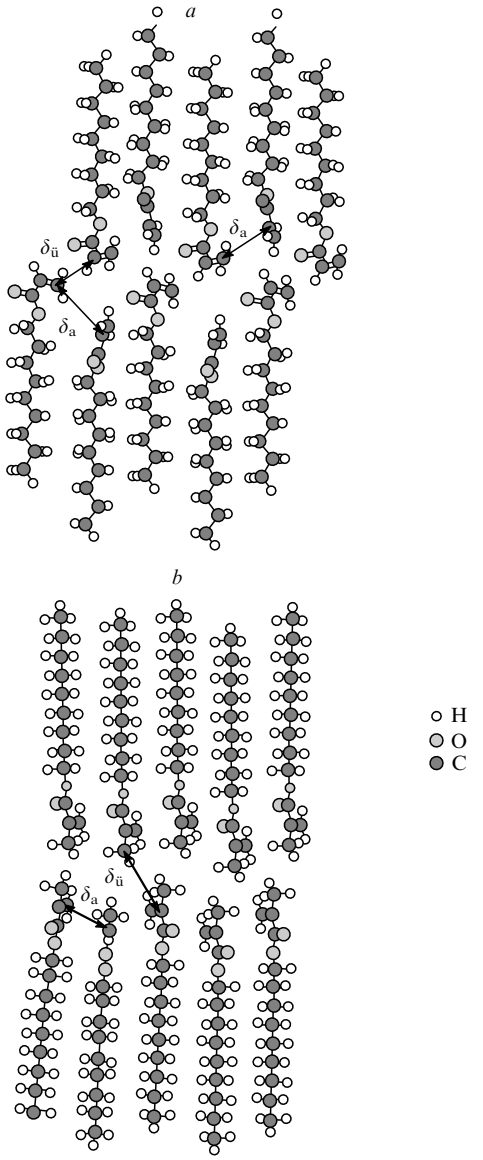


Figure 8. Monomolecular sectional view of the medium layer of a regular associate of NA (*a*) and NMA (*b*) in polymerisation of HAA and HAM.

nonyl acrylate (NA), nonyl methacrylate (NMA) and other alkyl acrylates and alkyl methacrylates (see Fig. 8), whereas the interassociate order of the double bonds in alkyl acrylates and alkyl methacrylates, including NA and NMA, is substantially different (Table 1).

It is believed that it is these characteristic features of the interassociate order of the double bonds of associated molecules that are favourable for polymerisation of NA and other higher alkyl acrylates and, by contrast, are unfavourable for polymerisation of NMA and other higher alkyl methacrylates. Apparently, these factors control the addition of polymeric radicals at the double bonds of the monomers. It was found that the incorporation of additive molecules into associates not only changes the positional order of the double bonds in the sites of localisation of the additive molecules by increasing the distance between the carbon atoms at the double bonds to 0.6–0.9 nm but also changes the molecular dynamics of all other associates. Molecular dynamics simulation of the thermal motion of molecules in regular associates of HAA and HAM showed that the inclusion of the molecules of BA or ethylhexyl acrylate (EHA) [BMA or ethylhexyl methacrylate (EHMA)] into regular NA (NMA) associates leads to their destabilisation (Fig. 9) by shifting

Table 1. Average distances between the carbon atoms at double bonds (δ) and the angle characterising the mutual orientation of the double bonds (θ) in the adjacent molecules in associates of alkyl (meth)acrylates (δ_a, θ_a) and between associates (δ_m, θ_m).

Associates	δ_a /nm	θ_a /deg	δ_m /nm	θ_m /deg
n-Alkyl acrylates				
BA	0.352	3	0.392	81
NA	0.343	1	0.365	88
DcA	0.340	1	0.358	89
CA	0.403	0	0.379	92
n-Alkyl methacrylates				
BMA	0.348	3	0.675	177
NMA	0.378	1	0.684	183
DcMA	0.358	1	0.624	182
CMA	0.392	1	0.648	182

Note. The distances δ and the angle θ in the models were determined with an accuracy of ± 0.001 nm and $\pm 2^\circ$, respectively; BA is butyl acrylate, DcA is decyl acrylate, CA is cetyl acrylate, BMA is butyl methacrylate, DcMA is decyl methacrylate, CMA is cetyl methacrylate.

the dissociate ⇆ associate equilibrium toward the non-associated monomers. For n-alkyl acrylates, this should lead to a decrease in the concentration of precursors and to a corresponding decrease in the polymerisation rate. In the case of HAM, the inclusion of the above-mentioned molecules should decrease the concentration of anti-precursors and increase the polymerisation rate.

The results of computer simulation of fluroalkyl (meth)acrylates also confirmed the existence of rather stable structures influencing the kinetics of polymerisation processes.

The hypothesis,[105] which was proposed in the 1950s after the discovery of the kinetic anomalies in polymerisation of the monomers crystallised in the phase transition region, was then extended to the high-temperature region far from the phase transition due to the discovery of new kinetic anomalies.[89–91, 106] Its computational apparatus was devised on the basis of experiments on specially chosen model monomers and their mixture.[93–95, 100] This hypothesis can be considered to be reliable as applied to TRP.

In conclusion, let us note the brave attempt [107] to represent the associated structure of a reaction medium as pseudopolymer chains with a limited lifetime τ_{ph} (blinking chains), whose units are linked *via* intermolecular interactions. For example, these chains can appear upon binding of alcohol molecules to form linear associates through hydrogen bonds.[108–110] It is assumed that the behaviour of blinking chains is somewhat analogous to that of usual macromolecules formed by covalent bonds. Hence, these chains can be described using the concepts and approaches developed in the physics of polymers, including scaling approaches. For chemical reactions proceeding in such a pseudopolymer medium, the relations were found in which the reaction order and other parameters reflect the characteristic features associated with the polymer statistics rather than with the laws of chemical kinetics.

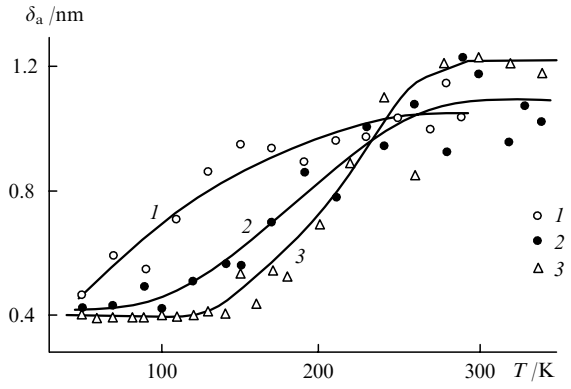


Figure 9. Temperature dependence of the distances between the double bonds (δ_a) in associates.
(*1*) BA, (*2*) NA + BA, (*3*) NA.

V. Three-dimensional radical polymerisation as a tool of macromolecular design

In recent years, researchers involved in different fields of fundamental science (chemists, physicists, mathematicians), specialists in computer simulation and engineers have focussed their efforts on the macromolecular design, *viz*., the chemical construction of macromolecules and the target synthesis of macromolecules with predicted structures and properties. In the area of highly cross-linked polymers formed by TRP, the macromolecular design is based on data from fundamental science, which made it possible to reveal the characteristic features of the kinetics and mechanism of TRP, whose distinguishing feature is the microheterogeneity. To use these data as an efficient tool of macromolecular design, it is necessary to transform them into mathematical (computer) models of TRP. Such models of TRP can be divided into two groups.

The first group of models developed in the period from 1977 to 1983 is based on the maximum simplified concepts.[1, 11, 45] Microgel particles acting as autonomous microreactors are approximated by spheres of the average radius r. It is assumed that the polymerisation process is localised in the peripheral layer of this sphere (with the thickness h, which remains unchanged with conversion). The calculated estimates showed that the number of microreactors remains virtually constant in the course of the polymerisation, so that the conversion increases due to an increase in r. When r reaches the value at which the spheres come into contact with each other, their loose peripheral layers acting as efficient reactors partially overlap with each other and their cores, which consist of highly cross-linked polymers with the maximum conversion (and, hence, which cannot interpenetrate), are packed to form a tetragonal or (which is less probable) hexagonal structure. In this stage, the polymerisation process is localised (reaction zone) in cavities of the structure composed of spheres (more precisely, in the inner near-surface layer of these cavities with the thickness h). It is assumed that at a rather high conversion, these cavities are spherical (of the average radius r'). Evidently, r' decreases in the course of further transformation. Within the framework of this model (percolation model), the rate constants of all elementary steps (initiation, propagation, termination) do not vary with conversion, because the conditions in the reaction zone (in loose near-surface layers above the dense highly cross-linked polymer) remain unchanged during polymerisation and only the total volume of the reaction zone changes (first it increases until the spheres come into contact with each other and then decreases). Correspondingly, the overall (experimentally observed) reduced polymerisation rate $W/[M]$ first increases (autoacceleration) and then decreases (autoretardation). In this case, both stages can be described by the following simple mathematical expressions:

autoacceleration

$$W = W_0\left(1 - \frac{C}{C_{lim}}\right) + W_r(4\pi N)^{1/3}h\left(\frac{3C}{C_{lim}}\right)^{2/3}, \qquad (1)$$

where W_0 and W_h are the polymerisation rates in the starting reaction mixture and spherical layers with the thickness h, respectively, C is the instantaneous conversion, C_{lim} is the limiting conversion, N is the concentration of spherical microreactors (microgel particles, grains);

autoretardation

$$W = W_0\left(1 - \frac{C}{C_{\lim}}\right) + W_r(4\pi N)^{1/3} h\, 3^{2/3}\left(1 - \frac{C}{C_{\lim}}\right)^{2/3}. \quad (2)$$

The region between autoacceleration and autoretardation cannot be described by such simple expressions.

The number of microreactors (microgel particles) formed in the reaction system reaches a constant value $N_{\lim}$ in the early stages of TRP (at $C < 1\%$). This parameter depends on both the kinetic parameters and reaction conditions.

In the absence of inhibitors,

$$N_{\lim} = \frac{W_i k_t}{(f-1)k_p^2[M]_0}, \quad (3)$$

where W_i is the initiation rate, f is the functionality and $[M]_0$ is the initial concentration of the monomer.

In the presence of the inhibitor X

$$N_{\lim} = \frac{(k_X[X])^2}{(f-1)k_p^2[M]_0}, \quad (4)$$

where k_X is the rate constant for the trapping of radicals as chain carriers.

Equations (1)–(4) indicate the manner in which the morphology of the polymer can be controlled. For example, a coarse-grained structure can be transformed into a fine-grained structure by increasing W_i or (and) adding additives X. The main advantage of this model is that it accounts for the microheterogeneous character of TRP.

Another group of mathematical (predominantly, computer) models deals with more complex equations.[111–120] Generally, it is assumed that k_p and k_t depend on the conversion. The character of the dependences is established on the basis of the corresponding concepts of molecular physics. Some of the physical constants remain unknown and serve as fitting parameters in the further comparison of the results of calculations with experimental data. From the applied viewpoint, this semiempirical theory has certain advantages. Thus, the above-mentioned equations are suitable for planning macromolecular design (but they are of limited use due to the empirical origin of the parameters). In the best-developed model, the rate constants of elementary steps are described by the following equations:[118]

$$k_p = \frac{k_{p0}}{1 + \exp[A_p(1/\upsilon - 1/\upsilon_{cp})]},$$

$$k_t = \frac{k_{t0}}{1 + \{R_d k_p[M]/k_{t0} + \exp[-A_t(1/\upsilon - 1/\upsilon_t)]\}^{-1}}.$$

Here, k_{p0} is the true kinetic rate constant, *i.e.*, k_p in the absence of diffusion control; A is the parameter determining how fast the diffusion-controlled kinetic constant decreases with increasing diffusion hindrance; υ is the average partial free volume of the system; υ_{cp} is the critical free volume for the chain propagation reaction determined as the value of υ at which $k_p = (1/2)k_{p0}$; $R_d k_p[M]$ is the component accounting for the contribution of the reaction-diffusion mechanism; [M] is the instantaneous concentration of double bonds and R_d is the parameter characterising the reaction diffusion.

To calculate the partial free volume at a particular conversion, it is necessary to know the following six characteristics of the material: the densities of the monomer and polymer (ρ_m and ρ_p, respectively), their glass transition temperatures (T_{gm} and T_{gp}, respectively) and the differences between the expansion coefficients in the high-elasticity and glassy states (α_m and α_p).

The parameter R_d was evaluated [121] from the results of non-stationary experiments (post effect) as follows:

$$R_d = \frac{k_t}{k_p[M]}.$$

VI. Critical conversion in three-dimensional polymerisation

The theory of polymer-network formation is one of the most important lines of investigation into the TRP mechanism. This theory has been developed in the studies of Dušek and co-workers,[10, 115, 122–143] Kloosterboer,[144–146] Boots and co-workers,[113, 145–147] Macosko and co-workers,[148–152] Lee and co-workers,[153–156] Hamielec and co-workers,[157–163] Chompff and co-workers [164] and Okay and co-workers.[114, 165–170] The results of these studies were generalised and analysed in the reviews.[120, 170, 171]

Some concepts of the theory of network formation are based on the Flory–Stockmayer model of polymerisation processes (for example, of stepwise reactions). Attempts to apply these concepts to TRP-type chain polymerisation processes were based on doubtful assumptions and rough approximations. Recently, it has been demonstrated [172–178] that calculations of the critical conversion α_c (gel point) for TRP with the use of the Flory–Stockmayer equations gave incorrect results even if these equations were specially adapted to this process. The equations, which work well for polycondensation (stepwise process), differ substantially from those derived in the studies [172–178] specially for TRP (chain process). Expressions relating α_c to the kinetic parameters of TRP stages (initiation, propagation, quadratic and linear chain termination and chain transfer) were deduced in the studies.[172–178] The problem was solved by the moments method followed by the generalisation of the numerical solutions in the form of equations. The starting model was based on the scheme of radical polymerisation including stationary-state conditions as the only assumption.

The critical conversion α_c in the formation of cross-linked polymers, which characterises the transition of the system from the flowable state to the state with the equilibrium modulus of elasticity, is an important parameter of the system both from the technological and theoretical standpoints.[179, 180] The formation of an insoluble gel in technological processes complicates the preparation of polymers. By contrast, the relation between the critical conversion, on the one hand, and the structural and kinetic parameters of the process, on the other hand, enables one to prepare cross-linked polymers with required physical-mechanical characteristics. Theoretically, the gel point determines the fluidity threshold in the polymer system formed and, hence, it is important to reveal the dependence of this value on the kinetics of the process and structural characteristics of the product.

The problem of the determination of the critical conversion was solved by Flory and Stockmayer [181] for polycondensation reactions of the type

$$R^1A + R^2B \longrightarrow R^1ABR^2, \quad (5)$$

which give rise to bonds between the functional groups A and B. The reactions can either be accompanied by elimination of by-products or proceed without the formation of the latter, groups A and B being either different or identical. If the number of functional groups per molecule of the starting reagents is larger than two, branched and cross-linked polymers can be generated. At a particular degree of conversion, higher-order (starting from the second) moments of the molecular-mass distribution of macromolecules approach infinity. This degree of conversion is called critical. The experimental critical conversions are determined from the results of viscosimetric measurements (the viscosity approaches infinity) or relaxation measurements (the appearance of the equilibrium modulus of elasticity). In recent years, the determination of the gel point on the basis of the frequency dependence of the relaxation modulus have gained wide acceptance.[182] It is believed that the critical conversion corresponds to the equality of $G'(\omega)$ and $G''(\omega)$.

The critical conversion and the structure of the network depend on the character of the functional-group distribution for

the starting reagents,[183] which can be expressed in terms of the average ($\overline{f_n}$) and weighted average ($\overline{f_w}$) functionalities [179, 183]

$$\overline{f_n} = \frac{\sum_i im_i}{\sum_i m_i}, \quad \overline{f_w} = \frac{\sum_i i^2 m_i}{\sum_i im_i}$$

where m_i are the concentrations of the starting reagents bearing i functional groups.

For polycondensation with related functional groups, it was found that

$$\alpha_c(\overline{f_w} - 1) = 1. \quad (6)$$

In the case of functional groups of different nature

$$\alpha_c^2 r(\overline{f_{aw}} - 1)(\overline{f_{bw}} - 1) = 1, \quad (7)$$

where r is the ratio between the concentrations of the interacting functional groups,

$$r = \frac{\sum_i im_{ai}}{\sum_j m_{bj}} < 1,$$

the indices a and b correspond to different types of functional groups.

The cross-linking of polymer chains is a special case. Generally, the critical conditions are expressed as follows:

$$\alpha_c(\overline{P}_w - 1) = 1, \quad (8)$$

where $\overline{P}_w$ is the weighted average degree of polymerisation of macromolecules subjected to cross-linking. It is implicitly assumed that the cross-linking can involve any unit of the polymer chain.

Equations (6)–(8) were derived by both the statistical method and kinetic calculations.[179, 180] These equations were also supported by the experimental data. The prerequisite to their applicability is the absence of intramolecular reactions.

The three-dimensional polymerisation, which can be represented by the scheme

$$M + R_i \longrightarrow R_{i+1}, \quad (9)$$

(M is the monomer, R_i is the active chain, the index i denotes the number of units in the chain), is generally described by Eqn (8), in which the critical branching proposed by Flory and Stockmayer [181, 184] is used as α_c. The relation between α_c and the conversion was established by solving the kinetic equations of the consumption of the functional groups of monomers.[185] Hence, calculations were based on probabilistic considerations, which are of limited usefulness in the case of polymerisation.[179, 180] The procedure for kinetic calculations of the gel point was developed in the studies.[1, 11, 45, 180, 186–189]

In the studies,[186–188] the gel point was calculated assuming

$$\frac{dN}{dt} = 0.$$

Evidently, these calculations should overestimate values, because, as in polycondensation, the second moments of the molecular-mass distribution (and, consequently, the functional-group distribution) approach infinity at lower conversions than the 'zero' concentration of polymer chains.[179–181]

The correct requirement for the infinity of the second moment of the molecular-mass distribution was used in the studies.[1, 11, 45, 180, 189] The following equations were derived:

$$\alpha_c = \frac{(k_t W_i)^{1/2}}{(n-1)k_p[M]_0}$$

and

$$\alpha_c = \frac{\{(k_t + k_t^1)[R] + k_m[M]\}^2}{k_p[M]\{(3k_t + k_t^1)[R] + 2k_m[M]\}}.$$

In these cases, the chain length was determined from the following kinetic parameters of the polymerisation process: the initiation rates W_i; the rate constant of chain propagation (k_p), the rate constants of chain termination by disproportionation (k_t^1) and recombination (k_t) and the rate constant of chain transfer to the monomer (k_m); the functionality of the monomer (n). It should be noted that in the latter case, the conversion with respect to the monomer rather than with respect to the functional groups was considered as the degree of conversion. Besides, it was noted that the equations in the above-given form can be deduced only for special conditions.

The above-mentioned equations were not confirmed experimentally. However, their validity was not questioned by researchers, because it is known that these conditions are not realised in the case of three-dimensional polymerisation.[1, 11, 45, 179, 180] Thus, intramolecular cyclisation proceeds rather vigorously due to fast chain growth by the radical mechanism and because of a low concentration of the chains in the early stages of TRP.[179, 190] It is believed that repeated cross-linking within the same pair of chains (formation of multiple junctions and ladder macromolecular structures) also decreases the effective concentration of interchain cross-links thus increasing the critical conversion. Hence, the radical polymerisation can be considered as a typical microheterogeneous process.[1, 11, 20, 45, 117, 168]

At the same time, polymerisation and polycondensation are radically different from the kinetic viewpoint.[179] A comparison of Eqns (5) and (9) shows that two functional groups are consumed in the course of the former reaction, whereas only one group is consumed in the latter case (in this reaction, the concentration of active centres remains unchanged). Hence, one functional group per monomer molecule is sufficient to prepare a polymer chain by polymerisation. In the polycondensation reaction of a monofunctional monomer, the chain is terminated. This fact casts doubt on whether the approaches, which were developed for studying polycondensation, can be extended to an investigation of polymerisation processes.

The study of living three-dimensional radical polymerisation demonstrated [191] that Eqn (8) is not fulfilled in this case as well,[192] although cyclisation is of little importance and the microheterogeneous character of the process is not manifested.[192, 193]

This fact served as the basis for stating the problem, whose solution revealed the critical conditions (gel point) for TRP. The analysis carried out in a number of studies [172–178] demonstrated that the critical conversion is related to the kinetic conditions of polymerisation in a complex way. Depending on the ratio between the rates of initiation and termination of a material chain, the gel point is determined by only one of the following parameters: (1) initiation rate, (2) termination rate. The former situation takes place if chain branching can occur, *i.e.*, at a high concentration of a multifunctional monomer, the process being substantially influenced by the kinetics of accumulation of active centres. In the latter case, the length of the material chain is of importance, because the number of pendant functional groups (probable branching points) per polymer chain is a controlling factor at a low concentration of the multifunctional monomer. However, the weighted average functionality of the starting monomer mixture is, on the whole, the governing factor.

The results of the solution of this problem are given in Table 2 in the form of equations for α_c in different processes. The criteria conditions limit the field of application of each equation. It should be emphasised that these equations are not analytical but were derived by generalising numerical solutions.

It is evident that the equations listed in Table 2 differ from all solutions obtained with the use of the Flory–Stockmayer theory. As mentioned above, an experimental comparison is hampered by side processes of the formation of small rings, which have a strong effect on α_c (shift toward higher values). However, under partic-

Table 2. Equations for critical conversion α_c.

Process	Φ_{22} small	Φ_{22} large	Criteria conditions
Living polymerisation, instantaneous initiation	$\frac{\alpha_c^2\Phi_{22}}{I_0} \approx 1$	$\frac{\alpha_c^2\Phi_{22}}{I_0} \approx 1$	$\frac{k_i}{k_p} > \sqrt{I_0\Phi_{22}}$
The same + chain transfer	$\alpha_c \approx \frac{1}{2}\frac{k_X X_0}{k_p\Phi_{22}}$	$\frac{\alpha_c^2\Phi_{22}}{I_0} \approx 1$	$\Phi_{22} >< \frac{(k_X X_0)^2}{k_p^2 I_0}$
Living polymerisation, slow initiation	$\frac{\alpha_c^2\Phi_{22}^2 k_p}{W_i} \approx 1$	$\frac{\alpha_c^3\Phi_{22}^2 k_p}{W_i} \approx 1$	$\frac{k_i}{k_p} > \sqrt{I_0\Phi_{22}}$
The same + chain transfer	$\alpha_c \approx \frac{1}{2}\frac{k_X X_0}{k_p\Phi_{22}}$	$\frac{\alpha_c^3\Phi_{22}^2 k_p}{W_i} \approx 1$	$\Phi_{22} >< \frac{(k_X X_0)^3}{k_p^2 k_i I_0}$
Slow initiation, chain termination by recombination	$\alpha_c \approx 0.33\frac{\sqrt{k_t W_i}}{k_p\Phi_{22}}$	$\frac{\alpha_c^3\Phi_{22}^2}{W_i} \approx 1$	$\Phi_{22} >< \frac{\sqrt{k_t^3 W_i}}{k_p^2}$
Slow initiation, linear chain termination	$\alpha_c \approx \frac{1}{2}\frac{k_{tY} Y_0}{k_p\Phi_{22}(0)}$	–	–
Replacement effect, chain termination through disproportionation	$\alpha_c = \frac{\sqrt{k_t W_i}}{k_{p2}\Phi_{22}}$	–	$\frac{k_{p1}\Phi_{22}}{\sqrt{k_t W_i}} < \frac{k_t}{k_{p2}}$

Note. Φ_{22} is the second moment of the functionality distribution for the starting reaction mixture (at $t = 0$); $\Phi_{22} \equiv \Phi_{22}(0) = \sum i(i-1)m_i$, where m_i is the initial concentration of i functional monomers (oligomers); W_i is the initiation rate; I_0, Y_0 and X_0 are the initial concentrations of the initiator, inhibitor and agent of chain transfer, respectively; k_i, k_p, k_t, k_{tY} and k_X are the rate constants of initiation, propagation, quadratic and linear termination and transfer of the chain, respectively; k_{p1} and k_{p2} are the rate constants of propagation for free and pendant double bonds in the processes in which the reactivities of the starting molecules containing two double bonds change after the one of these double bond has reacted; $\varepsilon = k_{p2}/k_{p1}$.

ular conditions (for example, if the probability of cyclisation is low), it is nevertheless reasonable to perform such a comparison.

The results obtained with the use of these equations and equations based on the Flory–Stockmayer theory were compared with the results of experiments performed under conditions in which internal cyclisation is supperessed.[176, 178] Two examples of such a minimisation are considered below.

Inhibited polymerisation of dimethacrylates. Radical polymerisation of triethyleneglycol dimethacrylate initiated by dicyclohexyl peroxydicarbonate in the presence of large amounts of inhibitors (benzoquinone or TNT) was carried out in cylindrical evacuated sealed tubes (250 mm in height and 3–3.5 mm in diameter). The conversion was detected from the contraction (shift of the meniscus was followed with an accuracy of 0.1 mm; the total shift at the instant of gel formation in the inhibition range under examination was 3–10 mm). The gel point was detected from the loss of flowability. A comparison with other methods showed that this approach gives a rather accurate estimate of the critical conversion.[192]

In the region of the longest lengths of growing polymer chains (at the smallest parameters $k_{tY}Y$), there is a large discrepancy (several orders of magnitude) between the calculated and experimental critical conversions, but then these values converge as the chain length decreases ($k_{tY}Y$ increases), and the best agreement is attained with the use of the equation

$$\alpha_c = \frac{1}{2}\frac{k_{tY} Y_0}{k_p\Phi_{22}(0)}, \qquad (10)$$

where k_{tY} is the rate constant of linear chain termination involving molecules of this inhibitor, Y_0 is the starting concentration of the inhibitor (at $t = 0$).

Calculations were also carried out with the use of the Flory–Stockmayer formula

$$\alpha_c = \frac{1}{\rho(\overline{P}_w - 1)}, \qquad (11)$$

where ρ is the molar fraction of the cross-linking agent, $\overline{P}_w$ is the weighted average degree of polymerisation of primary polymer chains, *i.e.*, chains which can be generated in the absence of a cross-linking agent at the instant corresponding to the gel point. This value was determined by gel permeation chromatography at degrees of conversion lower than α_c followed by extrapolation to zero conversion.

Since the experimental values of α_c are overestimated primarily due to cyclisation[179] (interchain cross-linking of pendant double bonds), it is believed that the probability of cyclisation decreases as the length of the growing polymer chain decreases and $k_{tY}Y$ increases. Hence, a comparison with the experiment at the largest values of $k_{tY}Y$ demonstrated that Eqn (10) is most precise. At the same time, this result indicates that the above-described calculations gave the correct estimate of the critical conversion not only in the range of parameters where Eqn (10) is valid, but also in the range where all relations presented in Table 2 are true.

This is all the more important because the discrepancy between the experimental and calculated values of α_c is often[194] considered as a test for estimating the percentage of cyclic structures in polymer networks, α_c being calculated with the use of the Flory–Stockmayer formula (8). Evidently, the use of the relations presented in Table 2 enables one to eliminate erroneous conclusions.

The experimental and calculated values of α_c for the inhibited polymerisation of triethyleneglycol dimethacrylate are given in Table 3.

Table 3. Experimental and calculated α_c for inhibited polymerisation of triethyleneglycol dimethacrylate (the molar initiator : inhibitor ratio is 2, dicyclohexyl peroxydicarbonate as the initiator).

Concentration of inhibitor /mol litre^{-1}	$k_{tY}Y_0$ /s^{-1}	Experiment	Calculations by Eqn (11)	Calculations by Eqn (10)
Trinitrotoluene as an inhibitor [a]				
0.05	5	~0.01	3.6×10^{-3}	8.9×10^{-4}
0.1	10	0.06	7.2×10^{-3}	1.8×10^{-3}
0.2	20	0.08	1.4×10^{-2}	3.6×10^{-3}
0.5	50	0.11	3.6×10^{-2}	9.0×10^{-3}
Benzoquinone as an inhibitor [b]				
0.005 (4) [c]	10	0.065	7.2×10^{-3}	1.8×10^{-3}
0.005 (2) [c]	10	0.055	7.2×10^{-3}	1.8×10^{-3}
0.005 (1) [c]	10	0.045	7.2×10^{-3}	1.8×10^{-3}
0.01	20	0.085	1.4×10^{-2}	3.6×10^{-3}
0.05	100	0.125	7.2×10^{-2}	1.8×10^{-2}
0.01	200	0.135	1.4×10^{-1}	3.6×10^{-2}
0.03	600	0.16	4.3×10^{-1}	7.2×10^{-2}
0.05	1000	0.19	7.2×10^{-1}	1.8×10^{-1}

[a] $k_{tY} \simeq 10^2$ litre mol^{-1} s^{-1}. [b] $k_{tY} \simeq 2\times10^3$ litre mol^{-1} s^{-1}, $k_p \simeq 350$ litre mol^{-1} s^{-1} (see Ref. 204), $[M]_0 \simeq 4$ mol litre^{-1}, $\Phi_{22}(0) \sim 8$ mol litre^{-1}. [c] The kinetics of polymerisation were recorded by high-precision calorimetry; initiation rates $10^7 W_i$ (mol litre^{-1} s^{-1}) are given in parentheses.

Copolymerisation of divinylbenzene with styrene. It was expected [195] that the probability of cyclisation would decrease to a negligibly small value and the polymer network would have an ideal structure with decreasing concentration of divinylbenzene (*m*-DVB) used as a polyfunctional agent in the initial comonomer mixture. Verification of this conclusion was searched for in the agreement between the calculated [according to Eqn (11)] and experimental values of α_c.

The criteria condition for estimating α_c at chosen kinetic constants dictates the choice of the equation

$$\alpha_c \approx 0.33 \frac{\sqrt{k_t W_i}}{k_p \Phi_{22}}, \qquad (12)$$

which was used in calculations. The results are given in Table 4.

Table 4. Experimental and calculated α_c for copolymerisation of *m*-DVB with styrene.

[*m*-DVB] (mol.%)	$10^3 \overline{P}_w$	$\Phi_{22}(0)$	Experiment	Calculations by Eqn (11)	Calculations by Eqn (12)
1	1.19	0.154	0.215	0.0425	0.032
0.5	0.79	0.077	0.333	0.133	0.065
0.25	0.74	0.039	0.488	0.271	0.128
0.17	0.67	0.026	0.549	0.435	0.192

Note. Block copolymerisation initiated by AIBN (4×10^{-2} mol litre^{-1}) at 60 °C, $W_i = 4 \times 10^{-7}$ mol litre^{-1} s^{-1}, $k_p = 200$ litre mol^{-1} s^{-1}, $k_t = 10^7$ litre mol^{-1} s^{-1}, $\Phi_{22} = 15.4$ mol litre^{-1} for pure *m*-DVB.

Analysis of the data in Table 4 casts doubt on the conclusion [195] that an ideal network is attained at low concentrations of *m*-DVB (the last row in the table). The conclusion about the attainment of an ideal-network state upon copolymerisation of dimethacrylates with monomethacrylates [196] is also in doubt. In this case, agreement between the experimental values of α_c and those calculated by Eqn (11) was observed at an even lower concentration (0.03 mol.%) of the bifunctional component (dimethacrylate). Calculations according to Eqn (12) gave lower α_c in this case as well. Consequently, contrary to the conclusions drawn in the study,[196] the contribution of cyclic structures is rather high. This contribution is also essential, if the length of primary chains can be decreased by several orders of magnitude due to an extensive chain transfer in the course of the polymerisation process,[196] although there is a tendency for cyclisation to be suppressed. For example, the ratio of the experimental critical conversion in the polymerisation of dimethacrylates to the calculated value decreases from 100 (at $\overline{P}_w = 1000$ in the absence of a chain transfer agent) to 13 ($\overline{P}_w = 142$) and then to 7–8 ($\overline{P}_w = 64$) in the presence of highly efficient chain transfer agents (dodecanethiols). In the case of diallylic monomers, which serve as active chain transfer agents, this ratio decreases to 5.2–5.5 at the smallest values $\overline{P}_w = 39–49$. This tendency is manifested not only upon a decrease in the chain length but also upon an increase in its rigidity.[197]

In the case of the above-considered inhibited polymerisation of dimethacrylates (see Table 3), the agreement between the calculated and experimental values of α_c is observed at $\overline{P}_w$ of less than 10. Apparently, this is the main reason for the fact that the contribution of cyclisation is close to zero, *i.e*., an ideal structure of the network is attained.

VII. Living three-dimensional radical polymerisation as a tool of macromolecular design

The discovery of living radical polymerisation (in the 1980s), reliable evidence for its occurrence in particular polymerisation processes obtained in 1993 and subsequent rapid progress in studies in this field of polymer science led to the development of a new tool of macromolecular design, *viz*., living TRP.¶ It appeared that living chain TRP radically changes the kinetic characteristic features, mechanism and structure (both topological and morphological) of the polymer formed. Correspondingly, the properties of the polymer material (physical-mechanical, sorption, thermomechanical, *etc*.) are sharply changed due to the transformation of the detailed mechanism of polymer chain growth, *viz*., the instantaneous chain growth of macromolecules (taking place in the case of usual TRP) is transformed into a slow stepwise process. The term 'instantaneous' is used in reference to processes satisfying the condition $\tau \ll t$ (where τ is the interval from the onset of the growing chain to its death due to quadratic or linear termination, t is the polymerisation time). The term 'slow' is taken to mean that the process meets the condition $\tau \geqslant t$. As a result of this transformation, the main factor responsible for the appearance of microheterogeneity is eliminated. Since it is the microheterogeneity that determines the main specific features of TRP, elimination (even partial) of the above factor leads to radical changes. From this viewpoint, living TRP as a tool of macromolecular design is considerably superior to usual TRP in efficiency.

Using dimethacrylates and their copolymers as examples,[198–200] it was established that the transformation of usual TRP into living TRP leads to a sharp change in the properties, *viz*., the molecular mobility increases and, correspondingly, the properties controlled by molecular mobility change. The modulus of elasticity decreases (both in the glassy and high-elasticity states at $T > T_g$). The glass transition temperature decreases by 20–40 °C. The rate of diffusion of the solvents and their equilibrium sorption increase. The temperature dependence of the rate constant of the quadratic termination of free radicals stabilised in a polymer matrix follows an alternative law (the character of the function changes); in this case, the radicals are generated by irradiation of the polymer with γ radiation (^{60}Co source) within the framework of the special techniques used in structure–physical investigation called radiation probing.[45]

The properties of the polymerisates prepared in the living chain and usual modes (according to the results of a studies [198–200]) are given in Table 5. Polymerisates of the typical reagent of TRP, *viz*., triethyleneglycol dimethacrylate (TGM-3), with the conversion $C = 0.80 \pm 0.02$ were prepared in the presence of AIBN as the initiator at 90 °C. To perform the living chain polymerisation, $CuBr_2$ and tetramethylthiuram disulfide were added to the initiator. The latter new agent of living radical polymerisation proposed in the study [200] provides a virtually complete transformation of usual TRP into the living chain mode at a particular component ratio.

In addition, Table 5 gives the characteristics of highly cross-linked macromolecular structures formed upon copolymerisation of triethyleneglycol dimethacrylate (TGM-3) with styrene (copolymerisation constants $r_1 \simeq r_2 \simeq 0.5$, equimolar mixtures, alternation of the units) in the presence of initiators (peroxides) at 125 °C. A benzoyl peroxide–2,2′,6,6′-tetramethylpiperidin-1-oxyl system (nearly equimolar ratio) was used as the agent of living TRP. This system, which has been intended only for reaction mixtures containing no less than 50 mol.% of styrene, was used with advantage.[191]

Living TRP is an efficient tool of macromolecular design for preparing highly cross-linked macromolecular structures with high molecular mobility (which are used, for example, in gel chromatography or for the preparation of materials with enhanced relaxation). Apparently, these changes in the properties are associated with either the absence or low concentration of high cross-linked regions ('grains') in living cross-linked polymers.

¶ The history of this discovery, the stages of development, analysis of the state-of-the-art of this scientific field and prospects in this area of investigation have been surveyed in the review.[191]

Table 5. Characteristics of usual and living TRP using homo- and copolymerisation as examples.

Parameter	Homopolymerisation		Copolymerisation	
	usual [a]	living [b]	usual [c]	living [c]
E /MPa	2122	1328	1652 / 1314	1486 / 403
σ ($\varepsilon = 10\%$) /MPa	104	58.9	77.1 / 52.3	62.8 / 17.0
W_g (%) during one hour	1.24×10^{-3}	0.42	0.14 / 1.38	0.22 / 2.00
S (%)	< 1	16.5	15 / 35	38 / 46
T_g /°C			138 / –	96 / –
$E_g(T > T_g)$ /MPa			43.6 / –	10.7 / –

Note. Physical-mechanical tests were carried out in the mode of uniaxial compression at 25 °C (glassy state) with a deformation rate $\dot{\varepsilon} = 10^{-4}$ s^{-1}; E is the modulus of elasticity, σ is stress on deformation $\varepsilon = 10\%$; W_g and S are the diffusion rate and sorption of benzene vapour, respectively, at 25 °C for 24 h. Free radicals (methacryl) were generated in polymer matrices with the initial conversion $C \simeq 80\%$ under the action of ^{60}Co γ radiation (dose was 2 Mrad).

The temperature dependence of the rate constant of recombination: [a] linear; [b] non-linear; [c] parameters at $C = 0.85 \pm 0.02$ and $C = 0.78 \pm 0.02$ are given above and below the bar, respectively.

This new tool has gained acceptance only recently,[192, 193, 198–202] because both theoretical and, in particular, experimental bases of living TRP are not sufficiently advanced. Although living radical polymerisation has been studied extensively, only ~3% of more than 400 studies published up to the year 2000 inclusive were devoted to living TRP.

Problems associated with living chain TRP are due, primarily, to two factors. First, information on the behaviour of agents of living radical polymerisation under conditions of highly cross-linked reaction media is scarce. It can be assumed that the diffusion hindrance and specific phenomena, such as microsyneresis and microredistribution of components of initiating systems, influence elementary steps of reversible trapping of radicals serving as chain carriers, which is the essence of the mechanism of living radical polymerisation. Second, (meth)acrylates are most commonly used in TRP, whereas the action of many agents of living radical polymerisation is limited to styrene, its derivatives and styrene-containing reaction mixtures. Hence, there is a need to search for new agents or adapt the available agents to conditions of TRP. The problem is that most of agents suitable for TRP of (meth)acrylates contain copper, iron, cobalt and other variable valence metal halides as basic components, which are insoluble or poorly soluble in cross-linked reaction media.

Living TRP was examined in the study.[203] Using polyethyleneglycol dimethacrylates as examples, it was demonstrated that the methyl α-bromophenylacetate–Cu(I)Br–1,1,4,7,10,10-hexamethyltriethylenetetramine system can serve as an efficient agent of living TRP of methacrylates starting with 70 °C. A comparison of the kinetic characteristic features of polymerisation, the critical conversions (gel points), molecular-mass characteristics of sol fractions and the kinetics of accumulation of stabilised radicals serving as chain carriers for usual and living TRP demonstrated that autoacceleration–maximum rate–autoretardation kinetic curves typical of usual TRP are transformed into curves with a maximum rate at at small conversion ($C \to 0$) if the living-chain mode is used. Subsequently, the rate decreases more rapidly than one would expect (assuming the first-order reaction with respect to the monomer), *i.e.*, the process shows evidence of autoretardation. The characteristic kinetic evidence for the living chain mode, *viz.*, the linear time dependence of $\ln([M]_0/[M])$ ($[M]_0$ and [M] are the initial and instantaneous concentrations of the monomer, respectively), is true only up to the conversion $C \simeq 40\%$. This gives grounds to assume that the later stages of TRP ($C > 40\%$) proceed in the usual fashion (due to the influence of a highly cross-linked macromolecular structure of the reaction medium). In living chain polymerisation, the critical conversion was shifted from < 1% to ⩾ 5%, which is consistent with other experimental data [198] and the new theory of gel formation.[172–178] Analysis of TRP by gel chromatography showed that a sol fraction in the course of usual TRP consists of a pure monomer in all stages of the polymerisation process starting with $C \to 0$ and up to $C > 50\%$, which is consistent with the microheterogeneous mechanism of TRP (see Section II). On going to the living chain mechanism, M_n of the sol faction linearly increases with conversion (the characteristic feature of living radical polymerisation [191]) to a critical value and then slightly decreases in the range $10\% \leqslant C \leqslant 40\%$ (from $M_n = 8000$ as a maximum at $C = 10\%$ to $M_n = 6000$ at $C = 40\%$). In the above-mentioned C region, the M_w/M_n ratio remains equal to ~2.5.

Presumably, the data from ESR measurements can be used for obtaining quantitative estimates. However, this was not done in the study.[203] It was found that the kinetics of accumulation of the free methacryl radicals $[R^\bullet] = f(t)$, where t is the polymerisation time, is described by curves with a maximum $[R^\bullet]_{max}$ attained at $C \simeq 50\%$ both for usual and living TRP. When the temperature changes from 70 to 90 °C, $[R^\bullet]_{max}$ decreases by a factor of 3.5 and by more than an order of magnitude in the case of usual and living TRP, respectively. However, quantitative estimates are of most interest. These estimates can be made by comparing the data on the reduced polymerisation rates

$$\frac{W}{[M]} \equiv W',$$

where [M] is the instantaneous concentration of the monomer with $[R^\bullet]$ at the same t. Actually, taking into account that

$$W = k_p[R^\bullet][M],$$

the instantaneous rate constant of chain propagation can be represented as follows:

$$k_p = \frac{W'}{[R^\bullet]},$$

where $[R^\bullet]$ is the concentration of radicals as chain carriers which can add molecules M. The concentration of the $[R^\bullet]_\Sigma$ radicals measured by ESR includes not only $[R^\bullet]$ but also the dead methacryl radicals immobilisation in a highly cross-linked structure in microregions with frozen mobilities of both $R^\bullet$ and M.[11, 13, 63] Hence, it can be written that

$$k_p \geqslant \frac{W'}{[R^\bullet]_\Sigma},$$

i.e., using $[R^\bullet]_\Sigma$ measured by ESR instead of the unknown concentration $[R^\bullet]$, the lower limit can be estimated as

$$k_p \equiv k'_p \quad \left(k_p \geqslant k'_p = \frac{W'}{[R^\bullet]_\Sigma}\right).$$

The k'_p constants thus estimated from the published experimental data [203] are given below. In the case of usual TRP performed at 70 °C, k'_p decreases from 9800 to 380 litre mol^{-1} s^{-1} in the range of $55\% \leqslant C \leqslant 75\%$. In the case of living TRP at the same temperature and in the same C range, k'_p is in the range of 60–70 litre mol^{-1} s^{-1}. If the data obtained in the study [203] are considered to be reliable, this result is unexpected. It is known [25] that in the course of usual TRP, k_p decreases (see Ref. 204) from 300–500 at $C \to 0$ to < 10 litre mol^{-1} s^{-1} at

$C > 50\%$. Since $k_p > k'_p$, $k_p > 9800$ (!?) at $C = 55\%$. For living polymerisation at 70 °C, $k'_p = 60-70$ ($k_p > 60-70$) seems to be normal as related to the results of the study,[25] because the molecular mobility of a cross-linked macromolecular medium increases in going from TRP to living chain polymerisation. However, the results of the study [203] of living TRP at higher temperatures also gave unexpected results. At $C \geqslant 50\%$, k'_p is in the range of 250–500 at 80 °C ($k_p > 250-500$, which is inconsistent with the prediction) as the conversion increases to the limiting values. At 90 °C, $k'_p = 1500-3000$ (!?).

To summarise, studies of living TRP are at their infancy.[172–177] Hence, the use of TRP as an efficient tool of macromolecular design of highly cross-linked polymer structures can only hold promise for the (hopefully close) future.

VIII. Conclusion

In the late 1950s–early 1960s, TRP attracted considerable attention due to the development of a new class of unsaturated polyester resins, *viz*., polyester acrylates, which were later called oligoester acrylates. Extensive systematic studies on the basis of a large number of oligoester acrylates in combination with the development of new experimental techniques enabled researchers first to reveal the main kinetic features of TRP and then to discover its main distinguishing feature, *viz*., microheterogeneity. Later on, the presence of microheterogeneity was repeatedly confirmed by both experiments and calculations. These results were generalised in the monograph.[11] In more recent studies of TRP, new original procedures were developed [45,49–51] for the investigation of the microheterogeneity and these procedures were applied to molecular design. These studies were surveyed in the monograph.[45]

Beginning in 1990s, interest in TRP has quickened all over the world resulting in a more than tenfold increase in the number of publications. This is associated with the development of new technological approaches, for example, in rapidly progressing materials science (construction of materials for information storage, biomaterials, fiber-optic coatings, *etc*.). It is TRP that has proved to be best suited for solving new technological problems owing to its distinguishing features, among which are the possibilities of performing reactions in the superfast mode at any (including low) temperatures, control of the process by initiation (including easily controlled sources of photochemical initiation), *etc*. Besides, the discovery of living radical polymerisation has opened up new opportunities for macromolecular design.

The following modern trends in studies of TRP should be noted. Fundamental studies of the kinetics and mechanism of TRP are carried out with the use of new experimental possibilities associated with the development of reliable fast-acting efficient methods for kinetic studies, such as fast-responce calorimetry, spectroscopy, *etc*. It should be noted that no radically new data on the kinetic characteristics and mechanism of TRP have been obtained since 1977.[1,11] Both the correlations between the kinetics and conformational properties of the starting multifunctional monomers and microheterogeneity as the principal features of TRP, which have been described and discussed earlier in the study [1] and monographs,[11,13] were confirmed in many studies of a large number of materials with the use of modern techniques. Three-dimensional radical polymerisation was investigated primarily using two classes of monomers, *viz*., divinylbenzene and its derivatives (including copolymerisation with styrene), on the one hand, and multifunctional (di-, tri-, tetra-) methacrylates and acrylates, on the other hand. The quantitative identification of cyclisation and a decrease in the reactivity of the pendant vinyl group in the course of TRP are major achievements of studies of the first group of compounds (divinylbenzene).[151,168,169,194]

In studies of compounds belonging to the second group (acrylates and methacrylates), considerable efforts have recently focused on the examination of superfast modes of TRP under conditions of photochemical initiation. It was found that at high photoinitiation rates, the initiating radicals R_i serve as main partners in the quadratic chain termination $R + R_i \rightarrow$ death reactions (where R_i is a radical of small size due to which it is highly mobile in a cross-linked medium; R is a polymeric low-mobile chain carrier). This fact radically changes the TRP process. Thus, autoacceleration disappears and the reaction rate order with respect to initiation decreases from 0.5 (normal) to ~ 0 (anomaly).

It should be noted that considerable efforts in the studies of both groups of compounds have been directed to computer simulation of TRP.[111–120] This direction of investigation is progressing rapidly, which is of great importance for extending the possibilities of macromolecular design.

Of special note are the development of procedures for performing living radical polymerisation involving both the adaptation of the known agents of living TRP to complex conditions of cross-linked media and the construction of new agents specially designed for TRP. Prominence is given to detailed studies of the kinetics and mechanism of living TRP.

Applied studies are carried out primarily in the field of materials science. These studies are aimed at using cross-linked polymers for producing materials for microelectronics and information storage systems, polymers for paint-and-varnish coatings, films and packings, biomaterials, materials for aspherical lenses, polymeric carriers for control drug delivery, fiber-optic coatings, ultraviolet curable adhesives, dental materials, abrasive-resistant coatings, polymeric hosts for luminophores and liquid-crystalline structures. The properties of TRP products and fields of application of these products were considered in the studies.[205–222]

Problems of three-dimensional radical copolymerisation are beyond the scope of the present review and will be surveyed in the future.

In conclusion, it should be noted once again that there are two radically different approaches to the interpretation of the dependence of the reduced polymerisation rate on the conversion within the framework of the microheterogeneous mechanism (microheterogeneous model) of TRP. One approach is based on the assumption that elementary steps of TRP (chain initiation, propagation and termination) are diffusion-controlled. Hence, their effective rate constants depend on the conversion and they change in the course of polymerisation. The functions $k = f(C)$ depend on the choice of a physical model for the diffusion control of elementary steps (according to Smolukhovskii, within the framework of the free volume theory or on the basis of the reaction-diffusion model). This approach does not explicitly take into consideration the microheterogeneity of the reaction medium and does not radically differ from the known theories for the gel effect developed for linear polymerisation of usual (monofunctional) vinyl monomers in high-viscous media.[223] The trivial kinetic features of TRP (autocatalysis in the early stages, autoretardation at high conversions, the dependence of $W/[M]$ on the initiation rate at fixed C) and the results of non-stationary kinetic measurements of elementary (actually, effective) rate constants of chain growth and termination are in satisfactory agreement with the results obtained with the use of models relying on the correlation between the diffusion-controlled rate constants and the state of the reaction medium determined by the conversion.

However, TRP involves unusual processes and phenomena (which are discussed in the present review and have been described and analysed in detail in the monograph [45]), which cannot be interpreted on the basis of homogeneous models with the constants $k = f(C)$. This gave impetus to the development of the microheterogeneous model of TRP. The simplest version of this model involves two types of local microreactors in which polymerisation processes occur, *viz*., microreactors with a high-viscous reaction medium (peripheral layers of microgel particles) and microreactors with a reaction medium consisting of the virtually pure starting monomer (oligomers). Because of this, the microheterogeneous model deals with only $(k)_0 = f(C = 0)$ and

$(k)_g = f(C = C_g)$, where the index g denotes the gel, instead of the rate constants $k = f(C)$ changing continuously in the course of TRP (homogeneous model). Hence, the rate constants of the elementary stages of TRP (chain initiation, propagation and termination), $(k)_0$ and $(k)_g$, in the case of the microheterogeneous model are independent of the depth of polymerisation. The occurrence of autoacceleration in the early stages and autodeceleration in the later stages of TRP (interpreted within the framework of the homogeneous model as a result of the dependence of k on the conversion) is associated first with an increase (at conversions lower than the critical value) and then with a decrease (at conversions higher than the critical value) of the total volume of microreactors of the first type (microgel particles).

Apparently, both models (homogeneous and microheterogeneous) are limiting cases of TRP. In actuality, the microheterogeneity of TRP is most pronounced for oligomers with short and(or) rigid oligomeric blocks in polymerisation with low (no higher than 10^{-7} mol litre^{-1} s^{-1}) initiation rates. For oligomers with long and(or) flexible oligomeric blocks or upon polymerisation with very high initiation rates (higher than 10^{-6}–10^{-5} mol litre^{-1} s^{-1}), the microheterogeneity is less pronounced. In recent experiments on living chain TRP, sources of the appearance of microheterogeneity in copolymerisation with the specially chosen comonomers as well as in polymerisation under conditions leading to the formation of very short chains (inhibition, chain transfer, catalytic chain transfer) were eliminated to an extent that the homogeneous model of radical polymerisation became quite suitable.

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