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State-of-the-art in the study of three-dimensional radical copolymerisation

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Abstract. The state-of-the art in the study of three-dimensional radical copolymerisation of multifunctional vinyl compounds with various monomers has been analysed. The mechanisms of relationships between copolymerisation kinetics with structure-physical transformations of the reaction medium and structures of cross-linked polymers are discussed. The key role of spectroscopic monitoring methods in the *in situ* studies of structure – kinetics relationships in three-dimensional radical copolymerisation is demonstrated. New approaches to control over these processes based on the use of chain transfer catalysis and living radical polymerisation are considered. The bibliography includes 178 references.

I. Introduction

The use of three-dimensional radical copolymerisation (TRCP) of multifunctional compounds (M_1) containing several double bonds with monomers (M_2) significantly extends the capabilities of directed design of network polymeric structures by varying the structures of starting compounds and the compositions of oligomer – monomer mixtures. High-tech processes based on TRCP are currently employed in the production of polymeric sorbents, membranes, laser videodisks, contact lenses,[1] gradient optical materials,[2] elements of computer optics,[3] microelectronics [4] and a variety of composite materials for special technique.[5] Commercial production or, in essence, synthesis of such articles demands high level of integration of such diverse processes as chemical reactions involved in TRCP, formation of a copolymer structure, microsyneresis of reaction components, vitrification of the reaction medium and diffusion-controlled exchange of monomers in gel polymer systems. Therefore, studies of TRCP as an integral complex of interrelated chemical and structure-physical transformations is a topical problem.

The majority of papers published thus far are devoted to determination of copolymerisation constants for the comonomers M_1 and M_2, analysis of mechanisms of gel formation, elucidation of structures and properties of copolymers formed, theoretical description and computer simulation of various TRCP processes. Some of them are considered in reviews,[1,4,6] but structure – kinetics relationships, which play a key role in the control over TRCP processes have not been taken into consideration. The increasing number of publications on this problem suggests the advent of a qualitatively new stage of research which is characterised by *in situ* analysis of structure – kinetics relationships in TRCP using spectroscopic monitoring in a real-time mode and development of novel efficient methods for the control over these processes using chain transfer catalysts and reagents for living radical polymerisation.

This review is devoted to the analysis of the most recent trends in the study of mechanisms of TRCP and encompasses a broad range of reaction systems $M_1 + M_2$ with oligomers and monomers differing significantly in the structures and properties.These systems allowed an analysis of effects of chemical (*e.g.*, relative reactivities of the C = C bonds in M_1 and M_2) and physical factors (*e.g.*, the lengths of oligomeric fragments and alkyl substituents, the presence of sites of strong intermolecular interactions in M_1 and M_2, *etc.*) on the kinetics of TRCP and structures and properties of the network copolymers formed.

A comprehensive analysis of TRCP reactions in $M_1 + M_2$ systems demands knowledge of homopolymerisation of the corresponding multifunctional compounds M_1. The expediency of studies into both copolymerisation and homopolymerisation of compounds M_1 is dictated by the similarity of their topologies and formation of pendant double bonds which differ from the double bonds in the starting oligomers M_1 in effective reactivities.† A detailed description of the state-of-the-art in the study of three-dimensional radical homopolymerisation is given in a review. [7]

II. A microheterogeneous mechanism of three-dimensional radical copolymerisation and structures of copolymers

1. Topological features of three-dimensional radical copolymerisation

It is known [8] that radical copolymerisation of monomers M_1 and M_2 yields linear macromolecules. With the exception of special cases of distortions in the uniform distribution of reactants,[9–11]

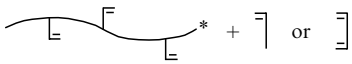
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† Effective (as opposite to true) reactivities of monomer – polymer systems depend on external factors (*e.g.*, diffusional characteristics of the reaction medium, conformational mobility of the polymer network, cage effect, *etc.*) rather than on the electronic structures of the reacting bonds.

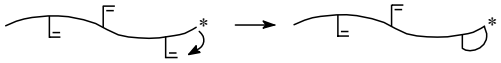
their compositions and alternation of the monomeric units in the polymer chain are determined by the composition of the initial monomer mixture and values of reactivity ratios of the monomers (r_1 and r_2, respectively). A totally different situation is observed on the transition to TRCP, where one of the components contains two (or more) reactive C=C bonds. In this case, the copolymerisation of a cross-linking reagent M_1 and a monomer M_2 is branched into different topological channels:[6]

1. Growth of linear chains carrying pendant double bonds and terminal radicals:

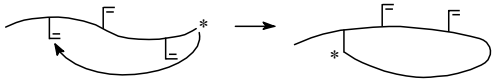


(1)

2. Primary intramolecular cyclisation:

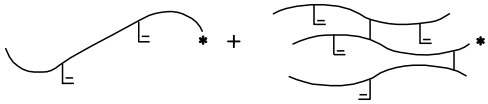


(2a)



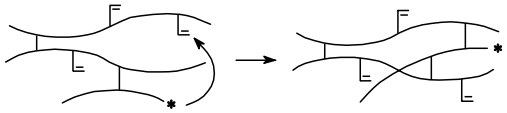
(2b)

3. Intermolecular chain cross-linking:



(3)

4. Secondary cyclisation in branched macromolecules, microgel particles and macrogel:



(4)

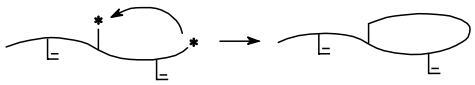
Primary intramolecular cyclisation (2a,b) is fairly inefficient as regards the formation of a network. This reaction results in a shift of the experimental gel point from a theoretical value calculated on the basis of the Flory–Stockmayer theory towards higher degrees of conversion.[6] Under these conditions, the formation of a microheterogeneous copolymer structure occurs at the topological level. Therefore, numerous papers deal with the analysis of factors determining the probability of this reaction.

The contribution of reactions (2a,b) is especially pronounced in early steps of TRCP where the probability of the bimolecular reaction (3) is very low because of a small concentration of the polymeric chains and growing macroradicals. In this step, effective reactivities of pendant C=C bonds in the vicinity of the terminal radical may exceed those of the C=C bonds of the oligomer M_1. Effective reactivities of the pendant double bonds also depend on the length and rigidity of the oligomeric fragment (spacer) which connects them with the main chain as well as on the flexibility of the main chain and the number of the rings formed.[1] The role of these factors is determined by the number and structure of the comonomer M_2 units which significantly influence the flexibility and conformation of chains in the growing macroradicals.[12, 13]

The feasibility of cyclisation during copolymerisation of ethylene glycol dimethacrylate (**1**) with styrene (**2**) has been established.[14] However, a completely soluble polymer devoid of double bonds and with rings in the main chain could be obtained only at low concentrations of the cross-linking reagent. Copolymerisation of dimethacrylate **1** and triethyleneglycol dimethacrylate (**3**) in highly dilute solutions resulted in cyclolinear polymers with M_w of $\sim$ 20 000.[15] An analysis of a hydrolysate of a polymer obtained from the dimethacrylate **3** revealed that the overwhelming majority of pendant double bonds are involved in intrachain cyclisation and the probability of formation of a ladder-type chain polymer is very low.

The dependence of the probability (DP) of intramolecular cyclisation on the length of the polymer chain of dimethacrylate **3** has been established.[16] The degree of polymerisation was controlled using a catalytic chain transfer agent and the number of double bonds was established by IR spectroscopy. It was found that only the products with DP < 9 had pendant methacrylate groups in each monomeric unit. With an increase in the DP to 15, the residual unsaturation of the products decreased to the level characteristic of the bulk polymer. This suggests that cyclisation in growing polymeric chains during polymerisation of dimethacrylate **3** occurs by route (2b).

The majority of papers devoted to cyclisation in TRCP consider only the reaction of the terminal radical and the pendant double bond. However, mathematical simulation of radical polymerisation reactions of oligomeric dimethacrylates on a cubic lattice[17] revealed that recombination of terminal and pendant radicals also contributes to cyclisation.

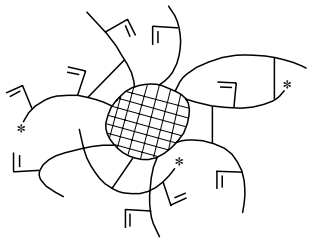


(5)

It was noted that at high initiator concentrations the intramolecular quadratic termination of radicals (5) is the main reason for cyclisation.

The probability of bimolecular intermolecular cross-linking (3) in the initial steps of (co)polymerisation is negligibly small, but increases rapidly with an increase in the concentration of primary polymeric chains. The interactions of growing macroradicals with the pendant double bonds of the polymeric chains result in the formation of branched macromolecules. The Monte Carlo simulation of topological structures of branched polymers in the pre-gelation step revealed[18] that the branching parameters strongly depend on the initiation rate of radical polymerisation of multifunctional monomers. Low initiation rates favour the formation of long-chain slightly branched polymers, whereas high initiation rates favour the formation of short-chain polymers with higher degrees of branching. The results of the simulation correlate qualitatively with the branching parameters of macromolecules isolated in the pre-gelation step of diallylic oligomers.[19, 20]

Favourable conditions for the reaction (4) between the radicals and pendant C=C bonds of different branching chains appear in branched macromolecules containing a large number of pendant double bonds. This process commonly referred to as secondary cyclisation[21] or intramolecular cross-linking[6] results in the formation of microgel particles, which consist of a dense nucleus and a loose shell.



The consumption of double bonds in the cross-linking and primary and secondary cyclisation during polymerisation reactions of multifunctional compounds can be calculated on the basis of a kinetic model of network formation.[21] These calculations showed (Fig. 1) that primary cyclisation prevails in the initial steps due to enhanced reactivities of pendant C=C bonds in the vicinity of growing radicals, which stimulates the formation of microgel particles. The contribution of intermolecular cross-linking and secondary cyclisation increases with an increase in the degree of conversion and polymer concentration, as a result of

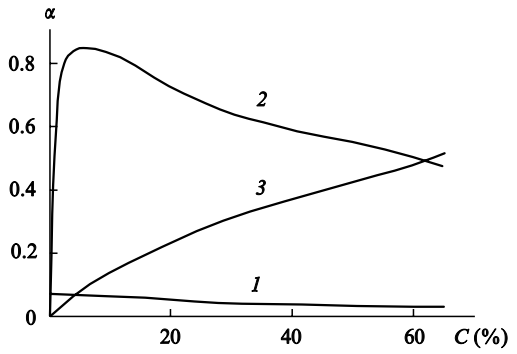


Figure 1. Dependence of the conversion of pendant double bonds (α) in cross-linking (*1*) and primary (*2*) and secondary cyclisation (*3*) on the overall conversion of the double bonds (C).[21]

which the macrogel is formed. Correspondingly, the homogeneity of the network increases with an increase in the contribution of secondary cyclisation and a simultaneous decrease in primary cyclisation.

2. Structural and kinetic heterogeneity of the reaction medium in three-dimensional radical copolymerisation

The true mechanism of three-dimensional (co)polymerisation is much more complicated than a model mechanism,[21] which takes into account only the topological peculiarities of network formation.[6,21] A crucial role in the formation of structures and properties of densely cross-linked polymers is assigned to microheterogeneous three-dimensional radical copolymerisation and structure-physical transformations, such as microsyneresis and vitrification of the reaction medium.[22–24]

From the moment of formation of microgel particles, the reaction medium becomes structurally and kinetically microheterogeneous due to lower mobility of the particles and a concomitant sharp decrease in the radical termination constant. As a result, the reaction is switched over to an autoacceleration mode (the gel effect).

Microgel particles can be regarded as microreactors consisting of two reaction zones, *viz*., an inner zone and a peripheral (near-surface) zone, which differ essentially in the effective reactivities and polymerisation rates of double bonds of a multifunctional oligomer.[23] The peripheral zone is characterised by higher rates of addition of double bonds of an oligomer to radicals localised on the surface of gel particles and thus unable to undergo recombination with analogous radicals of other particles. Slow polymerisation involving pendant double bonds occurs inside the microgel, its rate is limited by low mobility of the double bonds and steric hindrances, which prevents their addition to the radicals immobilised inside the microgel particles. Evidence for the existence of such limitations can be derived from the mode of attachment ('tail-to-tail'[25] or 'head-to-head'[26]) of the monomeric units, which is not typical of linear radical polymerisation. Steric constraints are important factors which control the stereoregularity of addition of the methacrylate groups and the topology of the netwok in the course of polymerisation of dimethacrylates.[27,28] They also determine the conformational state of network junctions, conformational dynamics and relaxation properties of the network itself.[27,29]

Pendant double bonds formed in a fast reaction of the radicals localised on the surface of microgel particles with one of the double bonds of the multifunctional oligomer M_1 are involved in a slow polymerisation inside the microgel particles. Consumption of the free oligomer and an increase in the size of a microgel particle result in a decrease in the effective size of the 'fast' reactor and an increase in the size of the 'slow' reactor to the size of a macrogel. As a result, the kinetics of three-dimensional polymerisation and copolymerisation of dimethacrylates switches over from an autoacceleration mode to an autoretardation mode.[23,30]

The structure–kinetic peculiarities of microheterogeneous three-dimensional radical polymerisation confer on it features of informal similarity with phase transition reactions, particularly crystallisation of polymers.[31] Based on this analogy, it was proposed to analyse the kinetic polymerisation curves conversion–time [$C(t)$] in the Avrami coordinates:[23]

$$C = 1 - \exp\left(-\sum_i k_i t^{n_i}\right), \qquad (6)$$

where k_i is the specific rate of polymerisation in the ith structural zone (*e.g*., in solution, on the surface or inside the microgel particle, *etc*.), which is proportional to the ratio of the rate constants for chain growth and chain termination (k_b) in this zone and n_i is the parameter which characterises the effect of the structure of the reaction medium on the rate of polymerisation in the ith zone.

Within the framework of this model, the value $n = 1$ corresponds to polymerisation under homogeneous conditions.[32,33] The value $n = 3$ entails total analogy to the polymerisation and phase transition where all the growing radicals are localised on the surface of polymer particles dispersed in the oligomer solution. In this case, $k_b = 0$ and the reaction proceeds in an autoacceleration regime. With an increase in the particle size, the particles merge and the contribution of the near-surface fast chain growth reaction diminishes and autoretardation of the polymerisation occurs. This structure–kinetic transition from near-surface to bulk polymerisation is manifested in a reduction of the parameter n due to diffusion-controlled constraints of the chain growth.

Studies into three-dimensional polymerisation of dimethacrylates have shown that, prior to autoretardation, the kinetic dependences plotted in the Avrami coordinates have one or two linear segments; their slopes yield the values of the parameter n in the range $1 \leqslant n \leqslant 3$ (see Refs 23 and 34). The autoretardation step is characterised by a gradual decrease of n to zero, which corresponds to termination of the reaction. The changes in the values of n are due to structural evolution of the reaction medium from a homogeneous solution of a polymer in an oligomer to the dispersion of microgel particles and the formation of a macrogel, which is accompanied by changes in the contributions of reactions occurring in different morphological zones to the overall reaction rate. The correctness of this statement was confirmed by *in situ* structural analysis of the reaction medium using light scattering techniques, NMR spectroscopy and dielectrometry.[22,35,36] The parameter n is highly sensitivite to changes in the structure-phase state of the reaction medium induced by solvents, precipitants, temperature, growth-limiting agents, *etc*.[23,34] Electron microscopic studies revealed a direct correlation between the numeric values of the parameter n and morphological characteristics of the polymers formed.[37] The validity of the use of the Avrami equation in the analysis of structure–kinetics relationships was confirmed by the fact that a similar equation was obtained with the help of an analytical method based on a kinetic scheme of three-dimensional radical polymerisation.[21]

In addition to topological and kinetic reasons, the microheterogeneous mechanism of three-dimensional radical polymerisation and copolymerisation has a thermodynamic reason which is related to the violation of the Flory–Rener[38] condition, *viz*., compatibility of a microgel with low-molecular-weight components of the reaction medium in the course of polymerisation. When the extent of the cross-linking inside microgel particles reaches a certain critical level, these components are displaced towards less densely cross-linked regions on the periphery of the microgel (syneresis). Because of diffusion-controlled limitations in macrogel formation, this process is not developed into separation of the system into two macroscopic phases, but is stopped in the microscopic level.[39] This process commonly referred to as microsyneresis results in structural and kinetic microheterogeneity of the reaction medium due to local vitrification in the central region

of microgel particles and violation of the homogeneous distribution of the reactants in the bulk of the reaction medium.

The redistribution of extrinsic molecular probes between zones with different network densities in the polymerisation of dimethacrylate **3** was established by the appearance of additional bands in the electronic absorption spectra of anthracene molecules localised in different zones of the polymeric matrix with different network densities.[27,28] The values of network densities calculated from absorption band frequencies of extrinsic anthracene molecules were equal to 1, 1.155 and 1.262 rel.u. The heterogeneity of molecular packing of the polymer of dimethacrylate **3**[28] was confirmed[40] by transmission electron microscopy, which revealed a bimodal distribution of heterogeneities according to their size (their diameters were 10 and 50–100 nm). These heterogeneities were related to the appearance of microgel particles preceding the macrogel formation.

Kinetic microheterogeneity of the initiation reaction can be due to involvement of initiator molecules in microsyneresis process[41] and increasing local concentrations of the initiator in less densely cross-linked areas. In this case kinetic heterogeneity can be further enhanced, since decomposition rates of radical polymerisation initiators increase with a decrease in the coefficient of molecular packing of the polymeric matrix.[42–44] Higher initiation rates of a monomer and pendant double bonds in areas with loose networks may result in homogenisation of network density over the bulk of the polymer. A significant improvement of the properties of network polymers after annealing and a relatively small increment in the conversion of the double bonds also suggest that in later polymerisation steps the reaction is predominantly localised in microzones with loosely cross-linked networks.[30]

In the case of three-dimensional copolymerisation, local relative concentrations of the comonomers M_1 and M_2 in the vicinity of growing radicals differ from their bulk-average concentrations due to microsyneresis.[12] This effect is manifested at higher effective reactivities of double bonds of the cross-linking reagent M_1 in comparison with the monomer M_2. It was shown[12,45] that microsyneresis observed in the copolymerisation of dimethacrylate **3** and butanediol dimethacrylate (**4**) with 2-methyl-5-vinyltetrazole (**5**) is accompanied by elimination of a less reactive compound **5** from the reaction zone of the microgel and a selective gel effect owing to consumption of double bonds of dimethacrylates **3** and **4** and pendant methacrylate groups. Specific heterogeneity of compositions of network copolymers formed is a natural consequence of microsyneresis and concomitant disturbances in the uniform distribution of comonomers.

The phenomenon of microphase separation of reaction components in the course of three-dimensional radical polymerisation and copolymerisation has found practical application in the production of liquid-crystal displays and synthesis of interpenetrating polymeric networks (IPN). One of the approaches to the production of such displays consists of polymerisation of diacrylates in solutions containing liquid-crystalline components.[46] The formation of a network induces phase separation and appearance of microdrops of a liquid-crystalline phase. By varying polymerisation conditions, one can control the degree of microphase separation and dispersity of liquid-crystalline inclusions into the network polymer matrix. Controlled microphase separation underlies the formation of structure and properties of interpenetrating polymeric networks one of which being formed by a three-dimensional radical (co)polymerisation mechanism, while the mechanism for the other is polycondensation (*e.g.*, urethane formation). Variation of relative rates of formation of these networks allows control over the degree of microphase separation of the reaction system components, phase morphology of IPN and their properties.[47,48]

3. Structures of network (co)polymers

In the context of this review, which is devoted to the analysis of structural and kinetic correlations in TRCP and their significance for the establishment of structure and properties of network copolymers, it seems expedient to highlight the role of reactivity ratios. If linear copolymerisation is carried out under homophasic conditions, the consumption of the monomers, the instantaneous composition of the copolymer formed and the distribution patterns of the monomeric units in the polymer chain are characterised by copolymerisation constants of the monomers r_1 and r_2.[49] Therefore, much attention is given to determination and refinement of these values for different comonomer pairs. The r_1 and r_2 values for many monomers are collected in reference books and are used in the design of experiments and simulation of copolymerisation processes.

In contrast to linear copolymerisation, three-dimensional copolymerisation cannot properly be described in terms of reactivity ratios of double bonds of a cross-linking reagent M_1 and a monomer M_2 because of the microheterogeneous mechanism of the three-dimensional copolymerisation, formation of pendant double bonds, microsyneresis of reaction components and vitrification of the reaction medium. These factors altogether largely determine effective reactivities of the double bonds in the starting oligomers M_1 and comonomers M_2 and pendant double bonds of the (co)polymer formed. The extent to which various factors affect the copolymerisation kinetics of individual reagents is different and depends on the composition of the original oligomer–monomer mixture and degree of conversion.[12,13,50]

Therefore, in order to minimise the specific effects of TRCP on r_1 and r_2 it is necessary that the values of the reactivity ratios of M_1 and M_2 were determined at low degrees of conversion ($< 1\%$) and at small concentrations of the cross-linking reagent ($< 1\%–3\%$). However, in this case, too, the differences in the reactivity ratios obtained by different authors are rather significant. Thus[51] the corresponding values for the copolymerisation of dimethacrylate **1** with methyl methacrylate (MMA, **6**) are as follows: $r_1 = 1.34$, $r_2 = 0.67$ (Ref. 51) or $r_1 = r_2 = 1$ (Ref. 52). Such discrepancies are due to the difficulty in isolation of the copolymer from the reaction mixture and different methods used for the determination of its composition and the content of pendant double bonds.

The ambiguity of the term 'monomer reactivity ratios', when speaking of the preparation of network copolymers, is spectacular as regards the differences in the values of r_1 and r_2 determined *in situ* in different steps of copolymerisation of *N*,*N*′-methylenebis(acrylamide) (**7**) and acrylamide (**8**) in D_2O using high-resolution ^{1}H NMR.[53] At a nearly zero conversion, $r_1 = 3.36$, $r_2 = 0.57$, whereas the corresponding values for the gel formation step ($C = 0.35$) are $r_1 = 1.77$ and $r_2 = 0.64$. It was suggested[53] that high reactivity of the double bonds in compound **7** at $C \approx 0$ favours the formation of microblocks of units **7** containing pendant double bonds as well as nonuniform distribution of the cross-links. The decrease in r_1 in the gelation step is attributed to microsyneresis and a decrease in effective reactivities of the double bonds.

It was suggested[12] that the ratio of copolymerisation rates of the cross-linking reagent and the monomer (w_1/w_2) was used as a parameter which takes into account all the structure-physical factors and characterises relative reactivities of double bonds. *In situ* determination of time dependences $w_1(t)$ and $w_2(t)$ throughout the whole polymerisation allows quantitative estimation of changes in the relative reactivities of the double bonds in the course of structural evolution of the reaction medium.

A comparison of experimental values of w_1/w_2 for different oligomer–monomer systems ($M_1 + M_2$) with those calculated from the Mayo–Lewis model (using experimental values of r_1 and r_2 for linear copolymerisation of the corresponding analogues) revealed their close fitting only for the very first reaction steps.[12,13,45] With an increase in the degree of conversion, both the experimental and calculated values diverge considerably. Thus in the copolymerisation of dimethacrylates **3** and **4** with deuterated methyl methacrylate (D-MMA) ($r_1 = r_2 = 1$ for linear copolymerisation of unlabelled and deuterated methyl methacrylate) this divergence amounts to 50% at high concentrations of the

cross-linking reagent. Obviously, in the three-dimensional copolymerisation the true reactivities of reagents determine the distribution of monomeric units in linear and branched macromolecules with pendant double bonds only in the initial steps of the reaction.[12] In turn, effective reactivities of M_1, M_2 and pendant double bonds begin to depend on the structure-physical state of the reaction medium with an increase in the degree of conversion, the appearance of microgel particles and the formation of a bulk polymer.

The topological, kinetic and thermodynamic factors altogether determine the microheterogeneous mechanism of three-dimensional copolymerisation and the structural heterogeneity of the network copolymer formed. It was found that the heterogeneity of moderately and strongly cross-linked networks increases with an increase in the density of the chemical cross-links.[54, 55] However, a specific type of non-homogeneity in a loosely cross-linked copolymer of methacrylate **6** with dimethacrylate **1** as a cross-linking reagent (0.1% – 0.5%) was observed.[56] Data from scanning near-field fluorescent microscopy suggest that local densities of segments within the copolymers under study exceed manyfold their average densities over the whole ensemble of chains. The segments vicinal to the cross-links form clusters ($\sim$ 10 nm) which merge to form heterogeneous structures the size of which amounts to several hundred nanometres. Presumably, the cross-links in such loose networks function as sites favouring supramolecular stacking of linear segments of polymer chains.

Convincing evidence in favour of microheterogeneity of network polymers was obtained by various methods which characterise different aspects of heterogeneity and differ in their resolution capacity. For example, microscopic methods allow revealing the microheterogeneity of polymer networks at the supramolecular level, whereas NMR and IR spectroscopy, at the molecular level.

High-resolution ^{1}H NMR provides direct information on the distribution of cross-links in model network copolymers prepared with involvement of a deuterated monomer M_2.[13] This method is based on the dependence of the width of the NMR line on the energy of magnetic dipole interactions between neighbouring H-containing units of the cross-linking reagent M_1. Since the units of deuterated M_2 function as non-magnetic diluents, the interaction of H-containing M_1 units and the width of the NMR line both depend on the distribution of the cross-links within the network. The efficiency of the method increases when network or linear copolymer analogues are analysed (Fig. 2).

The NMR line in linear copolymers prepared by copolymerisation of methyl methacrylate with a deuterated monomer (D-MMA) and containing up to 20% of H-MMA units remains narrow, which points to their statistical distribution among D-MMA units of the polymer chain. This is consistent with the values of their copolymerisation constants: $r_1 = r_2 = 1$. A further increase in the percentage of MMA units is accompanied by gradual broadening of the NMR line due to an increase in the number of MMA units constituting diads, triads and more lengthy sequences and the enhancement of their magnetic dipole interactions. In the case of network copolymers of triethylene glycol dimethacrylate with D-MMA, the broadening of the NMR line begins at dimethacrylate concentrations as low as < 5 mol.%. This points to a spatially heterogeneous distribution of cross-links in the bulk of the network copolymer. Apparently, such a heterogeneity can be accounted for by intramolecular cyclisation and microsyneresis, which results in the expulsion of D-MMA from microgel particles and a concomitant increase in the local concentration of the cross-links.

By virtue of their structural heterogeneity, network polymers and copolymers contain microzones which differ in local free volumes and mobilities of individual network elements. Using the polymer of dimethacrylate **3** as an example, it was shown [57, 58] that dynamic heterogeneity of network polymers causes the broadening of the time spectra of dielectric and mechanical α-relaxation. The microheterogeneity and the loss tangent a network increase

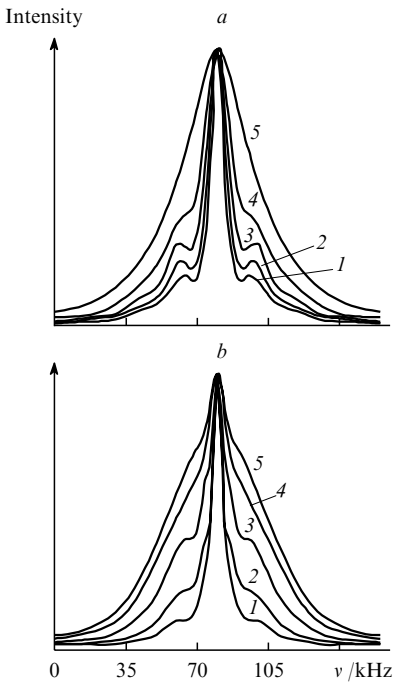


Figure 2. Dependence of linewidths in the NMR spectra of copolymers D-MMA with MMA (*a*) and with triethylene glycol dimethacrylate (*b*) on the concentrations of MMA and dimethacrylate.[13]
Concentrations of MMA (*a*) and dimethacrylate (*b*) /mol.%: (*1*) 1, (*2*) 5, (*3*) 20, (*4*) 50, (*5*) 100.

with an increase in its density.[58, 59] The width of the loss angle peak of a copolymer of **2** with divinylbenzene (**9**) prepared at 95 °C increases significantly with an increase in the concentration of compound **9** (from 5 mass % to 12 mass %). The glass-transition temperature of the copolymer (T_g) increases from 115 to 130 °C. The degree of deviation of T_g from the polymerisation temperature depends primarily on microheterogeneity of network polymers.[58] Synthesis of a microheterogeneous network polymer with T_g = 135 °C by polymerisation of diethylene glycol dimethacrylate (**10**) at room temperature supports this statement.

IR spectroscopy provides direct information about molecular structures of network polymers and copolymers. Studies of IR spectra of densely cross-linked polymers based on dimethacrylates

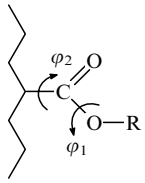
$$CH_2=C(CH_3)C(O)O-X-OC(O)C(CH_3)=CH_2$$

revealed that these spectra cannot be represented as a sum of the corresponding spectra of the linear poly(methyl methacrylate) (PMMA, **11**) and the oligomeric block X.[27, 28] The peculiarities of the IR spectra of poly(dimethacrylates) could be interpreted in terms of their cellular structure, which determines the conformation of atomic groups and stereoregularity of addition of methacrylate units.[27, 28] It was shown that syndiotactic addition of methacrylate units, which is thermodynamically more favourable than isotactic, is a more preferable route in linear radical polymerisation of the monomer **6** under ordinary conditions.[60] However, three-dimensional polymerisation of dimethacrylates shows a strong tendency of the probabilities of syndio- and isotactic addition of methacrylate groups to level off,[27, 28] which points to a greater contribution of thermodynamic factors responsible for the formation of the network structure in comparison with factors determining the stereospecificity of chain growth reactions in the linear polymer of **11**. In the case of three-dimensional polymerisation, the stereoregularity of the reaction of R* with C=C is controlled by steric factors and shrinkage stresses in the vicinity of the growing macroradicals.[16] When these stresses reach a certain critical level, the syndiotactic addition of methacrylate groups becomes thermodynamically less favourable and is replaced by

isotactic addition. The resulting changes in the packing conditions of atomic groups lead to alleviation of local stresses and a switchover of the chain growth reaction to a thermodynamically more favourable, *viz*., syndiotactic, route. Such a feedback between local stresses in network polymers and thermodynamics of a chemical reaction may bring about periodic switching of the chain growth reaction from one route of the addition of methacrylate groups to another. The microblock structure of polymethacrylate chains formed in this reaction seems to be the least significant (from the standpoint of structural hierarchy of network polymers) manifestation of the microheterogeneity of these processes.

The effects of steric hindrance and internal stresses on the stereoregularity of the addition of acrylate groups during the formation of network metallopolymers by radical polymerisation of zinc diacrylate have been established.[61]

The conformational state of methacrylate groups occupies a special place among characteristics of molecular structures of network (co)polymers based on oligodimethacrylates. These groups are localised in network nodes and their conformational dynamics determines largely the relaxation and physical-mechanical characteristics of poly(dimethacrylates).[29] The conformational states of methacrylate groups in network and linear polymers differ significantly [27, 28, 62] as can be evidenced from the differences in their IR spectra at the region of absorption bands of the C(O)O – R groups (1100 – 1300 cm^{-1}). Their frequencies depend on the values of the internal rotation angles φ_1 and φ_2.



The bands at 1197 and 1172 cm^{-1} in the absorption spectrum of the polymer **11** (Fig. 3) correspond to the vibrations of *cis*- and *gauche*-isomers which differ in the angle φ_1, whereas the bands at 1246 and 1275 cm^{-1} correspond to the oscillations of the ester group in conformations differing by the rotation angle φ_2 relative to the main chain.[62, 63, 64] Similar absorption bands are present in the IR spectrum of poly(dodecyl methacrylate) (**12**). However, in contrast to the polymer **11**, the intensity of the band corresponding to its *gauche*-isomer exceeds markedly that of the *trans*-isomer. This suggests that stabilities of ester-group isomers in linear polymers are determined by intermolecular interactions of alkyl substituents.

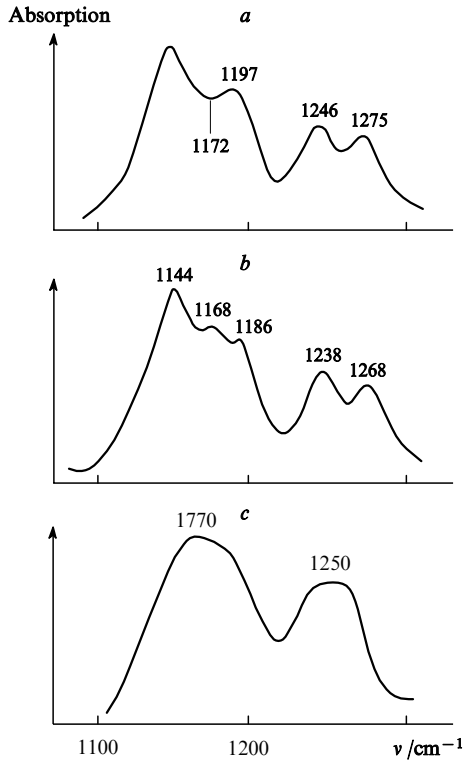
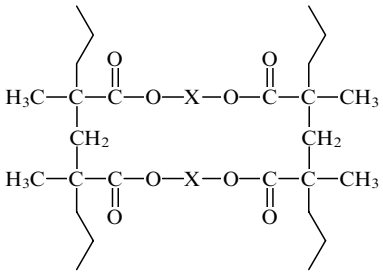


Figure 3. IR spectra of polymers of MMA (*a*), dodecyl methacrylate (*b*), butanediol dimethacrylate (*c*).[62]

In contrast to linear polymers **11** and **12,** the IR spectrum of a network polymer of dimethacrylate **4** (Fig. 3 *c*) contains only one broad absorption band around 1200 – 1140 cm^{-1} instead of several bands corresponding to individual isomers. This suggests a broad distribution of ester group conformations in network nodes over all possible values of the angle φ_1. The change in relative intensities of a pair of bands corresponding to ester groups with different rotation angles φ_2 relative to the main chain is also noted. This situation is typical of many densely cross-linked polymers, although some of its manifestations depend on the length and flexibility of the oligomeric block X.[29] It may thus be concluded that the conformational state of ester groups in network polymers is determined by the packing of several adjacent nodes and the spatial architecture of the network cells rather than by local energy minimum of intermolecular interactions, as in linear polymers.



Obviously, such packing is provided by cooperative conformational dynamics and is limited by local free volume. The global energy minimum of the network cells is reached through variation of conformation energies of all of its constituent ester groups and the oligomeric blocks X.

The differences in the stereoregularity of the addition of methacrylate units and the conformation energies of ester groups in linear PMMA and in network polymers can be the reason for differences in specific heats of polymerisation of MMA and methacrylate groups in dimethacrylates.[16, 45, 62]

In some cases, chemical cross-links and the cellular structure of the network prevent approach of atomic groups to each other and intermolecular interactions in a rigid glassy matrix. This phenomenon commonly known as the loosening effect of chemical crosslinks [65] is manifested in a decrease in the molecular packing coefficient (MPC) for copolymers of **1** with MMA with an increase in the concentration of the cross-linking reagent.[66]

Concentration of **1** (mass %)	3	10	20
MPC	0.689	0.671	0.648

The copolymer with a maximum content of **1** manifests the highest compressibility in the glassy state due to the loosening of chemical cross-links. At the same time, a copolymer with a lower content of **1** manifests higher compressibility in a high-elasticity state.[66]

In densely cross-linked polymers of dimethacrylate, the loosening effect is manifested as higher amplitudes of torsional vibrations of atomic groups [65] and the dependence of the mechanism of water absorption on the network density.[67] It has been shown [30] that the loosening effect makes a significant contribution to physical-mechanical and sorption characteristics of a polymer of dimethacrylate **1** and copolymers of **1** with styrene.

Chemical shrinkage of the reaction medium has a strong impact on the structure and properties of network (co)polymers prepared by radical polymerisation of vinyl compounds.[4, 68–71] The reason should be sought in the fact that the distances between monomer molecules are determined by the sum of the van der Waals radii of outer atoms (~3.4 Å), while the distance between the monomeric units in the polymer chain depends on the length of the C–C bond (~ 1.5 Å). In turn, shrinkage depends on the size of the monomer molecule and decreases on going from MMA to butyl methacrylate (**13**) from 21.01 vol.% to 15.33 vol.%.[70]

In the linear polymerisation, shrinkage and polymerisation occur simultaneously, while in the case of three-dimensional polymerisation, shrinkage can lag behind as a result of which excess free volume can form in the polymer gel.[4, 69] In this case, the lag is caused by a virtually instantaneous addition of the double bond to the radical, while the relaxation of the excess free volume is limited by the low rate of cooperative rearrangements of the network. It was found that the higher the rate of photopolymerisation the greater the lag in shrinkage.[69] The maximum conversion of double bonds increases owing to the appearance of excess free volume and an increase in molecular mobilities of reaction components.

If three-dimensional polymerisation is accompanied by vitrification of the network polymer formed, the relaxation of the volume of the reaction medium to the equilibrium state is freezed virtually completely resulting in the appearance of internal stresses within the system.[16] These significantly deteriorate the quality of the articles prepared by TRCP and considerable attention is given to their analysis.[71, 72] It was found[72] that photopolymerisation of multifunctional (meth)acrylates is accompanied by the appearance of internal stresses following onset of vitrification, which increase monotonically and progressively throughout the reaction. The rates of stress appearance increase with an increase in the functionality of the monomer, a decrease in the length of the oligomeric chain and a decrease in the concentration of the plasticiser. These trends are much more pronounced for methacrylates than for acrylates. It was thus suggested that the level of internal stresses increases with an increase in the elasticity modulus of the polymer formed.[72]

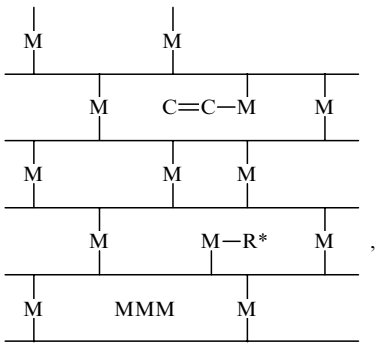
The total level of shrinkage stresses can be estimated as the energy of formation of an excess free volume ΔV in a network polymer with a bulk modulus K (see Ref. 16).

$$U \approx K\Delta V.$$

However, this expression is valid only for a model of a homogeneous network. In practice, the distribution of stresses in the bulk of a polymer is non-homogeneous due to the microheterogeneity of the three-dimensional polymerisation mechanism. Shrinkage stresses are usually concentrated in network zones at the junction of microgel particles. These particles can be regarded as microreactors where the chemical shrinkage occurs in a direction opposite to the propagation of the polymerisation front.[27] Therefore, the superposition of polymerisation fronts of several microreactors can bring about tensile stresses in the passing chains connecting different zones of the polymer formed in different microreactors. Quite probably, these stresses stimulate the cleavage of polymer chains and initiate the formation of microcracks in attempted synthesis of supercross-linked polymers of dimethacrylate.[68]

The heterogeneous distribution of stresses in the bulk of a polymer is the reason for specific features of thermal degradation of MMA copolymers with ethylene glycol, butanediol and hexanediol dimethacrylates where the content of the latter varies from 0.5 mol.% to 27 mol.%.[73] The degradation of copolymers occurs in two steps. In the first step, the degradation rate decreases progressively as the degree of cross-linking increases irrespective of the length of the cross-linking reagent, which is characteristic of moderately dense networks. In the second step, the degradation rate changes abnormally: it increases progressively with an increase in the degree of cross-linking and a decrease in the length of the spacer. Such a two-step degradation mechanism can be attributed to the presence of alternating loosely and densely cross-linked zones in the copolymer; cleavage of chemical bonds in the latter zones is induced by internal stresses.[73]

Considerable internal stresses can be developed in network polymers prepared by radical polymerisation of multifunctional metal-containing monomers of the type C=C–M–C=C, where M is an atom of a metal or a complex.[61, 74] Because of a small distance between the double bonds of organic ligands and their strict spatial fixation by a bridging atom M, the target polymer has a rigid small-meshed structure



which prevents chemical shrinkage and volume relaxation. As a result, growth of the polymer chains occurs under conditions of strong steric limitations and at higher internal stresses.

Direct evidence for the presence of internal stresses in a network polymer prepared from zinc diacrylate was obtained in the analysis of low-frequency IR spectra in the region of oscillations of the central fragment –O–M–O– (see Ref. 61). Instead of two narrow bands at 300 and 410 cm^{-1} characteristic of the monomer, the spectrum of this polymer contained one broad band at 340 cm^{-1}, which suggests distortions in the geometry of the bridging group induced by internal stresses. It was found[74] that internal stresses developed upon radical polymerisation of the $PdCl_2Y_2$ complex (Y is 2-methyl-5-vinyltetrazole) induce the cleavage of the metal–ligand bond and evolution of the inorganic microphase (MMM). An X-ray diffraction analysis of this complex has shown that the high level of internal stresses that appear upon polymerisation is due to strong steric shielding of the C=C bonds.[75] The inorganic microphase evolved in network polymers by virtue of internal stresses represents special manifestation of mechanochemical syneresis.

Since the reason for internal stresses in three-dimensional (co)polymerisation is incomplete shrinkage, total shrinkage can be reduced through the use of oligomers with a greater length of the spacer and plasticisers.[72] The total level of shrinkage and internal stresses can successfully be decreased using two-step synthesis of network (co)polymers. Its first step includes the synthesis of oligo(methacrylates) containing a large number of reactive double bonds from dimethacrylates.[28, 76] The use of such precursors in paint-and-varnish compositions employed as polymeric coatings improves their quality due to elimination of shrinkage stresses.[77] Slightly cross-linked gels based on dimethacrylates are used for the preparation of gradient light-focusing optical materials.[2] To do this, cylindrical gels are placed into a vessel filled with a solution of a monomer with a lower refraction index. A parabolic gradient of the monomer concentration is developed due to diffusion and is fixed by photopolymerisation. Non-shrinking spiroorthoester vinyl compounds proved to be valuable materials in the production of high-precision optics.[78] Radical polymerisation of these compounds at the double bonds is accompanied by the ring opening and the formation of a carbonyl group, which has larger size than that of the original ester ortho group. As a result, this reaction occurs without shrinking or is accompanied by a small increase in the volume. Non-shrinking compositions are prepared by copolymerisation of spiroorthoesters with ordinary vinyl monomers.[78]

Three-dimensional radical (co)polymerisation is widely employed for compression moulding of miscellaneous articles; therefore, much attention is given to the study of relationships between physical-mechanical properties of network copolymers and the structure of the starting oligomers and polymerisation conditions. An attempt has been made [24] to estimate the contribution of the structure of the starting oligoester methacrylates, intermolecular interactions and MPC into physical-mechanical characteristics of network polymers. The lack of a correlation between MPC and physical-mechanical characteristics of the polymers formed suggests that it is the distribution function of free volume rather than its absolute value that determines the properties of densely cross-linked polymers. Evidence for this assumption can be derived from the bimodal distribution of free volume in a polymer of triethylene glycol dimethacrylate as established by IR spectroscopy of adsorbed water.[67] It was found that the relative fractions of microvoids adsorbing small clusters $(H_2O)_n$ and of large pores absorbing water condensate depend on the polymerisation temperature.

Studies on physical-mechanical properties of network polymers based on oligocarbonate (meth)acrylates have shown [79] that the elasticity moduli determined from the initial portion of the deformation–stress diagram decrease with an increase in the spacer length and lowering of the energy barrier to internal rotation around the C–C bond. The elasticity modulus on compression is smaller than on stretching, which may be due to a greater contribution of the high-elasticity deformation component on compression. The differences in the chemical nature and lengths of oligomers and, correspondingly, molecular structures of polymer networks are especially apparent at initial portions of these diagrams. In regions of nonlinear dependence of stress *vs.* deformation, the differences in morphological characteristics of polymers predominate. A close relationship was found between the deformation-strength and relaxation characteristics of the polymers studied.[79] A similar correlation exists between thermomechanical and relaxation characteristics of network polymers based on oligomeric dimethacrylates.[57]

Studies of opticomechanical properties of model polymers based of diallyl and divinyl compounds of homologous series:

$$CH_2=CHCH_2OC(O)-(CH_2)_n-C(O)OCH_2CH=CH_2$$

$n = 2-8$, **14**

$$CH_2=CHC(O)O-(CH_2)_n-OC(O)CH=CH_2$$

$n = 2-6$, **15**

$$CH_2=C(CH_3)C(O)O-(CH_2)_n-OC(O)C(CH_3)=CH_2$$

$n = 2-6$, **16**

have been undertaken aimed at elucidation of the role of topological and morphological structures in the establishment of physical-mechanical characteristics of network polymers.[80]

Isochronic temperature dependences of the elasticity moduli $E = f(T)$ and optical sensitivity with respect to stress $D = f(T)$ have been determined [80] rather than deformation–tension dependences.[24, 79] Such a comprehensive approach has demonstrated non-additive changes in isothermic values of functions $E = f(n)_T$ and $D = f(n)_T$ on the number of the CH_2 groups in the homologous series of the polymers under study. There was no strict correlation between elastic and photoelastic characteristics and the length of the starting oligomers **14** and **15**.

The dependence of opticomechanical characteristics of densely cross-linked polymers on the structure of the starting oligomers is indirect rather than direct and is manifested as the peculiarities of topological structures of networks formed in three-dimensional polymerisation.[80] The differences in the properties of the polymers prepared from diallyl (**14**) and divinyl (**15**, **16**) oligomers are due to the fact that the former are prepared by cross-linking branched macromolecules, while the latter are synthesised by cross-linking primary microgel particles having colloidal sizes. A cage model of a network polymer was proposed [80] based on the established contributions of energy and entropic elasticities of deformed network polymers. According to this model, some interjunction chains have a rigid conformation, while the other undergo rotational-isomeric transitions and are responsible for the entropic elasticity of polymeric networks. This model has been rationalised taking into account the microtactic characteristics of polymeric chains and conformational structures of densely cross-linked polymers based on oligomeric dimethacrylates.[27, 28]

It was found [24, 79, 80] that the control of physicomechanical properties of network polymers by variation of the structures of the starting oligomers is inefficient due to microheterogeneity of the three-dimensional polymerisation mechanism, which determines topological and morphological structures of the final polymer. This stimulates a search for novel approaches to a control over topological and morphological structures of network polymers in the stage of their synthesis, *e.g.*, through the control over intramolecular cyclisation and intermolecular cross-linking reactions.[30]

III. Methods for *in situ* investigation of three-dimensional radical copolymerisation

Structural and kinetic studies of TRCP demand separate determination of the kinetics of consumption of double bonds of the cross-linking reagent M_1 and the monomer M_2 over the whole process. The sampling method and the analysis of the compositions of the copolymer and the monomer mixture in the course of the reaction applicable in linear copolymerisation cannot be used in this case, since insoluble network copolymers are formed in the earliest steps of TRCP. As for the calorimetric method widely used in the kinetic studies of three-dimensional homopolymerisation,[7] its application in TRCP is limited, since it allows one to measure the overall heat of the copolymerisation reaction and concomitant structural and physical transformations of the reaction medium.

The calorimetric method was used [81] for the study of copolymerisation of dimethacrylate **1** with styrene. By analogy with linear copolymerisation of styrene with MMA, the authors assumed that this reaction is azeotropic and used averaged values of molar heats to calculate the conversion:

$$Q = 0.5(Q_1 + Q_2),$$

where Q_1 and Q_2 are the known molar heats of homopolymerisation of styrene and MMA. However, these calculations did not take into account the fact that the heats of bond formation in the diads M_1M_2 in the copolymerisation of these monomers differ from those in the diads M_1M_1 and M_2M_2.[60, 82] One should also keep in mind that, apart from chemical reactions of the opening of C=C bonds, differences in the conformation energies of network polymers and its linear analogue and shrinkage stresses make significant contributions to the overall heat of three-dimensional copolymerisation.[83] The contribution of these structure-physical components to the heats of formation of network copolymers can apparently be ignored only in comparative studies of kinetics of copolymerisation of the same type of systems at the qualitative level.

Thus, the experimental base for the study of TRCP could not be formed by simple borrowing methods for investigations into linear copolymerisation, on the one hand, and the performance of three-dimensional homopolymerisation, on the other hand. Therefore, special methods of spectroscopic monitoring for *in situ* structure-and-kinetic investigation of TRCP have been developed to solve this problem.

1. IR spectroscopic monitoring

IR spectroscopic monitoring of TRCP is based on the construction of curves of double bonds consumption in the oligomer $[C_1(t)]$ and the monomer $[C_2(t)]$ from the decreage in the intensities of

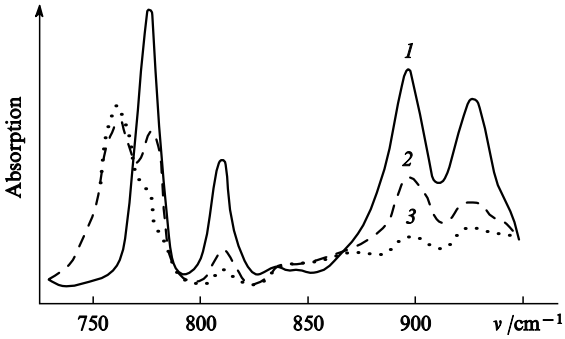


Figure 4. IR spectra of the original mixture (ethylene glycol dimethacrylate–styrene) (molar ratio, 1:2) (*1*), after 8 h polymerisation at 30 °C ([CPC] = 5 mass %) (*2*) and after 8 h annealing at 60 °C (*3*).[83]

absorption bands of the corresponding $C=CH_2$ groups. The main criterion in the choice of analytical bands is their minimum overlapping in the spectrum. In many oligomer–monomer systems, this criterion is met by the bands of deformation vibrations of hydrogen atoms in the region of 750–950 cm^{-1}. In the copolymerisation of ethylene glycol dimethacrylate with styrene and dicyclohexyl peroxydicarbonate (CPC) as an initiator, the intensities of all absorption bands related to deformation vibrations of $C=CH_2$ bonds of methacrylate groups (945, 812 cm^{-1}) and styrene (907, 780 cm^{-1}) shows a tendency to decrease reaching a constant level characteristic of residual unsaturation of the copolymer at a given temperature (Fig. 4).[83] Subsequent increase in the temperature results in 'thawing' of the mobilities of styrene, ethylene glycol dimethacrylate and pendant methacrylate groups, as a result of which copolymerisation continues up to the moment when the copolymer formed passes again into a glassy state (Fig. 4, curves *2* and *3*). Similar changes in the IR spectra are observed in the copolymerisation of triethylene glycol dimethacrylate with styrene.

The conversion curves of the methacrylate groups and styrene[83] are shown in Fig. 5. A decrease in the content of residual methacrylate groups on going from ethylene glycol dimethacrylate to triethylene glycol dimethacrylate suggests that the short oligomeric block significantly hinders the mobilities and decreases the effective reactivities of pendant methacrylate groups in comparison with a more lengthy oligomeric block.

Studies of TRCP of model systems based on monomers and multifunctional oligomers and carrying similar reactive groups (MMA with dimethacrylates, styrene with divinylbenzene) present considerable interest. However, the analytical bands of

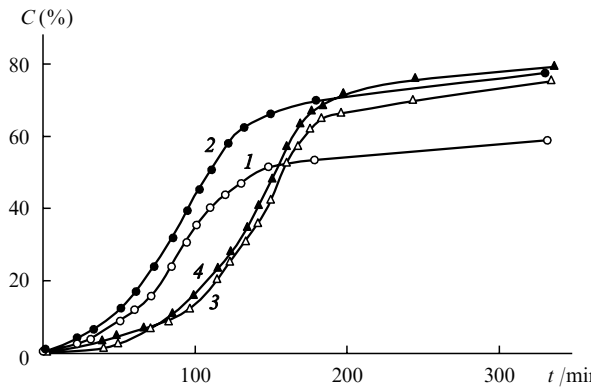


Figure 5. Copolymerisation kinetics of ethylene glycol dimethacrylate (*1*) with styrene (*2*) and triethylene glycol dimethacrylate (*3*) with styrene (*4*).[83]
Dimethacrylate : styrene ratio 2:1, T = 30 °C, [CPC] = 5 mass % (*1*, *2*) and 3 mass % (*3*, *4*).

the monomer and oligomer overlap completely. In this case, separate investigation of the copolymerisation kinetics can be carried out by replacing one of the comonomers by its deuterated analogue. Thus on going from MMA to D-MMA, the vibrational frequency of the C=C bond decreases from 1638 to 1592 cm^{-1}, which allows separate registration of copolymerisation rates of the double bonds of D-MMA and dimethacrylate.[13]

Monitoring of consumption of reactive groups using absorption bands of vibration overtones in the near IR region of the spectrum significantly expands the potential of the studies of (co)polymerisation in multicomponent systems. As the overtone frequences ν_{0-2} are associated with the main vibrational frequency ν_{0-1} by the ratio:

$$\nu_{0-2} \approx 2\,\nu_{0-1},$$

the absorption bands of the overtones are characterised by a better resolution than the neighbouring main vibration bands. Near-IR monitoring was used[48] in a study of two interpenetrating polymer networks one of which was prepared by radical copolymerisation of bisphenol A diglycidyl ether dimethacrylate (**17**) with styrene, while the other, by a reaction of diglycidyl ether of bisphenol A (**18**) with 4,4′-diaminodiphenylmethane (**19**). The kinetics of formation of each interpenetrating network could be studied by analysing overtones of vibration bands of the epoxy group, styrene and methacrylate groups at 6073, 6135 and 6166 cm^{-1}, respectively.

The achievements in the production of equipment for IR spectroscopy are so significant that they can meet virtually any demands of investigators in the field of three-dimensional (co)polymerisation. Modern Fourier spectrometers allow the registration of rates of superfast three-dimensional photopolymerisation reactions of acrylic and methacrylic compounds in microsecond time spans with time resolution of 10^{-3} s (see Ref. 84). Layer-by-layer scanning of polymeric coatings can be performed and the degree of conversion can be judged using real-time attenuated total reflectance-Fourier transform IR spectroscopy.[85] The use of optofibre connections permits one to conduct kinetic monitoring in polymerisation reactors located at a distance of up to 100 m from the spectrophotometer.[86]

An analysis of the kinetic data by spectroscopic monitoring is often confined to a discussion of the conversion *vs.* time dependences.[5,48,85] The presentation of experimental data in the copolymerisation rate–time coordinates makes it possible to increase the amount of information obtained by this method.[11–13] The ratio of copolymerisation rates in the oligomer M_1 and the monomer M_2 (υ_1/υ_2) is yet another important structure–kinetic feature of TRCP reactions which reflects the instantaneous composition of a copolymer. Valuable information about the state of a reaction system can be obtained from a comparison of experimental dependences of the rates *vs.* reaction time $(w_1/w_2)_{exp}$ with the dependences calculated on the basis of the Mayo–Lewis model according to the equation:

$$\left(\frac{w_1}{w_2}\right)_{cal} = \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}, \qquad (7)$$

where $[M_1]$ and $[M_2]$ are the current concentrations of the C=C bonds calculated on the basis of the experimental dependences $C(t)$.

IR spectroscopic monitoring allows one to follow the disturbances in the uniform distribution of reactants in TRCP. Such disturbances can be due to microsyneresis of the components from microgel particles (microreactors) and low molecular mobility of the medium in the vitrification step, as a result of which diffusional flows of the reactants to the active sites cannot compensate for the consumption of a more reactive monomer. Deviation of the experimental ratio of the reduced copolymerisation rates $(w_1/w_2)_{exp}$ from the values of $(w_1/w_2)_{cal}$ calculated by the Mayo–Lewis model is a criterion for the estimation of such disturbances.[12,45]

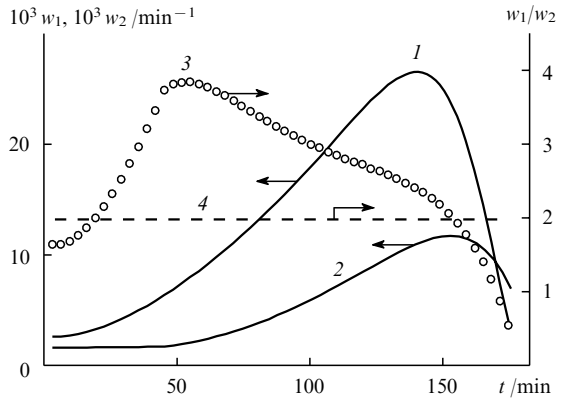


Figure 6. Copolymerisation kinetics of butanediol dimethacrylate (14.5 mass %) with 2-methyl-5-vinyltetrazole.[12]
(*1*, *2*) Copolymerisation rates (w_1 and w_2, respectively), (*3*) experimental values of w_1/w_2, (*4*) values of w_1/w_2 calculated from Eqn (7).

The TRCP of dimethacrylates with 2-methyl-5-vinyltetrazole is a special case of disturbances in the concentration homogeneity of the reaction medium.[12,45] Prerequisites for the appearance of concentration heterogeneities in such systems are significant differences in the reactivities of methacrylate groups of oligomers and vinyltetrazole (for linear copolymerisation of MMA with 2-methyl-5-vinyltetrazole $r_1 = 1.47$, $r_2 = 0.51$, respectively) and low content of the cross-linking reagent.

Figure 6 shows the experimental dependences of the reduced copolymerisation rates of butanediol dimethacrylate (**4**) and the monomer **5** as well as the experimental and calculated dependences of the ratios (w_1/w_2) *vs*. time. A comparison of curves *1* and *2* demonstrates that copolymerisation of methacrylate groups occurs as an autoaccelerating reaction from the very beginning, while the monomer **5** is polymerised initially at a constant rate. A possible reason for the selective gel effect in the polymerisation is disturbances in the initially uniform distribution of reagents in the vicinity of the growing macroradical due to the enrichment of the polymer chain with monomer units carrying pendant methacrylate groups due to low copolymerisation constant of vinyltetrazole.

As a result, the local concentration of methacrylate groups in the vicinity of the growing macroradical $[M_l]$ increases in comparison with their average concentration in a reactor $[M_m]$, the latter being determined by spectroscopic methods and used for the calculation of the reaction rates.

$$w = \frac{\upsilon}{[M_m]}.$$

This results in the overestimation of w values perceived as a selective gel effect. No such effect is observed at high concentrations of butanediol dimethacrylate. It was therefore concluded that high flexibility of the growing macroradical containing a large number of units of the monomer **5** is a prerequisite for its manifestation. Evidently, at high content of these units the macroradicals have a coil conformation, which favours intramolecular cyclisation. Selective gel effect can lead to the formation of a specific microheterogeneous network structure consisting of regions with higher concentration of the cross-links incorporated into a loosely cross-linked matrix enriched with units derived from 2-methyl-5-vinyltetrazole.[12]

The experimental values of w_1/w_2 significantly exceed the calculated values (see curves *3* and *4*, Fig. 6) over a broad range of conversions. This difference cannot be explained only by the increase in the local concentration of pendant methacrylate groups.[12] The exit of the monomer **5** from the reaction zone as a result of microsyneresis also seems to play a role in the concentration heterogeneity of the medium. Contrariwise, in the terminal step the experimental values of w_1/w_2, are much lower than the calculated ones.This can be due to higher mobility of the monomer **5** in comparison with dimethacrylate **4** and pendant methacrylate groups under conditions of vitrification of the reaction medium, as a result of which $[M_l]$ in the vicinity of the macroradicals becomes lower than $[M_m]$.

It was shown [12,13,45] that TRCP and the concomitant structure-physical transformations of the reaction medium may induce non-uniform distribution of the reactants in the vicinity of growing macroradicals and, as a consequence, compositional heterogeneity of copolymers. Thus topological peculiarities of TRCP play a role in the formation of compositional heterogeneity of network copolymers. These include cyclisation and selective gel effect in the initial steps of the process, microsyneresis of reactants, differences in the rates of diffusional transport of reactants to macroradicals in the step of vitrification of the reaction medium.

IR spectroscopic monitoring is a promising method for the *in situ* studies of structure–kinetic relationships in TRCP which consists of recording kinetic curves for the decomposition of initiators of the radical polymerisation $C_i(t)$.[50] The vibration bands of the C=O bonds of benzoyl peroxide and dicyclohexyl peroxydicarbonate lie in a convenient region for measurements (1770–1820 cm^{-1}) depending on the type of intermolecular interactions and do not overlap with the absorption bands of C=O in the decomposition products.[87] Their intensities are sufficiently high for registration of the dependences $C_1(t)$, $C_2(t)$ and $C_i(t)$ in one experiment. Combined analysis of these dependences enables the estimation of the contribution of a decrease in the decomposition rates of the initiator to inhibition of TRCP in the vitrification step.[50]

2. NMR studies of formation of network polymers

NMR spectroscopy is widely used for the *in situ* studies of copolymerisation kinetics and the structures of the copolymers formed. The conversion of the double bonds of comonomers is determined from the decrease in the intensities of signals for vinyl protons using high resolution ^{1}H NMR spectrometers.[88,89] Studies of ternary copolymerisation of hydroxyethyl methacrylate (**20**) with *N*-vinyl-2-pyrrolidone (**21**) and *tert*-butyl-2-hydroxycyclohexyl methacrylate (**22**) using this method made it possible to obtain conversion curves for each individual comonomer and to determine the instantaneous composition of the ternary copolymer at various degrees of conversion.[88]

The copolymerisation of acrylamide with bisacrylamide in D_2O has been studied in especially great detail.[26,53] This study revealed a nearly twofold decrease in effective reactivities of the double bonds of bisacrylamide with an increase in the depth of conversion due to accumulation of a great number of less mobile pendant acrylamide groups.[53] A large number of 'head-to-head' additions of the monomeric units testifies to the microheterogeneity of the copolymer structures at the molecular level.[26]

Pulse NMR was used [35,90,91] for the study of formation of network polymers during polymerisation of dimethacrylates. NMR data confirm the validity of the microheterogeneous mechanism of three-dimensional radical polymerisation [23,92] and enable more detailed investigations into formation of network polymers.

3. Dielectric relaxation spectroscopy

The effect of structure-physical transformations of the reaction medium on the kinetics of three-dimensional radical polymerisation is largely realised through changes in the molecular mobilities of the reactants.[36] On-line monitoring of three-dimensional polymerisation by dielectric relaxation spectroscopy in a broad frequency range (as a rule, from 1 to 10^5 Hz) provides comprehensive information about the evolution of structural and dynamic characteristics of the reaction medium. This allows one to follow *in situ* changes in the rotational mobilities of polar groups by changes in the dielectric conductivities ε and transla-

tional mobilities of impurity ions by changes in the electric conductivity σ and to observe microphase separation from the appearance of Maxwell–Wagner interlayer polarisation.[36, 57, 93–95] The informativity of this method increases appreciably when kinetic polymerisation studies are supplemented by calorimetry [36] and IR spectroscopy.[96]

The correlations between the features of molecular motion at different depths of polymerisation and kinetic characteristics of this process were established using a specially designed measuring cell [36] for simultaneous *in situ* registration of dielectric permittivity, conductivity of the reaction medium and heat evolution. It was found that a sharp decrease in the rate of linear polymerisation of MMA, which is due to the vitrification of the reaction medium, correlates with a sharp decrease in dielectric permittivity. This suggests that the freezing of the forward-rotational motion of MMA molecules over the whole bulk of the polymerisate is the main reason for autoretardation of the reaction.[36]

Three-dimensional polymerisation of oligomeric dimethacrylates, in contrast with polymerisation of MMA, is characterised by a broad range of autoretardation and an even broader (as regards conversion) zone of reduced dielectric permittivity.[36, 57] A broad range of dispersion of the dielectric permittivity testifies to the structural and dynamic heterogeneities of the polymerisates formed. Initial manifestations of a decrease in dielectric permittivity are due to the formation of fragments of a network with interjoint distances lower than the size of the kinetic segment (local vitrification). Further gradual decrease in dielectric permittivity down to maximum conversions suggests that fragments with a loose cross-linking where segmental mobility of the network components still remain in the polymer. This molecular mobility resource is used for enhancing the conversion in three-dimensional polymerisation and (co)polymerisation by increasing the temperature in the final step.[83]

The initial steps of three-dimensional polymerisation of dimethacrylates are often accompanied by abnormal increase in dielectric permittivity.[36, 57] The appearance of a positive increment $\Delta\varepsilon$ against the background of a general tendency of the dielectric permittivity to decrease owing to a decrease in the mobility of polar methacrylate groups included into the network is attributed to the formation of a microheterogeneous structure of the polymerisate, which restricts the mobilities of ionic impurities. An analysis of different models of microheterogeneous polymerisates revealed that these abnormalities can be explained by the 'reversal' of the matrix for the mechanism of interlayer polarisation and by using the theory of polarisation of the diffusion zone of the double electric layer.[97, 98]

A promising approach to the study of three-dimensional radical copolymerisation entails the use of complex techniques which include simultaneous monitoring of the reaction by dielectric relaxation and IR spectroscopy. The use of model oligomer–monomer systems allowing selective monitoring of molecular mobility of a polar cross-linking reagent (dimethacrylate) in a non-polar medium of the second monomer (styrene) seems to be a very informative approach.

4. Fluorescent probes

The use of fluorescent molecular probes for the study of polymerisation processes is based on high sensitivity of emission spectra parameters to intermolecular interactions and structure-physical state of the medium. The changes in the state of the nearest environment of luminophore molecules may bring about shifts in the maximum of the emission band, enhancement of the fluorescence intensity and changes in the anisotropy and fluorescence lifetime.[99] On-line measurements of these parameters in the course of polymerisation provide direct information about the structural evolution of the reaction medium.[100]

The fluorescence method was used for the study of the sol–gel transition in the copolymerisation of MMA with compound **1** [101–103] using pyrenemethyl pivalate as a probe. It was found that the intensity of fluorescence (I) at the moment of sol–gel transition (t_c) was sharply increased due to freezing of molecular mobility and an increase in the quantum yield of the fluorescence. A comparison of the experimental dependence t_c on the concentration of ethylene glycol dimethacrylate c_0 (see Ref. 101) with a calculated dependence obtained on the basis of a kinetic model of gel formation [104]

$$t_c = (kc_0)^{-1}, \tag{8}$$

where k is the combination of rate constants for all steps of the reaction, revealed that at the dimethacrylate concentrations above 0.5% the experimental values of t_c exceed manyfold the calculated values and are little dependent on the concentration of dimethacrylate in the reaction mixture (Fig. 7). These discrepancies are due to a decrease in the overall rate constant k caused by a decrease in the probability of involvement of pendant methacrylate groups in the molecular cross-linking.[101, 105]

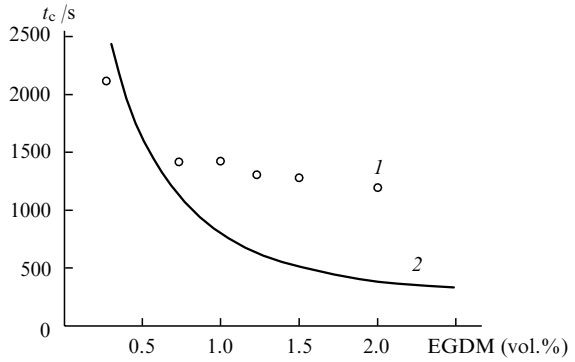


Figure 7. Dependence of the onset of gel formation in copolymerisation of MMA with ethylene glycol dimethacrylate (EGDM) at 75 °C on the concentration of dimethacrylate.[101]
(*1*) Experimental data, (*2*) curve calculated from Eqn (8).

The experimental dependences $I(t)$ were used [101–103] for determining the numerical value of a critical parameter β in the expression for the sol–gel transition in the framework of a percolation gel formation model:[106]

$$G = B(p - p_c)^{\beta}, \tag{9}$$

where G is the share of the gel fraction, B is the critical amplitude and p is the probability of formation of a bond between the adjacent junctions of the network. If $p = p_c$, this corresponds to the onset of formation of an infinite cluster, *viz*., the gel point. Assuming [101] that the reaction time t is proportional to the probability p, the time t_c corresponds to the gel point, and the fluorescence intensity corresponds to the amount of the gel formed, Eqn (9) can be converted into Eqn (10):

$$I = A(t - t_c)^{\beta}, \tag{10}$$

where A is a new critical amplitude. The values of β determined from the slope of the dependences:

$$\log I = \log A + \beta \log(t - t_c)$$

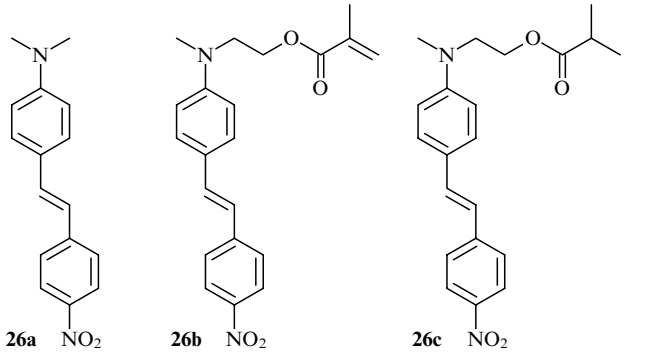
appeared to be the same for systems with different content of dimethacrylate; the average value of $\beta = 0.40 \pm 0.03$ was similar to that calculated on the basis of the percolation model.[106]

Copolymerisation of acrylamide with bisacrylamide in an aqueous solution was studied using 1-anilinonaphthalene-8-sulfonate (**23**) as a fluorescent probe.[99] The polymerisation was accompanied by a 20-fold increase in the fluorescence intensity with an increase in the volume fraction of the polymer in the hydrogel due to a decrease in the diffusion coefficient of the water molecules which play the role of fluorescence quenchers. There is a good correlation between the kinetic curves for the increment of I and the curves obtained using the dilatometric method. Both

methods gave similar values of rate constants for polymerisation and the reaction order with respect to the initiator.

An equipment for simultaneous *in situ* monitoring of conversion of double bonds and recording fluorescence spectra has been described.[100] In this equipment the differential scanning calorimeter and a spectrofluorimeter have a common measuring cell. 7-Nitro-2,1,3-oxadiazole dialkylamino derivatives (**24**, **25**) were used as fluorescent probes. That containing an acrylate group was incorporated into the network as a fluorescent label. Studies of photopolymerisation of dimethacrylates and other multifunctional oligomers revealed a good correlation between the increase in the fluorescence intensity and conversion of C=C bonds.

Both inert and reactive fluorescent probes (**26a**–**e**) based on 4-amino-4′-nitrostilbene were used for the study of microheterogeneity of the reaction medium in photopolymerisation of ethylene glycol, triethylene glycol, butanediol and hexanediol dimethacrylates.[107]



The inert probes **26a**, **26c** and **26e** simulated free oligomer molecules and participated in microsyneresis throughout the polymerisation; these concentrated in areas with a loose network and were surrounded by the oligomer molecules. The probes **26b** and **26d** containing methacrylate groups were incorporated into the network polymers formed and were distributed in the reaction medium more uniformly.[107]

The polymerisation of all dimethacrylates studied was accompanied by a shift of the maximum towards a short-wavelength region with a simultaneous broadening of the fluorescence band (λ_{max}); however, on reaching a $\sim 60\%$ conversion, the spectrum was slightly narrowed. In the authors' opinion,[107] the polymerisation results in the formation of a heterogeneous reaction medium in which the probe molecules are distributed between different microregions. As a consequence, the fluorescence spectrum represents a sum of spectra of probe molecules in different environments which vary from highly mobile regions enriched with the oligomer ($\lambda_{max} = 700-650$ nm) to regions consisting exclusively of rigid densely cross-linked polymer ($\lambda_{max} = 560-590$ nm). The changes in the spectral parameters of fluorescence are observed as a result of accumulation of a network polymer and the redistribution of probe molecules between different microregions. The probes **26a**, **26c** and **26e** are displaced from the areas with a high density of the network to more mobile loosely cross-linked areas. This can be evidenced from a smaller shift of λ_{max} in comparison with the shifts of λ_{max} in the case of probes **26b** and **26d**, which are immobilised in the network as a result of copolymerisation with dimethacrylates. A decrease in the width of the fluorescence band on reaching a $\sim 60\%$ conversion testifies to the tendency of the network density to equalise at greater depths of polymerisation. This tendency is consistent with the results of modelling and high-temperature annealing of network polymers.

IV. Control of three-dimensional radical copolymerisation and design of network macromolecular structures

Process control of three-dimensional radical copolymerisation and the formation of network copolymer structures entails control over growth, cyclisation and chain cross-linking reactions (1)–(5). Some authors (for bibliography, see Ref. 1) consider the intermolecular cross-linking reaction (3), responsible for the formation of macrogel, and secondary cyclisation (or intramolecular cross-linking) reaction (4), which results in the formation of microgel particles and a molecular network structure, as key objects for the control. However, the conventionality of such separation can be illustrated by the fact that the contribution of reactions (3) and (4) depends, in turn, on the lengths of the primary polymer chains formed in reaction (1).[6] Therefore, studies on three-dimensional radical (co)polymerisation are currently characterised by an intensive search for ways of control over the whole complex of reactions (1)–(5).

A characteristic feature of TRCP is the existence of tight structure–kinetic relationships realised at both topological and morphological levels of formation of the structure of the network polymer. Therefore, the studies devoted to the problem of control over TRCP processes can arbitrarily be divided into two groups depending on the factors (structure-physical or kinetic) used for this analysis. The conventionality of such division is determined by the fact that any changes in the structures of the starting monomers M_1 and M_2 and in the properties of the reaction medium (*e.g.*, type of solvent, nature of intermolecular interactions, *etc.*) determine the kinetics of the process. In turn, varying of the rates of initiation, growth and chain termination reactions is accompanied by changes in the structural and diffusional characteristics of the reaction medium, which influences the kinetics of the reaction in accordance with the feedback principle.

1. Structure-physical methods of control over three-dimensional radical copolymerisation

The structure-physical approach to the control over TRCP processes is based on variations of the types and intensities of intermolecular interactions in the reaction mixture. In practice, this approach is realised in several ways. Monomer units with bulky alkyl substituents, which create steric hindrance for the interaction of the growing radicals with pendant double bonds, are introduced into a copolymer chain in order to suppress cyclisation and intermolecular cross-linking. Monomers containing sites for strong intermolecular interactions resulting in the formation of a physical interaction network in the reaction medium are employed to stimulate intermolecular cross-linking and gel formation. And, finally, the contributions of cyclisation and intermolecular cross-linking can be controlled by varying the excluded volume factor through the use of solvents possessing different thermodynamic affinities for the copolymer formed.

Steric effects of alkyl substituents of methacrylate monomers on gel formation during their copolymerisation with multifunctional methacrylates have been studied.[108] It was shown that in copolymerisation of ethylene glycol dimethacrylate with dodecyl methacrylate (**27**) the intermolecular cross-linking can be completely suppressed due to steric hindrance created by the alkyl group of $C_{12}H_{25}$. This represents a new route to the preparation of reactive prepolymers carrying pendant methacrylate groups.

The effects of steric hindrance on the critical conversion (gel point) in the copolymerisation of allyl methacrylate (**28**) with MMA, dodecyl methacrylate, butyl methacrylate and hexadecyl methacrylate (**29**) have been studied.[109] The degree of polymerisation of the primary chains was maintained at the same level using a chain transfer agent, *viz*., dodecanethiol (**30**). A characteristic feature of the polymerisation of allyl methacrylate in comparison with dimethacrylates is that in the early steps of polymerisation a polymer is formed carrying only allyl pendant groups due to low reactivities of the allylic double bonds.[110, 111] Therefore, gel formation in the homopolymerisation of allyl methacrylate occurs later than in the polymerisation of dimethacrylates. In the copolymerisation of allyl methacrylate with MMA and butyl methacrylate, the experimental critical conversion corresponding to the gel point (C_c = 24.1%) coincided with that calculated with the use of the Stockmayer theory, whereas in the copolymerisation with methacrylates **27** and **29**, the gel point was shifted towards the critical conversion of 34.3% and 43.0%, respectively. It was shown [109] that as in copolymerisation of higher methacrylates with dimethacrylates, this shift is due to steric hindrance exerted by long-chain alkyl substituents, which prevents interaction of growing methacrylate radicals with pendant allyl groups.

The topology of the TRCP reaction strongly depends on the rigidity of the main chain of the copolymer macromolecule that is being formed.[6] This was established in comparative studies of gel formation during copolymerisation of dimethacrylates with MMA, on the one hand, and with *tert*-butyl methacrylate (**31**) and bornyl methacrylate (**32**), on the other hand. It was found that in copolymers prepared with involvement of the methacrylate units **31** and **32** cyclisation and inter- and intramolecular cross-linking are suppressed due to a decrease in the flexibility of the main chain and steric hindrance created by bulky substituents.

The effects of the physical network of the hydrogen bonds on intermolecular cross-linking and gel formation in three-dimensional copolymerisation have been studied.[112, 113] The copolymerisation of benzyl methacrylate (**33**) with 2 mol.% of hexanediol dimethacrylate was carried out in a solution of *tert*-butylbenzene in the absence and in the presence of 5 mol.% of (2-methacryloyloxyethyl) succinate (**34**).[112] The onset of gel formation occurred at conversions of 38.2% and 30.0%, respectively. The displacement of the gel point towards lower conversion values in the presence of the succinate **34** is due to the formation of hydrogen bonds between the carboxy groups of the succinate units **34** incorporated into the prepolymer and the growing macroradical. The presence of these bonds reduces the excluded volume effect thus favouring intermolecular cross-linking of the polymeric radicals with the pendant methacrylate groups of the prepolymer and the formation of macrogel.[112] A displacement of the gel point towards lower conversions under the influence of hydrogen binding of carboxy groups was also observed in ternary copolymerisation of hexanediol dimethacrylate with butyl methacrylate and the succinate **34**.

A combination of chemical and physical cross-linking makes it possible to realise the conditions of formation of network polymers which are consonant with the Flory–Stockmayer theory and to synthesise the networks close to ideal.[112] Copolymerisation of methacrylate **33** with 0.05 mol.% of poly(ethylene glycol) $(CH_2CH_2O)_{23}$ dimethacrylate (**35**) in *tert*-butylbenzene supplemented with 5 mol.% of the succinate **34** is an example. In the absence of the succinate **34**, no gel is formed even at maximum conversions of ~94%; however, in its presence, the network of hydrogen bonds favours the formation of a chemically cross-linked macrogel even at 58.4% conversion. The ratio of the experimental value of conversion, which corresponds to the gel point to the theoretical value is 1.9, which allows this network to be considered [112] as virtually ideal. The formation of such a network is favoured by the formation of a diphilic copolymer with a rigid non-polar primary chain built of units of methacrylate **33** and flexible polar pendant chains of dimethacrylate **35** in the pre-gel step.

Considerable attention is given to the study of three-dimensional copolymerisation of dimethacrylates with hydrophilic monomers containing hydroxy groups. The resulting hydrogels manifest good swelling properties in the presence of water. By virtue of their hydrophilic nature and good biocompatibility, such hydrogels find use in medicine and biology.[114]

Hydrogels based on hydroxyethyl methacrylate (**20**) are widely used in medicine. Large amounts of such hydrogels are used in the production of contact lenses,[115] while copolymers based on methacrylate **20** and dimethacrylates of ethylene glycol and diethylene glycol dimethacrylates are used as blood substitutes and drug depots.[116] Therefore, the regulation of processes of formation of the structure and properties of hydrogels based on methacrylate **20** should meet the most rigid criteria. Special attention is given to primary cyclisation, since it causes a significant deviation of mechanical properties, swelling index and diffusion characteristics of the copolymer from the corresponding parameters of an ideal network along with lower density of chain cross-linking. The effect of the composition of the monomeric mixture on primary cyclisation in photoinduced copolymerisation of methacrylate **20** with diethylene glycol dimethacrylate and poly[ethylene glycol(600) dimethacrylate] (**36**) has been studied.[114] A comparison of experimental results with the results of computer simulation of the reaction kinetics using a method developed by Elliot and Bowman [117] showed that the dependence of reactivities of pendant methacrylate groups on their spatial localisation, moment of 'generation' and length of the spacer as well as the differences in the local and averaged concentrations of polymeric radicals should be taken into consideration to fit the experimental data on the extent of cyclisation with the calculated values. The addition of a solvent increases the probability of cyclisation due to a decrease in the rate of the reaction of polymeric radicals with the monomer and an increase in the time of contact of the radical with the pendant methacrylate groups.[114]

The effects of the solvent on the formation of a network copolymer in the ternary copolymerisation of methacrylate **33**, ethylene glycol dimethacrylate and methoxytricosaethylene glycol methacrylate (**37**) have been studied.[6] The copolymer formed had a diphilic nature owing to a combination of a non-polar main chain and polar side chains of the comonomer **37**. As a result, the conformation of the copolymer depended on the nature of the solvent, which, in its turn, affected the cross-linking process. Thus the compression of the main chain and straightening of the side chain in a methanolic solution resulted in the formation of microgel particles.

Emulsion copolymerisation of styrene and MMA with divinylbenzene is used in the synthesis of reactive microgel particles having submicron sizes and carrying pendant C=C bonds.[118, 119] The microgels thus obtained are used in the production of polymeric coatings.

Three-dimensional radical copolymerisation in the presence of diluents is widely employed for the preparation of heterogeneous porous materials used as sorbents, membranes and materials for chromatography. Phase separation is the main driving force in the formation of a porous structure, while the morphology of the network polymer formed is determined by the microheterogeneous mechanism of copolymerisation.[1] Two-component mixtures consisting of a good solvent and a precipitant are often used for controlling the parameters of the porous structure of a copolymer in suspension copolymerisation.[120–122]

Hydrogen binding sites, which represent hydroxy groups localised in the oligomeric chain of dimethacrylate, have a pronounced effect on the TRCP processes and the structure and properties of the copolymers formed.[5] Studies of copolymerisation kinetics of such dimethacrylates by real-time IR spectroscopy revealed [5] that effective reactivities of methacrylate groups depend critically on the curing temperature. Thus in the initial steps, the rate of copolymerisation of methacrylate groups at 30 °C significantly exceeds that of styrene, whereas at 90 °C the difference is levelled off. A considerable effect of temperature on the relative

reactivities of the double bonds of comonomers can be explained [34] by the fact that low temperatures favour the formation of oligodimethacrylate associates stabilised by intermolecular hydrogen bonds and with methacrylate groups arranged favourably for the chain growth. An increase in temperature results in the dissociation of such associates and a decrease in effective reactivities of methacrylate groups.

Studies into mechanical properties of copolymers prepared at 30 and 90 °C and further cured to a state with identical conversion of the double bonds revealed that the strength and impact elasticity of the destruction of a low-temperature copolymer significantly exceed those of a high-temperature one. These differences correlate with the peculiarities of the microstructures of the copolymers as revealed in the analysis of the failure surface by atomic-force microscopy. Both copolymers have granular structures with the grain sizes of about 100 nm, the grain size in the low-temperature sample being larger. It was concluded [5] that the granular morphology of copolymers is due to the fact that TRCP occurs with the formation of microgel particles which then merge to form clusters. It was found also that microphase separation the early stages of which are temperature-dependent plays an important role in the formation of granular morphology.

Introduction of hydrogen-binding sites into network polymers based on dimethacrylates offers additional opportunities for modification of their properties owing to a combination of chemical physical networks. However, the problem of steric effects exerted by the rigid network of chemical bonds on the feasibility of realisation of an interpenetrating network of labile hydrogen bonds is still topical. Model hybrid networks based on triethylene glycol dimethylacrylate and containing COOH groups as potential junctions of a physical network were tested.[123] The carboxy groups were introduced in three different ways, *viz*., by copolymerisation of triethylene glycol dimethylacrylate with methacrylic acid, by polymerisation of dimethacrylate containing a solubilised copolymer of MMA with methacrylic acid and by thermal oxidation of residual double bonds in a homopolymer of triethylene glycol dimethacrylate. IR spectroscopic studies have shown that hydrogen bonds are formed both between the carboxy groups (dimers) and between the carboxy and ester groups; hydrogen bonds depleted by steric hindrance and a certain amount of free COOH groups are also present. The relative contents of different hydrogen bonds and free carboxy groups that cannot form H-bonds due to steric hindrance depend on the mode of introduction of these groups into the polymeric matrix.[123]

A significant effect on TRCP is produced by additives of various polymers introduced into the reaction medium in order to reduce shrinkage and modify the structure and properties of the network copolymers. A great number of papers are devoted to the effects of polymeric additives on curing of polyester resins which represent mixtures of unsaturated polyesters with styrene.[124–126] A characteristic feature of such processes is phase separation of the reaction mixture in the very early steps of the reaction and the formation of a biphasic structure where the components represent inclusions of the polymeric additives and the matrix represents a cured polyester resin.[126, 127] A polymeric additive can influence the topology and kinetics of network formation. The scope of this influence is determined by the concentration of the additive and its compatibility with the original reaction mixture and the network copolymer formed.[128]

A comprehensive structure–kinetic study of TRCP of a polyester and styrene in the presence of additives, *viz*., PMMA (**11**) and poly(vinyl acetate) (**38**) having a higher thermodynamic compatibility with the reaction medium has been carried out.[128] The reaction rate was recorded using differential scanning calorimetry; changes in the sizes of the microgel particles in the step preceding the formation of the macrogel were monitored by gel-permeating chromatography. It was found that the rate of copolymerisation decreases with an increase in the concentration of the additive, this effect being more pronounced for the polymer of **11**. The same factors determine the extent of reduction of microgel particles in early steps of the reaction. It was concluded [128] that poor compatibility of polymeric additives with the polyester results in compression of coils of polyester molecules in a mixture of styrene with the additive, which favours intramolecular cyclisation, reduction of the sizes of microgel particles and a shift of the onset of macrogel formation towards higher conversions.

2. Kinetic methods for the control over three-dimensional radical copolymerisation

The existence of a relationship between the kinetics of three-dimensional radical (co)polymerisation and structure formation of network (co)polymers has stimulated a search for efficient methods for the control over this process at different rates of initiation, growth and termination of polymeric chains.

The effect of the initiator concentration on the formation of microgel particles was studied for bulk polymerisation of ethylene glycol dimethacrylate.[129] This study included isolation and analysis of gel particles at different stages of the polymerisation process. The overall conversion of the double bonds was estimated using differential scannining calorimetry; the number of pendant methacrylate groups in gel particles was determined by IR spectroscopy. Dynamic light scattering studies have shown that a bimodal distribution of gel particles according to their size takes part in the reaction system in the very earliest steps of the reaction. It is of note that larger particles are formed upon aggregation of smaller particles.

The conversion of pendant double bonds in microgel particles increases in the course of polymerisation from 20% (at the overall conversion of double bonds of $\sim 1\%$) to 65% at the moment of formation of the macrogel (at the overall conversion of double bonds of 14%). An increase in the initiator concentration results in considerable broadening of the range of size distribution of macrogel particles: at the initiator concentration of 1%, the size of smaller particles ranges from 19 to 30 nm, whereas that of large particles is in the range 83–134 nm. If the initiator concentration increases to 5%, the ranges of the particle size increase to 11–32 and 44–154 nm, respectively, but the average size of larger particles diminishes from 105 to 80 nm, presumably at the expense of an increasing contribution of the quadratic radical termination reaction at invariably high rates of initiation and shortening of primary polymer chains involved in the formation of larger particles. The data obtained [129] suggest that the morphological structures of the polymers formed depend critically on the concentration of the initiator.

However, the experimental results reported by Chiu and Lee [129] do not correlate with the results obtained within the framework of a model of three-dimensional radical polymerisation.[24] According to this model, the reaction system contains, from the very beginning of polymerisation, only two components, *viz*., the starting oligomer and grains of a network polymer with the maximum possible degree of conversion. In the course of polymerisation, which occurs on the grain surface, the size of the grains increases and the latter begin to aggregate. Contrary to model concepts,[24] the degree of polymerisation of microgel particles increases gradually with time; the reaction of pendant methacrylate groups inside gel particles makes a significant contribution to the total conversion of the double bonds.[129]

It has been shown [130] that the experimental results obtained in the study cited [129] do not fit in kinetic and statistical network formation models, since they ignore the changes in structure–kinetic relations in polymerisation. However, it was found that these results can qualitatively be rationalised in the framework of a percolation model, which takes account of translational diffusion of monomeric and polymeric molecules, segmental diffusion of polymeric chains, excluded volume effect, formation of microgel particles and differences in effective reactivities of double bonds in the starting oligomer and pendant methacrylate groups. Presumably,[130] a more precise description of microheterogeneous

three-dimensional polymerisation should rely on a model which combines the advantages of the percolation model with those of the average field model.

The multimodal distribution of microgel particles according to their size [129] seems to be the most characteristic feature of three-dimensional radical polymerisation and copolymerisation. This was confirmed by the results of investigation of microgel particles obtained by copolymerisation of ethylene glycol dimethacrylate with MMA in toluene in which the cross-linking reagent was used at the concentrations of 9 mol.% and 15 mol.% (see Ref. 131). Data from exclusion chromatography suggest that in both cases the distribution of microgel particles according to their size changed gradually in the course of copolymerisation from monomodal to bimodal due to increasing fraction of larger particles. It was emphasised [131] that bimodal distribution of particles near the gel point provides conclusive evidence in favour of a coagulation macrogel-forming mechanism according to which small-sized (primary) particles aggregate to form larger particles. In earlier studies,[1] the formation of a macrogel in the course of TRCP was considered as a special manifestation of chemical aggregation of colloidal particles. The correlation between cross-linking and chain termination rate constants, on the one hand, and changes in the structures and sizes of reaction components, on the other hand, should be taken into consideration in describing the kinetics of gel formation as the interaction of microgel particles.[131]

IR spectroscopic monitoring was used [45] to study the effect of the initiator concentration on the copolymerisation kinetics of butanediol dimethacrylate with 2-methyl-5-vinyltetrazole (monomer **5**) over the whole range of conversion. It was found that the reduced copolymerisation rate of the methacrylate groups (w_1) in the initial steps of the reaction increases with the concentration of the initiator (dicyclohexyl peroxydicarbonate) (1 mass % – 3 mass %), this increase being more pronounced than that of the monomer **5** (w_2). This can be due to the fact that at high rates of initiation shrinkage lags behind copolymerisation in time, which leads to appearance of excess free volume in the vicinity of growing macroradicals. The mobilities and effective reactivities of pendant methacrylate groups increase correspondingly. The local concentration of the monomer **5** in the reaction zone may additionally decrease with an increase in the degree of cross-linking inside the microgel particles as a result of microsyneresis and a concomitant increase in the w_1/w_2 ratio. The differences in the effects of initiation rates on the copolymerisation kinetics of reaction components result in a significant effect of the initiator concentrations on the compositional and structural heterogeneities of network copolymers even if the compositions of original oligomer – monomer mixtures are identical.

An important role in the control over three-dimensional radical polymerisation is played by inhibitors and the polymer chain transfer agents. Their mechanisms of action are based on suppression of the intramolecular cyclisation reaction (2) by reduction of the lengths of primary polymeric chains. Trinitrotoluene (**39**) was found to be an effective regulator of structure formation in three-dimensional polymerisation of dimethacrylates.[23, 132] The addition of the polymerisation inhibitor **39** results in drastic changes in the kinetic and rheological characteristics of polymerisation of triethylene glycol dimethacrylate.[23] This is manifested in a shift in the onset of the gelation effect from the degree of conversion $\sim$ 1% to $\sim$ 15% with retention of fluidity of the polymerisate in this conversion range. In the Avrami coordinates, the polymerisation kinetics is characterised by the coefficient $n = 0.9$, which suggests homogeneity of polymerisation and the formation of short comb-like polymer chains with pendant methacrylate groups. Then, the system loses its fluidity, as a result of which the Avrami coefficient increases to 1.3 due to a decrease in the rate constant for quadratic termination of the macroradicals. The lack of the autoretardation step up to maximum conversions of $\sim$ 70% is a characteristic feature of the reaction carried out in the presence of 10 mol.% of the inhibitor **39.** Conventional microheterogeneous polymerisation of triethylene glycol dimethacrylate is described by a constant value of the Avrami index (1.6) even in the early steps up to a transition to the autoretardation mode at $\sim$ 40% conversion. The differences in the kinetics of ordinary and suppressed polymerisation of triethylene glycol dimethacrylate suggest that after addition of the inhibitor **39** the microheterogeneous formation of a network polymer can be replaced by a quasi-homogeneous one.

The effects of the inhibitor **39** on the copolymerisation kinetics of ethylene glycol and triethylene glycol dimethacrylates and oligocarbonate dimethacrylate as well as on the structures and properties of the polymers formed have been studied.[132] In this study, compound **39** suppressed the microheterogeneity of the reaction medium and favours the formation of polymers with more homogeneous structures. Compound **39** has an advantage over other, more rapidly consumed inhibitors in that it controls gel formation throughout the polymerisation time, since the value of the rate constant for the inhibition is $\sim$ 20 times lower than for chain growth.[132]

Chain transfer agents (alkanethiols and alkyl halides) are used to control three-dimensional (co)polymerisation much more frequently than inhibitors. Using chain transfer reactions, one can control successfully the degree of polymerisation of primary chains, prevent cyclisation and displace the gel point towards higher conversion values. Very often, this results in elimination of the gel effect. The main approaches to the use of chain transfer reactions for the control over three-dimensional thermally induced (co)polymerisation are discussed in a review.[6]

Considerable attention has recently been given to the role of the chain transfer reaction in three-dimensional photoinduced copolymerisation.[133, 134] The effect of initiation and chain transfer rates on the copolymerisation kinetics of hydroxyethyl methacrylate with 1 mass % of diethylene glycol dimethacrylate on the structure of the polymer chain was studied.[134] It was found that the lengths of the kinetic chains and the polymerisation rate decrease, while the rates of quadratic radical termination reactions increase in the presence of dodecane-1-thiol as the chain transfer agent. An increase in the initiation rate and a concomitant increase in the photoirradiation rate result in high concentration of short radicals, which also increases the probability of the chain termination reaction. Large number of short polymeric chains and the formation of a sol fraction significantly deteriorate the properties of network polymers of biomedical applications. Optimisation of conditions for their preparation demands selection of photoinitiation rates with account of the dependence of the chain termination reaction on the chain length.[134]

3. Chain transfer catalysts as regulators of three-dimensional radical (co)polymerisation and (co)polymer structures

The discovery of a catalytic chain transfer on a monomer in the linear polymerisation of MMA [135] has stimulated a search for possible applications of chain transfer catalysts in the control over three-dimensional polymerisation of oligodimethacrylates and the synthesis of soluble reactive polymers based on them.[28, 76, 136, 137] These and subsequent studies have demonstrated that the structure-forming role of chain transfer catalysts in linear and three-dimensional radical polymerisation differ substantially despite identical chemical mechanisms.

Low-spin cobalt(II) complexes with various macroligands proved to be highly efficient chain transfer catalysts in the polymerisation of methacrylates.[138] The type of ligand environment has a crucial effect on the rate constants of the catalytic chain transfer reaction, for the series of cobalt glyoximates these vary from 50 to 100 000. The steric factor, which determines the possibility of the interaction of cobalt with a growing polymeric radical, plays an important role. These data were taken into consideration in the design of catalysts that are efficient in the chain transfer from the methacrylate radicals, but completely inert with respect to styrene radicals.[138]

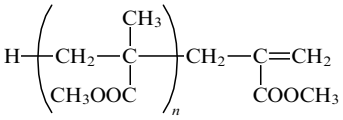
The pioneering study [135] was devoted to polymerisation of MMA in the presence of a cobalt – hematoporphyrin complex

[Co(II)P]. A two-step catalytic mechanism was proposed for the chain transfer from the growing radical R_n^* to the monomer M:

$$R_n^* + Co(II)P \longrightarrow Z_n + HCo(III)P, \quad (11)$$

$$HCo(III)P + M \longrightarrow Co(II)P + R_1^*. \quad (12)$$

According to IR spectroscopic data,[139] abstraction of the hydrogen atom from the terminal methyl group of the C-tertiary radical R_n^* in reaction (11) results in the formation of the unsaturated macromonomers Z_n:



40

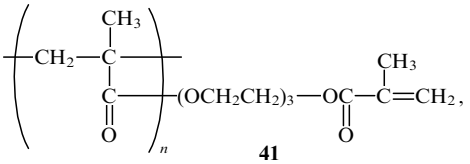
Because of the high value of the rate constant for the catalytic chain transfer (2.4×10^3), the Co(II)P added to the reaction medium in as low concentration as 6.6×10^{-4} mol litre^{-1} favours the formation of an oligomer P_n with a degree of polymerisation $n = 9$.[135] Preparation of an oligomer of the same degree of polymerisation in the presence of ordinary chain transfer agents of the thiol type demands $\sim$ 10 mass % of the latter, which is incorporated in the oligomer and thus presents serious technological problems.[140] The use of catalytic chain transfer agents not only eliminates these problems, but also enables access to reactive macromonomers of variable degrees of polymerisation which can be regulated by varying the concentration of the transfer agent.[138, 140]

Catalytic chain transfer reactions are widely used in the synthesis of macromonomers of the type **40** from various methacrylates.[141] Their reactivities differ significantly from those of ordinary unsubstituted methacrylates, since the radicals formed as a result of an attack on the vinyl group of the oligomers **40** have low growth rates due to steric shielding.[142] Therefore, the adducts formed in the reaction of the radicals R_n^* with macromonomers of the type **40** are prone to undergo reversible β-fragmentation, *i.e.,* elimination of the terminal fragment.[140, 143]

$$R_n^* + Z_k \rightleftharpoons Z_{n+1} + R_{k-1}^*. \quad (13)$$

Study of this reaction in a macromonomer **40**–butyl methacrylate mixture has led to suggestion [143] that macromonomers of the type **40** are involved neither in the copolymerisation with ordinary methacrylates nor in chain transfer catalysis through Co(II), but are themselves active participants of a catalytic chain transfer. A competition between catalytic chain transfer reactions through intermediacy of Co(II) and β-fragmentation is a characteristic feature of all reactions involving Co(II) complexes. Its role increases with an increase in the degree of conversion. Reaction (13) significantly extends the potential of radical polymerisation and allows one to perform synthesis of block and graft copolymers with acrylates, styrene and other monomers, which cannot normally be accomplished.[140, 143]

For the first time, the catalytic chain transfer reaction was used for the control over three-dimensional radical polymerisation of dimethacrylates.[28, 76] It was found that the polymerisation of triethylene glycol dimethacrylate in the presence of Co(II)P yields soluble linear oligo-*n*-methacrylates



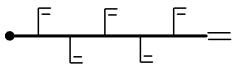
41

carrying a pendant methacryloyl group in each repeating unit. The degree of polymerisation of the oligomers **41** depends on the concentration of the chain transfer catalyst.

The oligomers **41** with degrees of polymerisation $n = 5-15$ manifest high reactivities. Substitution of oligomers **41** for dimethacrylates makes it possible to diminish chemical shrinkage and internal stresses within the polymer and to obtain networks with segmental structures made up of long and short polymethacrylate chains cross-linked with oligomeric chains. The polymers prepared from oligomers differ from ordinary triethylene glycol dimethacrylate-based polymers in syndiotactic attachment of their methacrylate groups and higher values of elastic moduli.[28] This testifies to gradual elimination of steric hindrances preventing the growth of polymethacrylate chains and alleviation of internal stresses associated with the two-step synthesis of the polymer. Possible applications of compounds **41** for improving the quality of paintwork materials based on oligoester acrylates are discussed.[77]

The addition of Co(II)P to triethylene glycol dimethacrylate in its bulk polymerisation strongly attenuates the gel effect which is shifted towards higher conversion values.[76] However, with an increase in the concentration of the catalyst up to the maximum limiting solubility values (5×10^{-3} mol litre^{-1}) the gel effect cannot totally be eliminated and insoluble network polymers are formed. Preparation of soluble products **41** and elimination of the gel effect can be achieved by polymerisation in DMF, which prevents aggregation of polymeric chains and the formation of a macrogel. In this context, degeneration of the gel effect can be regarded as a reliable test for the formation of multifunctional compounds **41**.[76]

The effect of the catalytic chain transfer reaction on polymerisation of ethylene glycol and diethylene glycol dimethacrylate with AIBN as the initiator has been studied.[29, 144] The addition of Co(II)P sharply decreases the polymerisation rate, diminishes the gel effect and changes the shapes of the kinetic curves (Figs 8 and 9). This suggests that Co(II)P significantly restricts the development of microheterogeneity of the reaction medium and the effect of the latter on the rates of chain growth and chain termination due to formation of multifunctional oligomers with pendant methacrylate groups.



42

The probability of intramolecular cyclisation decreases sharply after the formation of low-molecular-weight intermedi-

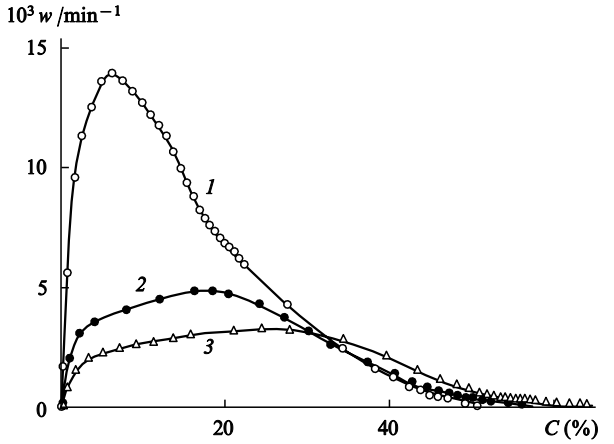


Figure 8. Kinetics of polymerisation of ethylene glycol dimethacrylate under ordinary conditions (*1*) and in the presence of 6×10^{-4} (*2*) and 3×10^{-3} mol litre^{-1} (*3*) Co(II)P.[30]
[AIBN] = 6.4×10^{-3} mol litre^{-1}, $T = 60$ °C.

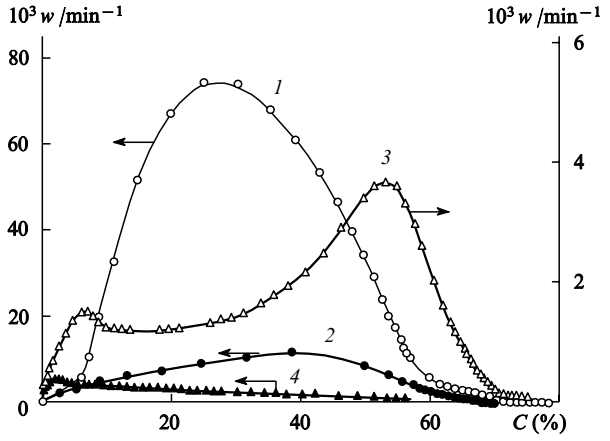


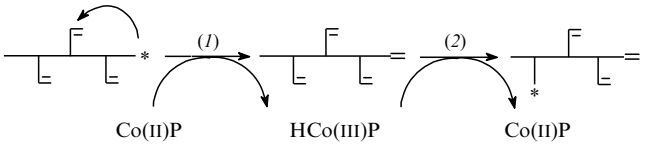
Figure 9. Kinetics of polymerisation of diethylene glycol dimethacrylate under ordinary conditions (*1*) and in the presence of 6.5×10^{-4} (*2*), 3.3×10^{-3} (*3*) and 13×10^{-3} mol litre^{-1} (*4*) Co(II)P.[144]
[AIBN] = 6.4×10^{-3} mol litre^{-1}, $T = 60$ °C.

ates **42** and prerequisites appear for the formation of more homogeneous polymers.

The extent to which the chain transfer catalyst influences the rate of polymerisation of ethylene glycol and diethylene glycol dimethacrylates and the shapes of kinetic curves vary significantly (see Figs 8 and 9). As a consequence, the effective rate constant for the catalytic chain transfer and the structure–kinetic relationships in three-dimensional radical polymerisation strongly depend on the structures of the starting oligomer and the polymer and physical characteristics of the reaction medium.

It is known that this rate constant decreases in linear polymerisation of methacrylates with an increase in the length of the alkyl substituent.[145] However, in the polymerisation of dimethacrylates, similar doses of Co(II)P more strongly inhibit the polymerisation rate of diethylene glycol dimethacrylate, an oligomer with a greater chain length (see Figs. 8 and 9). Higher efficiency of the chain transfer catalyst in the polymerisation of diethylene glycol dimethylacrylate can be ascribed to structural peculiarities of the growing polymeric radical, *viz*., the probability of intramolecular transfer of chains to the pendant double bonds of diethylene glycol dimethacrylate is higher than in the case of ethyleneglycol dimethacrylate due to the greater length of the spacer.[144]

Obviously, the role of a catalytic chain transfer in the formation of a more homogeneous network structure is not confined to the inhibition of intramolecular cyclisation (*1*):



An important role is ascribed to the probability of intermolecular cross-linking of the intermediates **42**, which involve pendant radicals formed in the intramolecular chain transfer reaction (*2*).

Polymerisation of diethylene glycol dimethacrylate in the presence of high concentrations of Co(II)P is accompanied by an appearance of two maxima on the kinetic rate curve $w(C)$ which correspond to 6% and 53% conversion of the double bonds. The first maximum is unrelated to a classical gel effect and appears as a result of formation of multiple terminal C=C bonds in a fast catalytic chain transfer reaction. The formation of such bonds is accompanied by a reduction of the thermal effect of polymerisation (Q) depending on the number-averaged degree of polymerisation ($\bar{P}$) (see Ref. 141)

$$Q = \frac{Q_\infty (\bar{P} - 1)}{\bar{P}}, \qquad (14)$$

where Q_∞ is the specific heat of polymerisation in the absence of a chain transfer catalyst.

Thus, the first maximum (Fig. 9, curve *3*) corresponds to the apparent gel effect and is manifested if Q_∞ is used instead of Q in the processing of calorimetric data. A true gel effect is observed at the conversion $C > 30\%$ and develops in response to enhancement of diffusional control over the catalytic chain transfer reaction. This, in turn, is due to a decrease in the molecular mobilities of bulky Co(II)P complexes resulted from an increase in the concentration of the network polymer and vitrification of the reaction medium.

The effect of diffusion on the catalytic chain transfer reaction in the linear polymerisation of methacrylates were studied.[145] It was found that the structure–kinetic relationships can be expressed by an empirical equation:

$$C_k k \eta^\alpha \approx \text{const}, \qquad (15)$$

where C_k is the catalytic chain transfer constant, k is the rate constant for the chain growth and η is the viscosity of the reaction medium ($\alpha = 0.5-1$). From the expression (15), it follows that the efficiency of the chain transfer catalyst decreases with an increase in the viscosity of the reaction system. However in the case of three-dimensional bulk polymerisation of dimethacrylates the structure–kinetic relationships are more complicated, because the reaction occurs in a microheterogeneous medium.[29, 144]

When polymerisation of ethylene glycol and diethylene glycol dimethacrylates is carried out in DMF in the presence of high concentrations of Co(II)P, the gel effect is abolished completely, which points to elimination of the topological factors responsible for the microheterogeneity of the reaction medium.[144] The multimodal molecular-mass distribution of polymerisation products suggests the presence of dimeric and trimeric forms of the starting dimethacrylates and of the major high-molecular-weight fraction (Fig. 10). The average molecular masses of the polymerisation products depend substantially on the structure of the starting dimethacrylate, the concentrations of Co(II)P and the content of DMF. According to IR spectroscopic data, the products contain large amount of pendant methacrylate groups and can be related to compounds of the type **42**. High reactivities of these compounds were confirmed by separate determination of copolymerisation kinetics of pendant methacrylate groups with D-MMA (Fig. 11).[146]

In contrast to dimethacrylates, which are used exclusively in the synthesis of statistical polymers, the multifunctional compounds **42** can be used as starting reagents in the design of a new generation of polymeric materials having the structures of graft copolymers. Three-dimensional nanosized copolymers with controlled levels of microheterogeneities possessing entirely novel properties can be prepared by varying structural parameters of the precursors **42** and comonomers.[146]

The use of catalytic chain transfer agents for the control over three-dimensional copolymerisation was first proposed by the

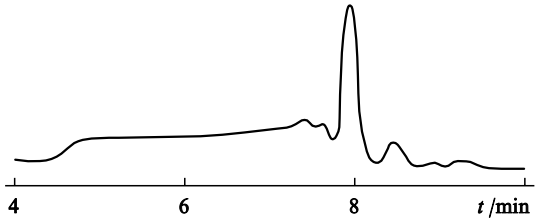


Figure 10. A gel-permeation chromatogram of polymerisation products of ethylene glycol dimethacrylate in the presence of 1×10^{-2} mol litre^{-1} Co(II)P and 40 mass % of DMF.[144]

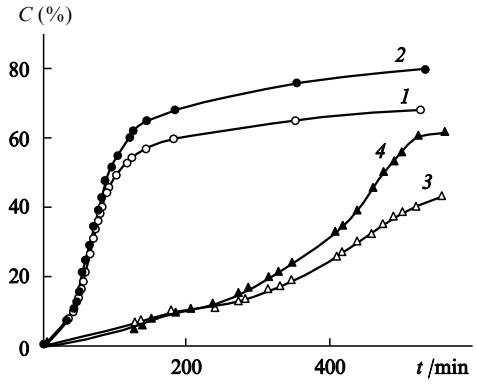


Figure 11. Copolymerisation kinetics of oligo-*n*-methacrylates based on ethylene glycol dimethacrylate (*1*, *3*) with D-MMA (*2*, *4*).[146]
Compositions of mixtures (mass %): (*1*, *2*) 64 : 36, (*3*, *4*) 74 : 26, T = 30 °C, [CPC] = 5 mass %.

present authors.[45] The use of oligomer – monomer systems, which differ considerably in the mechanisms of reactions of terminal radicals with chain transfer catalysts, seems to be especially promising in this respect. These systems include mixtures of dimethacrylates with styrene and acrylates, since reactions of catalytic transmitters with C-secondary styrene- and acrylate-derived radicals differ substantially from their reactions with tertiary methacrylate-derived radicals.[147–150]

It has been shown [147] that the coefficient of the chain transfer from the polymeric radical to the monomer in the polymerisation of styrene in the presence of Co(II)P is an order of magnitude lower than that in the polymerisation of MMA. In the authors' opinion, this is due to the involvement of the chain transmitter in the competing reactions of catalytic inhibition

$$HCo(III)P + R_m^* \longrightarrow P_m + Co(II)P \qquad (16)$$

and reversible inhibition due to the formation of a labile cobalt – carbon bond:

$$R_n^* + Co(II)P \longrightarrow R_n - Co(III)P. \qquad (17)$$

Reversible dissociation of the Co – C bond can lead to regeneration and further growth of the polystyrene radical, which corresponds to the passage of the reaction into a 'living' radical polymerisation mode.[148]

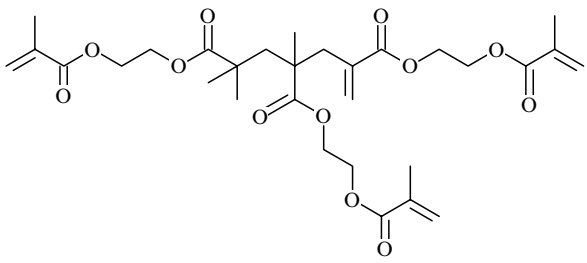
It has been shown [30, 151] that the addition of Co(II)P decreases drastically the rate of copolymerisation of ethylene glycol dimethacrylate with styrene in parallel with a shift of w_{max} towards higher degrees of conversion and an increase in the limiting conversion of the double bonds. An analysis of experimental results revealed that the formation of a network in the presence of Co(II)P is less subject to diffusion-controlled limitations in comparison with ordinary copolymerisation. As in the case of homopolymerisation of dimethacrylates,[29] the kinetic effects of Co(II)P are caused by a decrease in the microheterogeneity of the reaction medium due to the formation of intermediates of the type **42**. The sorption and physical-mechanical characteristics of the copolymers formed undergo significant modifications under the action of the chain transfer catalyst, which influences both the kinetics of copolymerisation and the formation of the network structure.[30]

In the bulk copolymerisation of dimethacrylate with styrene, the gel effect cannot completely be suppressed even by high concentrations of Co(II)P, which points to incomplete homogenisation of the reaction medium. The lack of the gel effect in the copolymerisation carried out in DMF suggests that the topological factors responsible for the microheterogeneity in the reaction of Co(II)P with macroradicals are eliminated virtually completely, as a result of which intramolecular cyclisation and cross-linking reactions are suppressed. The structures of reaction products obtained upon copolymerisation of an ethylene glycol dimethylacrylate – styrene mixture (1 : 1) in the presence of 20% of DMF provide supporting evidence. These reaction products represent multifunctional oligomers of the type **42** with M_n = 2270 and M_w = 14 350 (see Ref. 151).

The feasibility of preparation of soluble branched copolymers of MMA with tripropylene glycol diacrylate (**43**) in the presence of an ordinary (dodecanethiol) and a catalytic (cobalt difluoroboro dimethylglyoximate) chain transfer agents has been demonstrated.[152] This reaction was carried out in toluene (0.33 mol) with 0.15 mol of MMA and 5×10^{-3} mol of diacrylate (80 °C). The changes in the compositions and architectures of copolymers were recorded by NMR spectroscopy and chromatographic methods. It was found that linear copolymers with pendant acrylate groups are formed in the initial steps of the reaction. These groups react with the growing radicals to form branchings and loops. In turn, branched macromolecules can further be cross-linked through quadratic termination and recombination, which increases the molecular masses and polydispersities of the copolymers formed. Because of the differences in the reactivities of MMA ($r_1 \approx 2.0$) and diacrylate **43** ($r_2 \approx 0.5$), the concentration of the latter in branched copolymers increases with an increase in the degree of conversion, which favours further branching. The differences in the chain transfer constants for the reactions carried out in the presence of dodecanethiol for the methacrylate (~ 0.6) and acrylate (~ 1.7) radicals increase the probability of quadratic termination in the final period of the reaction due to consumption of the chain transfer agents and increasing concentrations of the growing acrylate radicals.

Although the persistent concentration of the catalytic chain transfer agents throughout the polymerisation reaction was noted [152] as its salient advantage, the problems of peculiarities of its interactions with acrylate and methacrylate were not touched upon. These include the possibility of formation of a cobalt – carbon bond between the terminal acrylate-derived radical of the copolymer and the transfer agents and the passage of the reaction into a living radical polymerisation mode upon reversible dissociation of this bond.[149, 150] The contribution of the aforementioned reaction should increase at higher conversions due to involvement of an increasing number of acrylate groups in copolymerisation. The β-fragmentation (13) resulting from the interaction of terminal C=C bonds in methacrylate branches of copolymers of the type **40** with various polymeric radicals [143] can also play a role in the character of the molecular-mass distribution and composition of branched copolymers.

The synthesis of superbranched polymers based on ethylene glycol dimethacrylate in the presence of cobalt glyoximate with a chain transfer constant of $\sim 10^3$ has been carried out.[153] By varying the concentration of the chain transfer catalyst, the author has succeeded in directing the polymerisation towards the formation of trimers of ethylene glycol dimethacrylate.



The reinitiation of terminal methacrylate groups of these trimers by a hydride transfer from the Co – H bond is accompanied by trimerisation and formation of new branching points. Cascade branching yields a soluble superbranched polymer with an average molecular mass ranging from several thousand to 40 000 Da. Soluble superbranched polymers are prepared by both bulk and solution polymerisation at dimethacrylate conversions

up to 70%. Special mention should be made of such remarkable characteristics of such superbranched polymers as high surface functionality and low viscosity, which is much lower than that of a linear poly(methyl methacrylate) of the same molecular mass.[153] Cascade radical polymerisation of dimethacrylates in the presence of a chain transfer catalyst can occupy a prominent place among more complex multistep procedures used in the synthesis of superbranched polymers and dendrimers.[154, 155]

Chain transfer catalysts based on triethylene glycol dimethacrylate can be used in the synthesis of linear polyesters.[156] However, the mechanism of their formation is still widely debated in the literature.[141] Note that linear polyesters can be prepared by catalytic chain transfer reactions (11) and (12) using hydride transfer to the pendant C=C bond of the terminal radical and the process occurs as alternating copolymerisation of these bonds with dimethacrylate molecules.

Studies on kinetics of three-dimensional radical (co)polymerisation of dimethacrylates in the presence of chain transfer catalysts [29, 30] have shown that the low-molecular-mass multifunctional intermediates **42** formed change dramatically the process of structure formation of network polymers in comparison with ordinary polymerisation where the role of transient species is played by microgel particles (Fig. 12 *a*). The formation of microgel particles in ordinary polymerisation of dimethacrylates and copolymerisation with styrene is the main reason for early manifestations of the gel effect, spatial heterogeneity of the network and formation of the microheterogeneous structure of the polymer. Using atomic-force microscopy, it was shown [157] that the degree of microheterogeneity of dimethacrylate–styrene copolymers increases with the concentration of the cross-linking reagent. This is accompanied by broadening of time relaxation spectra and an increase in fragility of the cross-linked copolymers.

The catalytic chain transfer reaction prevents the formation of microgel particles and development of the gel effect. In this case, the reaction medium represents a quasi-homogeneous solution of the intermediates **42** in the starting oligomer (Fig. 12 *b*).[151] The inhibition of intramolecular cyclisation sharply increases the probability of intermolecular cross-linking of the intermediates and favours the formation of a more uniform structure of the network (Fig. 12 *c*). It should be noted that not only the catalytic chain transfer reaction controls the morphology of the polymer by preventing the formation of large heterogeneous areas from microgel particles, but also stimulates the formation of a new in principle type of molecular networks consisting of short chains of the copolymer *1* cross-linked by the oligomeric chains *2*. By varying the concentration of a chain transfer catalyst, one can obtain chains *1* of any length and concentration and thus control the contribution of components *1* and *2* to the properties of the (co)polymers.

Comparative structure-physical studies of network polymers and copolymers prepared by conventional methods and in the presence of Co(II)P have shown that the structures and properties of the (co)polymers undergo significant modifications as a result of catalytic chain transfer reactions.[30, 151] The differences in the absorption kinetics of benzene and water induced by ethylene glycol dimethacrylate–styrene (4 : 1) copolymers synthesised by conventional methods and in the presence of Co(II)P provide an example (Fig. 13). The addition of Co(II)P also causes a ~ 10%

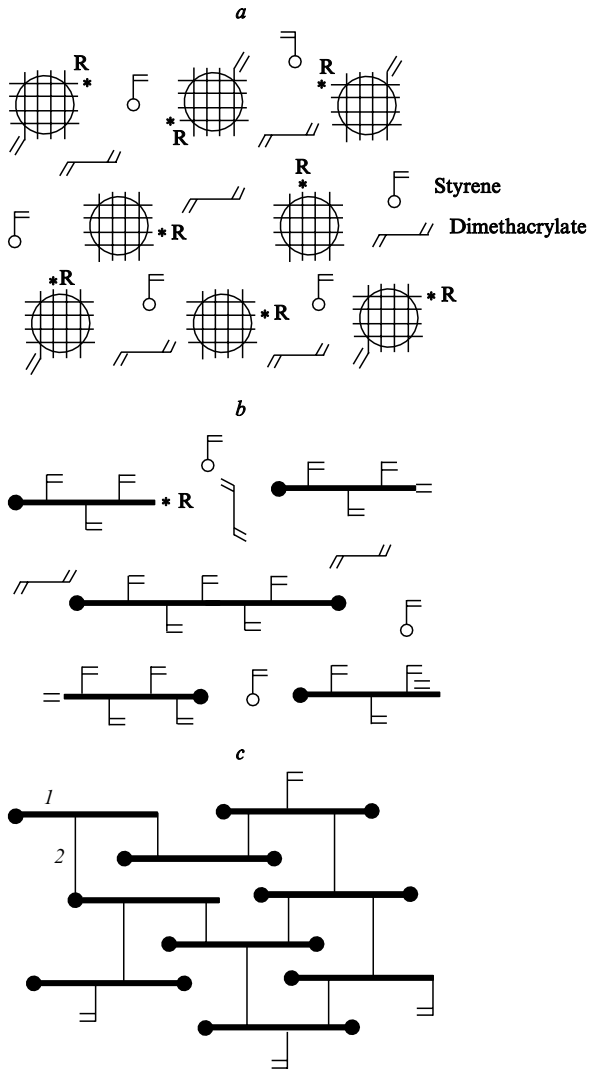


Figure 12. A scheme of synthesis of a network copolymer by conventional three-dimensional copolymerisation (*a*) and in the presence of a chain transfer catalyst (*b*, *c*).
For (*1*, *2*) see text.

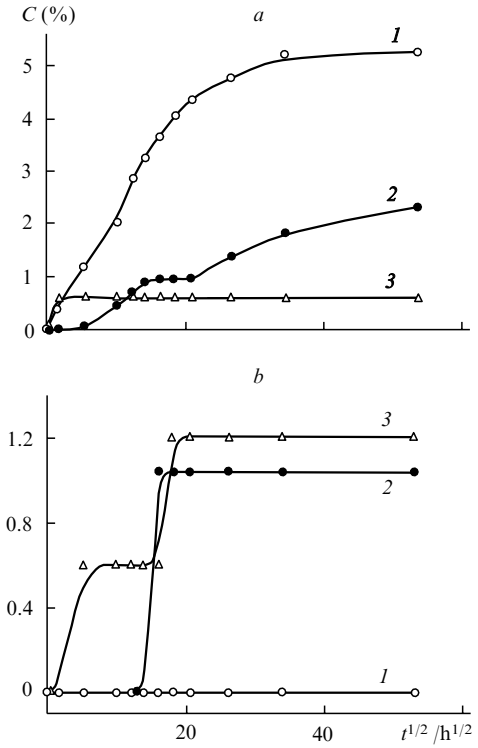


Figure 13. Kinetics of sorption of benzene (*a*) and water vapours (*b*) by copolymers of ethylene glycol dimethacrylate with styrene (4 : 1) prepared by ordinary copolymerisation (*1*) and in the presence of 3.4×10^{-4} (*2*) and 3.8×10^{-3} mol litre^{-1} Co(II)P (*3*).[30]

decrease in the elasticity modulus and a ~ 10% decrease in the forced elasticity modulus of copolymers. Homopolymerisation of ethylene glycol dimethacrylate in the presence of a chain transfer catalyst is accompanied by a ~ 30% decrease in the elasticity and forced elasticity moduli of the polymer. These data are at variance with the hypothesis [24] that a decrease in microheterogeneity of network polydimethacrylates will result in an increase in the elasticity modulus. Rather, they corroborate the hypothesis [158] that the microheterogeneities ('grains') play the role of reinforcing fillers in these polymers.

4. Three-dimensional radical (co)polymerisation in a 'living' chain growth mode

Significant achievements in the study of 'living' linear radical polymerisation in the past decade have paved the way to the synthesis of polymers with controllable structure and properties [159, 160] and stimulated attempts to use the 'living' polymerisation mode as a means of control over the formation of network (co)polymers. The agents of 'living' radical polymerisation influence substantially three-dimensional (co)polymerisation.[158] However, their efficiencies strongly depend on the structure-physical transformations of the reaction medium and can be brought to minimum through a decrease in the molecular mobilities of the reactants.[161]

The mechanism of 'living' radical (co)polymerisation is based on a reversible addition of growing polymeric radicals R* to low-molecular-mass radicals X* (see Refs 159 and 160).

$$R^* + X^* \rightleftharpoons R-X. \qquad (18)$$

Transition metal complexes, iminoxyl radicals and stable free radicals formed upon decomposition of the so-called iniferters (from Initiator Transfer Terminator Agent) can be used as polymerisation regulators X*.[159, 160] Owing to the high mobilities of the radicals X*, reaction (18) inhibits quadratic termination of polymeric radicals. Reiteration of decomposition and regeneration of a labile R–X bond induce the change in the fast chain growth mechanism into a slow step-by-step mechanism. The larger the number of steps in the chain growth mechanism the more completely the process meets the criteria of a true 'living' radical polymerisation, *i.e.*, the linear growth of the molecular mass of the polymer formed in parallel with the conversion of the monomer and narrow molecular mass distribution.[160]

There are hundreds of papers devoted to 'living' linear polymerisation of monofunctional compounds. The most recent advances are highlighted in several reviews [159, 160, 162, 163] which provide a detailed description of various types of compounds X and their applications as reagents for 'living' radical polymerisation and of mathematical models for predicting various parameters of the polymerisation reaction and the structures and properties of the reaction products. The use of polymers synthesised by ionic mechanisms, metathesis or polycondensation in 'living' radical polymerisation makes it possible to broaden the topology of the products (*e.g.*, linear, comb-like, superbranched, *etc.*, polymers) and compositions of copolymers (*e.g.*, statistical, regular, bulk, graft, *etc.*) and to ensure their controlled functionalisation.

However, the publications devoted to three-dimensional radical (co)polymerisation in a 'living' chain mode are not numerous due to the difficulties in conducting polymerisation in highly structured media. The main obstacle is that, in contrast to linear polymerisation, the mechanism of chain growth in three-dimensional polymerisation cannot be tested directly on the basis of such characteristics as molecular mass distribution, dependence of molecular masses of polymeric products on conversion, *etc.* Therefore, the contribution of the 'living' chain growth reaction to three-dimensional (co)polymerisation can be judged on the basis of indirect features, such as a critical conversion (gel point) shift,[164] suppression of autoacceleration of the reaction,[165] reduction of microheterogeneity of (co)polymerisation products and changes in their properties.[166] Some authors believe that these characteristics reflect the inhibition of intramolecular cyclisation due to a stepwise growth of the 'living' chains.[159] This hypothesis was corroborated in copolymerisation of styrene with 4,4′-divinylbiphenyl in the presence of an alkoxyamine, a 'living' radical polymerisation agent based on styrene and an iminoxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO).[167, 168] The calculated experimental copolymerisation constants suggest that the cyclisation involving the pendant double bonds, which usually proceeds at high rates in ordinary polymerisation, is fully suppressed on going to the living polymerisation mode. The final product, *viz.*, cross-linked polystyrene, is virtually devoid of topological defects, such as small rings.

Significant differences were found [168] in the characteristics of polystyrenes cross-linked by 4,4′-divinylbiphenyl prepared upon conventional radical copolymerisation and in the presence of 'living' radical polymerisation agents. The copolymers synthesised in the 'living' chain mode were characterised by higher elasticity and swelling moduli than the former. These differences were interpreted within the framework of a microheterogeneous mechanism. The copolymers obtained by 'living' polymerisation possessed a nearly statistical distribution of network junctions and were characterised as homogeneous, whereas copolymers prepared by conventional three-dimensional polymerisation were made up of densely crosslinked microgel particles connected by a loose network typical of microheterogeneous polymerisation.

The efficacy of alkoxyamines for performing 'living' radical copolymerisation of dimethacrylates with styrene has been found.[166, 169] Three-dimensional radical copolymerisation of styrene with dimethacrylates in the presence of alkoxyamines based on TEMPO, benzoyl peroxide (dicyclohexyl peroxydicarbonate) and styrene was studied by high-precision isothermic calorimetry, EPR and rheokinetics.[169] A shift in the gel point towards higher conversion values (> 10%) and high concentrations of the iminoxyl radical throughout the polymerisation with sufficiently high rates of the reaction provide conclusive evidence in favour of a 'living' copolymerisation process. Detailed structure-physical studies using mechanical, thermomechanical and diffusion-sorption methods have shown [166] that copolymers obtained in 'living' polymerisation possess higher elasticities and lower effective densities of the macromolecular network in comparison with copolymers prepared by conventional polymerisation. These differences were attributed [166] to the decrease in the microheterogeneity of the reaction medium and granularity of the cross-linked copolymers on going from the chain growth to the stepwise growth mechanism.

The use of alkoxyamines and iminoxyl radicals as agents for 'living' radical polymerisation is limited to styrene-containing systems; in addition, polymerisation should be conducted at high temperatures (~ 120 °C).[159, 160] Therefore, controlled radical polymerisation of acrylates and methacrylates in a 'living' chain growth mode usually includes transfer of a halogen atom (the so-called Atom Transfer Radical Polymerisation, ATRP).[160] The possibility to perform polymerisation at lower temperatures (~ 70 °C) is an obvious advantage of this method. ATRP has found extensive application in linear (co)polymerisation and proved to be an efficient tool for the synthesis of polymers with controlled molecular masses, low polydispersities and diverse architectures.[159, 162, 170, 171] However, only a few examples are known where ATRP has been used for the control of three-dimensional radical (co)polymerisation reactions.[161, 172, 173]

The ATRP of diethylene glycol dimethacrylate induced by methyl α-bromophenyl acetate using a Cu(I)Br – 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) complex as a catalyst has been studied.[161] This study included investigation of the time dependence of the conversion of double bonds by differential scanning calorimetry, *in situ* EPR spectroscopy and gel-permeation chromatography of the sol fraction isolated in different steps of polymerisation. An analysis of experimental results led the authors to the conclusion that this polymerisation proceeds in a 'living' mode and at persistent (low) concentrations of the growing

radicals only to conversions below 40%. Subsequent structurisation of the reaction medium and limitation of the diffusional mobility of the catalyst–ligand complexes disturb the equilibrium

$$R-M_n-Br + Cu(I)Br-HMTETA \rightleftharpoons$$
$$\rightleftharpoons R-M_n^* + Cu(II)Br_2-HMTETA$$

between growing and 'dormant' polymeric chains and direct the reaction to a conventional radical polymerisation route.[161]

The possibility of controlling three-dimensional radical bulk polymerisation of dimethacrylates by ATRP catalysts is limited due to a sharp decrease in their efficiencies with an increase in the viscosity of the reaction medium.[161] The use of solvents eliminates these limitations and opens up new opportunities for the design of network macromolecular structures in a 'living' radical copolymerisation mode. These possibilities were realised in the synthesis of star-shaped polymers with a functional microgel core.[172, 173] This approach [172] entails the addition of a bifunctional (cross-linking) reagent to a solution containing 'living' chains of a linear polymer. In the initial step, the molecules of the cross-linking reagent are attached to 'living' linear polymers; subsequent three-dimensional polymerisation yields microgel particles with chains of a linear polymer branching radially from its surface.

Star-shaped polymers with a microgel core were synthesised [172] by adding bis(acrylamides) containing spacers of different lengths and structures to a solution of 'living' PMMA chains prepared in the presence of an ATRP catalyst $RuCl_2(PPh_3)$. By varying the lengths of PMMA molecules and content of the divinyl compound, it was possible to obtain star-shaped polymers with molecular masses of 10^5-10^7 and macromolecular sizes ranging from 5 to 42 nm. This novel approach to the synthesis of star-shaped polymers enables incorporation of diverse functional groups (amide, ester, hydroxy, *etc*.) into the microgel core employing a cross-linking reagent with a spacer containing appropriate groups. This opens up new ways to the synthesis of star-shaped polymers attenuated to selective interactions of the 'guest–host' type. It was found [173] that biphilic star-shaped polymers with a diacrylamide core carrying ~ 70 radially branching PMMA chains with a degree of polymerisation of 100 can extract hydrophilic compounds, such as benzoic acid, benzyl alcohol and benzylamine from an aqueous solution to an organic phase. These polymers selectively interact with benzoic acid in the presence of ethyl benzoate (an equimolar mixture) by virtue of hydrogen bonding of the carboxy group to the $-NH-CO-$ groups.

Iniferters, which decompose upon UV irradiation or thermal treatment into two radicals, *viz*., an active R*, which initiates polymerisation of a monomer, and a passive radical X*, which is an active participant in linear termination of the macroradicals P_n^*, are widely used as initiators of 'living' radical polymerisation of vinyl monomers. The growth of 'living' chains is maintained owing to the fact that the rate of linear termination by a small mobile radical X* significantly exceeds that of diffusion-controlled quadratic termination of the macroradicals P_n^*, while the labile terminal bond in the adduct P_n-X dissociates with regeneration of the radical P_n^*, which ensures further chain growth up to the next chain termination.[160] Different types of iniferters and numerous examples of a macromolecular design based on them and their applications in linear radical polymerisation have been reviewed.[162]

The attempts to use iniferters to control three-dimensional radical copolymerisation are not numerous and confined to photopolymerisation of dimethacrylates.[58, 165, 174–176] *p*-Xylylenebis(*N*,*N*-diethyl dithiocarbamate), which dissociates irreversibly upon UV irradiation into an initiating C-radical and a carbamate-type S-radical terminating the growth of the polymeric chain, was used as an iniferter. The dependence of kinetics of 'living' three-dimensional (co)polymerisation of dimethacrylates on iniferter concentration, intensity of UV irradiation, temperature and spacer length has been studied.[165] It was found that the reaction is not autoaccelerated in the presence of the iniferter, and the polymerisation rate decreases 100-fold in comparison with ordinary photopolymerisation of dimethacrylates performed under identical conditions. A significant feature of this approach, which makes it different from conventional polymerisation, is that the polymerisation rate and the maximum conversion do not increase but rather decrease with an increase in the spacer length. This phenomenon is attributed [165] to the fact that the density of the cross-links increases in the presence of the iniferter much more slowly than in conventional polymerisation. Besides, the polymerisation rate is so low that the localisation of the methacrylate groups in the vicinity of the growing radical enhances their effective reactivities to a greater extent than the increase in their mobilities due to elongation of the spacer.

Poor reproducibility of the kinetic data obtained in the polymerisation reactions initiated by a photoiniferter ordinary photopolymerisation has been stressed.[165] This is attributed to the reversible chain termination in the presence of sulfo radicals; however, the contribution of this reaction to the overall heat of the process has not been taken into consideration in the calculation of conversions of double bonds on the basis of calorimetric data. It is therefore not surprising that the polymerisation kinetics of dimethacrylates measured by a spectroscopic method in the presence of the same iniferter [58] differs substantially from those results of calorimetric studies.[165] Studies of polymerisation kinetics of diethylene glycol and triethylene glycol dimethacrylates and of copolymerisation kinetics of divinylbenzene with styrene by the decrease in intensities of the absorption bands in the overtone vibrations of C–H bonds in the near IR revealed that the polymerisation rate decreases in the presence of a photoiniferter, although it does not eliminate the autoacceleration effect due to the diffusion control of quadratic termination of polymeric radicals.[58] Thus, the data available on the effects of iniferters on the kinetics of three-dimensional photopolymerisation of dimethacrylates are controversial. The mechanism whereby iniferters influence the kinetics of thermally induced three-dimensional polymerisation also needs to be further elucidated. The use of tetramethylthiuram disulfide as a free radical source imparts non-trivial kinetic features to the polymerisation of triethylene glycol dimethacrylate, which are manifested in particular in the appearance of two additional maxima on the polymerisation rate *vs*. time curve.[158]

Polymers synthesised in the presence of photoinifertes are convenient models for the study of dependences of their structures and properties on the degree of conversion, since they do not contain immobilised radicals able to initiate the polymerisation process at higher temperatures.[174–176] The heterogeneities of copolymers of poly[ethylene glycol(200) dimethacrylate] and poly[ethyleneglycol(200) acrylate] were established from the widths of the maxima on the temperature dependence curve of mechanical loss tangent.[165] The equality of this parameter in the copolymers prepared under ordinary conditions and in the presence of an iniferter prompted a conclusion that 'living' radical polymerisation of densely cross-linked networks neither influences the reactivities of pendant double bonds nor diminishes the microheterogeneity of the copolymer formed.[165]

Studies of temperature dependences of mechanical loss tangents revealed a high level of structural microheterogeneity of network polymers based on triethylene glycol dimethacrylate synthesised in the presence of a photoiniferter.[58] It is of note that the microheterogeneity of the polymer formed was not considered [58] as a structural defect,[24] but rather as a beneficial factor which enables the preparation of a polymeric material with the vitrification temperature exceeding the polymerisation temperature by ~ 100 °C. The feasibility of this synthesis is due to the coexistence of densely cross-linked microgel clusters with highly mobile loosely cross-linked network areas where further interactions of free radicals with pendant double bonds and oligomer molecules occur. As a consequence, at low curing temperatures a

heterogeneous system can produce a polymer with higher vitrification temperature than a homogeneous system.

It was found [160] that irreversible chain termination in linear radical polymerisation can be prevented through the use of both 'living' radical polymerisation agents and a structure-physical approach where 'living' chain mode is provided by restriction of translational mobilities of macroradicals. This approach was first realised in low-temperature polymerisation of butyl methacrylate in a glassy state induced by γ-irradiation.[177, 178] In this case, the mobilities of growing radicals appeared to be completely suppressed due to high viscosity of the reaction medium. When analysing the effects of chemical agents of 'living' radical polymerisation on three-dimensional polymerisation of multifunctional methacrylates, one should take into consideration the fact that this process has an intrinsic 'living' component of its own due to uninterrupted chain growth on radicals localised on the surface of microgel particles and immobilised in the network. This component, being an integral element of a microheterogeneous three-dimensional polymerisation mechanism, enhances the microheterogeneity of the polymer formed. 'Living' radical polymerisation agents suppress microgeterogeneity only in the step of growth of linear chains containing pendant methacrylate groups. With a decrease in the mobility and efficiency of these compounds (due to increased viscosity of the medium), the network formation goes under control of an ordinary microheterogeneity mechanism which retains some elements of 'living' polymerisation induced by structure-physical factors.

V. Conclusion

An analysis of literature data demonstrates significant achievements in the studies of kinetics and mechanisms of TRCP and the development of methods for the control over the structure and properties of network polymers. Progress in this area has been made owing to the use of IR spectroscopy and NMR monitoring based on separate registration of conversion curves of C=C bonds of the monomer and the cross-linking reagent. The use of *in situ* spectral monitoring allows one to measure instantaneous compositions of the copolymers formed in the course of copolymerisation, to follow changes in effective reactivity ratios induced by structure-physical transformations of the reaction medium and to detect violations in the homogeneous distribution of reaction components in the vicinity of macroradicals caused by microsyneresis and limitations in the molecular mobilities of the reaction components. Direct information about the redistribution of reactants due to microsyneresis and formation of a microheterogeneous structure of network copolymers can be obtained through the use of fluorescent probes and labels. The use of these tools has made it possible to establish the correlations between different parameters of the microheterogenous structure and characteristics of network copolymers.

The formation of structures of network copolymers occurs under conditions of superposition of chain growth, intermolecular cross-linking, cyclisation and intramolecular cross-linking involving pendant double bonds. Considerable attention has been given to experimental and theoretical studies of factors which influence the contribution of these reactions to the overall conversion of double bonds and, as a consequence, to the topological structure and microheterogeneity of the copolymer formed. It was found that the copolymerisation process can be controlled by varying the character of intermolecular interactions of growing polymeric radicals and macromolecules. Thus, the use of comonomers carrying carboxy groups favours intermolecular cross-linking due to the forward formation of hydrogen bonds in the reaction medium. Cross-linking and cyclisation can be suppressed by addition of comonomers containing bulky alkyl substituents, which create steric hindrance for the interaction of macroradicals with pendant double bonds. The control over the lengths of primary polymeric chains by chain transfer agents (thiols and alkyl halides) also limits the cyclisation and enables formation of a more homogeneous structure of a network polymer. However, these approaches have significant limitations: the range of copolymers obtainable is rather small in the former case and environmental safety requirements have not been met, in the latter case.

The discovery of catalytic chain transfer reactions and living' radical polymerisation reactions has revolutionised the situation in linear polymerisation and paved the way to the synthesis of copolymers of any architecture, which in turn gave a strong impetus to the development of versatile and environmentally safe methods for control over TRCP. Pioneering studies have shown that chain transfer catalysts inhibit cyclisation and the gel effect in bulk (co)polymerisation of multifunctional compounds and favour the formation of more homogeneous polymeric networks than upon conventional polymerisation. Data on the effects of the agents of 'living' radical polymerisation on microheterogeneity of the networks formed are scarce and controversial. The potential of these methods in the control over three-dimensional bulk polymerisation is limited, since at more advanced stages of the reaction the activities of chain transfer catalysts and agents of 'living' radical polymerisation decrease with a decrease in their mobilities on going to media with a higher degree of structurisation.

Diffusion-controlled restrictions in reactions of chain transfer catalysts and agents of 'living' radical polymerisation with polymeric radicals are eliminated when these reactions are carried out in solutions. This opens up broad prospects for the design of network macromolecular nanosized structures possessing complex architectures. The data cited in this review clearly demonstrate that these potentialities have partly been realised in the synthesis of a vast variety of superbranched reactive macromolecules and microgels, dendrimers and star-shaped copolymers with a functional microgel core.

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