Russian Chemical Reviews **78** (2) 165 – 194 (2009) © 2009 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2009v078n02ABEH003896

Structural aspects of polymer network formation upon curing of oligomer systems †

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Abstract. Modern concepts of the structure of polymer networks prepared upon oligomer curing are considered. The molecular, topological, supramolecular and colloid-dispersion structural levels of cured oligomer systems are discussed. The emphasis is placed on analysis of the structural features related to the mechanism and kinetics of network formation upon polymerisation and polycondensation. The bibliography includes 169 references.

I. Introduction

Opinions differ as to the structure of cured oligomeric systems (see, *e.g.*, Refs 1 – 25). Nevertheless abstracting from differences in terminology used in scientific publications to describe particular structural fragments and processes responsible for their formation and omitting some insignificant details, one can see that the approaches to assessment of structural features of cured oligomers, developed by researchers from various scientific schools, have much in common. Analysis of experimental data carried out for different levels of structural hierarchy of polymers makes it possible, to a first approximation, to reduce modern concepts of the structure of cured polyfunctional oligomeric systems to the following.

The molecular level of structural hierarchy is governed by the chemical nature of components, but owing to random character of curing processes the same initial reactants are transformed to products with different molecular structure and, therefore, physical properties.[2, 25 – 28] When polymer networks are synthesised from synthetic oligomers, it is in principle impossible to obtain an individual compound with a specified molecular structure.

By varying the conditions for and kinetic characteristics of oligomer curing processes one can vary the supramolecular structure (mutual spatial arrangement of chemically identical macromolecular fragments, which is responsible for, in particular, the packing density of a polymer[25]).

The topological structure is a key characteristic of polymerisation products.[2, 25] It is described leaving particular chemical compositions and spatial arrangement of macromolecules apart. When on the topological level, the structure of a polymer network can be considered as a graph[29] with inclusion of the distribution functions over the number and functionality (degree of branching) of vertices (network nodes), over the length of edges (chains connecting cross-link points), over the ring size, *etc.*, without specifying their chemical nature. This level of structural organisation is strongly affected by the curing conditions.

Finally, the formation of polymer networks is usually accompanied by some phase transitions and changes in state. This results in systems of different morphologies, which also influence the properties of polymers on the colloid-dispersion structural level, which in turn is to a great extent determined by the curing regime.[6, 12]

The present review concerns structural aspects of polymer network formation, related to the kinetic features of oligomer curing processes.

II. Structural features of cured oligomeric systems

1. Molecular level

The molecular level of structural organisation of cured oligomeric systems is governed by the nature and chemical structure of components, the functionality of oligomer molecules, the network formation mechanism, *etc.* Of

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Received 11 August 2008
Uspekhi Khimii **78** (2) 176 – 206 (2009); translated by A M Raevskiy

† Dedicated to the memory of Yurii Sergeevich Lipatov.

course, the properties of cured systems based on oligomers differing in chemical structure (*e.g.*, oligoether epoxides and oligoether acrylates) or oligomaleinate/fumarates and phenol–formaldehyde oligomers, as well as oligoether acrylates differing in oligomer block length or methacrylate group number in the molecule are different. This is first of all due to the different energies and lengths of covalent bonds, different energies of intermolecular interaction and different chemical nature of cross-link points. It is this principle that underlies the Askadskii method,[27] according to which the repeating unit of a polymer (or the repeating fragment of a polymer network) is represented by a number of anharmonic oscillators involved in different types of intermolecular and chemical interaction. Mention should also be made of van Krevelen's empirical method,[28] which relates the properties of a polymer to its molecular structure.

Of course, the molecular level predetermines differences in the topological structure of cured oligomers of different chemical structure.

2. Topological level

The topology of cured oligomeric systems is determined by the chemical nature and functionality of the initial components and by the kinetics of their curing. A significant role is also played by such parameters, as the molecular mass distribution (MMD) and the functionality type distribution (FTD) of the initial components, because they specify the lengths of chains between cross-link points, as well as the concentration and the degree of branching of chemical cross-link points.

Various methods of simulation of complex topological structure of polymer networks prepared by curing of oligomers have been proposed (see, *e.g.*, Refs 30–40).

Sivergin *et al.*[30,39,40] reported Monte Carlo simulation of the formation of a fragment of the network structure in the case of three-dimensional polymerisation. It was shown that the topological structure is characterised by a large number of rings and 'tails'. The macrobody of a real three-dimensional polymer includes a large number of such weakly bonded fragments.

The schemes of a macrobody shown in Fig. 1 *a*,*b* were obtained as follows.[38] Tetra- or bifunctional reactants simulating di- and monovinyl oligomers, respectively, were placed in the sites of a two-dimensional or three-dimensional lattice. (Each double bond gives rise to two kinetic chains.) Initially, active centres appeared randomly, reacted with the nearest functional groups and moved, thus forming a kinetic chain, until (i) arrival at sites where the nearest environment contained no unreacted functional groups (bricking up of active centre) or (ii) meeting another active centre (chain termination).

The system shown in Fig. 1 *a* initially contained only tetrafunctional reactants while the system shown in Fig. 1 *b* contained 90% of bifunctional ones. In both cases, 44% of oligomers were included in the polymer after curing, but it appeared that the degree of conversion with respect to functional groups was 47% in the case *a* and 30% in the case *b*.

The use of both systems leads to highly inhomogeneous topological structure. Namely, the polymer is localised within some large clusters (case *a*) or is distributed over a few tens of clusters with a relatively small proportion of large clusters (case *b*). In essence, this study revealed the occurrence of a microgel mechanism of polymerisation.

For comparison, Fig. 1 *c* presents the results of polycondensation of tetrafunctional monomer. Clearly, in this case the topological structure is much more homogeneous, that is, the polymer is composed of a few hundreds of sol fragments (macromolecules and small clusters).

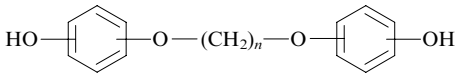
Rings are important structural fragments of polycondensation networks. Kinetic calculations,[41,42] Monte Carlo simulation[43] and experiments with polyethers, polyamides, *etc.*[44–48] showed that almost all bifunctional monomers eventually form cyclic macromolecules. Polycondensation of monomers of higher functionality leads to formation of



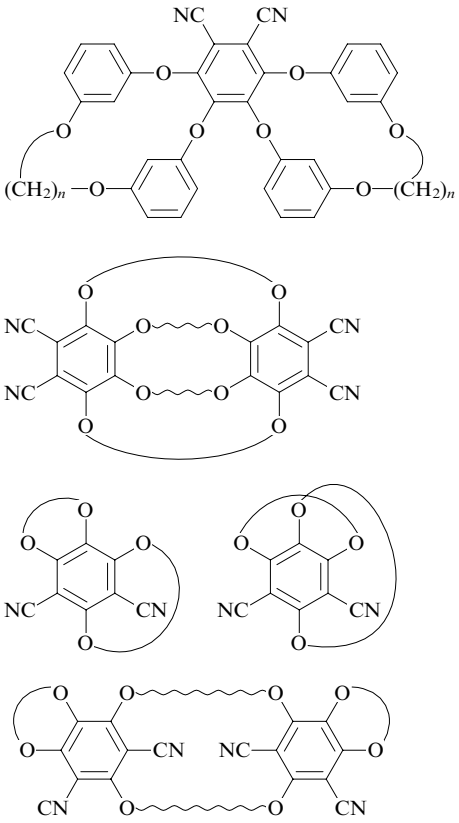
X (*1*), + (*2*), 0 (*3*).

Figure 1. Schematic representation of the structure of a polymeric body obtained upon polymerisation of a tetrafunctional oligomer (*a*), a blend containing bifunctional (90%) and tetrafunctional (10%) oligomers (*b*) and upon polycondensation of the tetrafunctional oligomer (*c*).[38] Polymer units included in clusters (*1*), other units (*2*) and 'pendant' functional groups (*3*); voids denote the unreacted oligomer.

topologically complex rings[44] as in the case of, *e.g.*, products of the interaction of bisphenols of the general formula

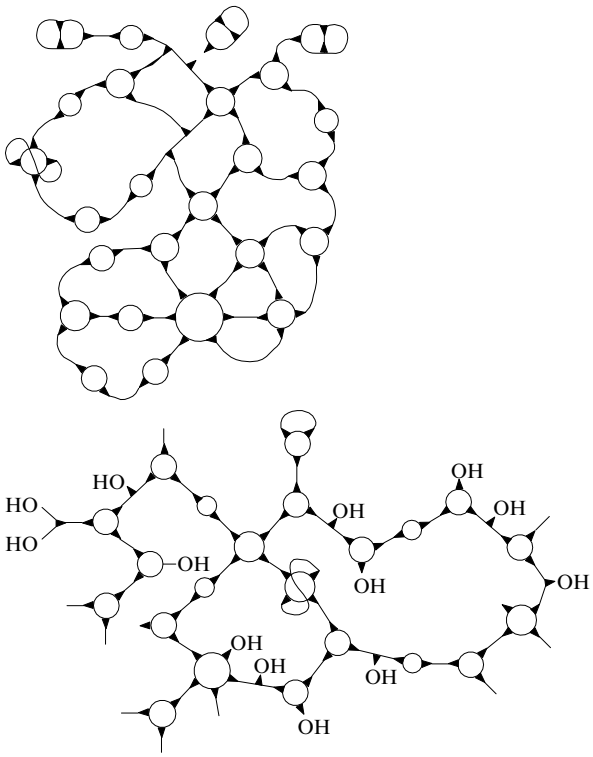


with 1,2- or 1,3-dicyanotetrafluorobenzene:



These reactants were used to obtain cyclic products containing up to 12 rings; the corresponding distribution functions are shown in Fig. 2.

Oligomers of higher functionality [1,1,1-tris(4-hydroxyphenyl)ethane and 2,6-difluoro- or 2,6-dichloropyridine] were used for the synthesis of polycycles which in essence represent network fragments,[49,50] *e.g.*,



(bridging fragments and rings are denoted by lines and circles, respectively).

The distribution problem of rings of different topology was solved by Erukhimovich[51,52] who theoretically analysed the probabilities of formation of all possible cyclic structures comprised of bi, tri- and tetrafunctional oligomers. The equation proposed is as follows:

$$N_x^{(c)} = Az^x x^{c-L}, \quad (1)$$

where $N_x^{(c)}$ is the number of rings of particular topology having the size x, A is the normalising factor, z is the distribution parameter, c is the ring complexity index and L is the number of bridging fragments.

For trivial rings, one has $c = -3/2$; in this case one deals with the known Stockmeyer–Jacobson distribution

for reversible polycondensation

$$N_x^{(-3/2)} = Ax^{-5/2},$$

and for irreversible polycondensation

$$N_x^{(-3/2)} = Ax^{-3/2}.$$

The topological structures of polycondensation networks were studied by computer simulation. As an example, Fig. 3 presents a two-dimensional scheme of a network structure obtained[34,35] for a mixture of reactants $A_2 + B_4$ simulating the curing of epoxy oligomers (A_2) with diamines (B_4).

The scheme was obtained under the following conditions. Tetrafunctional molecules were placed in sites of a regular lattice and their functional groups B randomly reacted with groups of the bifunctional reactant A (uniform distribution of the bifunctional reactant over the entire

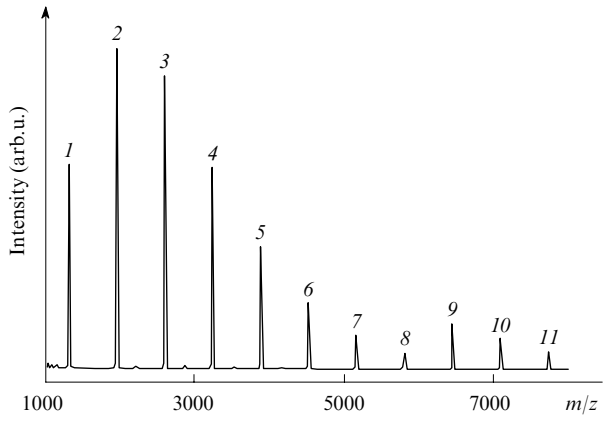


Figure 2. Mass distribution for products of the interaction of 1,2-dicyanotetrafluororbenzene and bisphenol according to matrix assisted laser desorption/ionisation time-of-flight mass-spectrometry data.
Products contain 2 to 12 rings (positions *1–11*, respectively).[44]

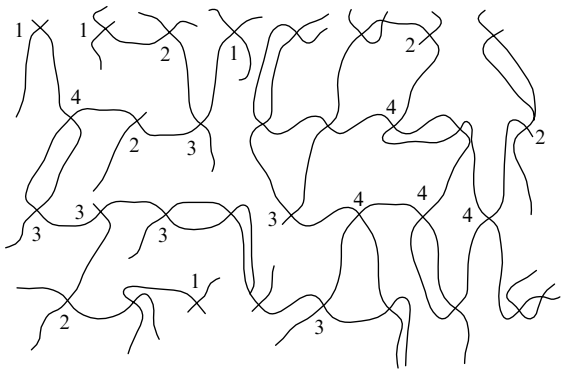


Figure 3. Two-dimensional scheme of epoxyamine polymer.[34] Figures denote the functionalities of particular cross-link points, which are determined by the number of B-groups bonded to the network chains.

system was assumed). However, if one A-group of the bifunctional component reacted, the second A-group could react with a B group located in a neighbouring cross-link point. In turn, the probability for a given site to interact depends on the local concentration of unreacted A-groups. The experimental conditions also allowed the probabilities of the reaction of the bifunctional reactant with the site after the first, second and third addition to be included. Despite the prescribed stoichiometric ratio of the reactants

$$K_{st} = \frac{A}{B} = 1,$$

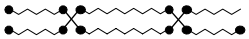
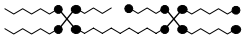
the network obtained was highly inhomogeneous and contained (i) a large number of rings characterised by a broad size distribution; (ii) unreacted B-groups, which is responsible for the formation of cross-link points of different functionality; (iii) 'pendant' tails, *etc*. (see Fig. 3). Figures in this Scheme denote the functionalities of particular cross-link points, which are determined by the number of B-groups bonded to the network chains rather than 'tails'!

A schematic representation of topological fragments of a network proposed by Lantsov[33] (Table 1) takes into account the possibility of deviation of the coefficient K_{st} from 1.

The calculated formation probabilities of particular structures were compared with experimental data obtained by pulsed NMR spectroscopy taking a number of epoxy-amine networks as examples. The percentage of protons of different mobility, which depends on the degree of connectivity between the fragments, was determined. In some cases, theoretical values obtained using different methods of taking into account the contributions of particular topological structures were in good agreement with experimental data (Table 2). Probably, these structures correspond to a real topology of the networks obtained under different conditions.

Figure 4 presents a schematic representation of a fragment of the topological structure of a polyurethane network obtained by curing of isocyanate, glycol and a trifunctional reactant.[53] The topological structure can be even more complicated owing to association of some rigid urethane blocks. Such an associate is surrounded by flexible glycol chains, one of which can penetrate within the rigid-chain associate. As a result, each microdomain (microphase) will

Table 1. Possible network fragments and their notations.[33]

Fragment	Cross-link point	'Tail'	Chain
	$CLP_{43} + CLP_{34}$	$1\,T_3$	$2\,C_4 + 2\,C_{43} + 1\,C_3$
	$CLP_{41} + CLP_{14}$	$3\,T_1$	$3\,C_4 + C_{41}$
	CLP_4	–	$4\,C_4$
	CLP_3	$1\,T_3$	$3\,C_3$
	CLP_2	$2\,T_2$	$2\,C_2$
	CLP_1	$3\,T_1$	$1\,C_1$
	CLP_0	$4\,T_0$	–

Note.  denotes a cross-link point (CLP), denotes a 'tail' (T) and  denotes a chain (C). The structure of the subscript is as follows: the first decimal digit denotes the functionality of the cross-link point and the second decimal digit characterises the connectivity between a given cross-link point and a neighbouring cross-link point. Figures preceding the letters 'T' and 'C' denote the numbers of these elements in a given fragment.

Table 2. Calculated and experimental percentages of protons (P) for networks obtained by curing of epoxy oligomer ED-24 with dichlorodiaminophenylmethane at different content (φ) of phenyl glycidyl ether with inclusion of the contributions of different topological fragments of the network.[33]

T/°C	φ/vol. fraction	P		Network fragments [a] whose contributions are included
		experiment	calculations	
130 – 180	0.25	0.6	0.59	all except CLP_4, CLP_3, C_{44}, C_4
160 – 180	0.325	0.5	0.49	all except CLP_4, CLP_3, C_{44}, C_{43}, C_{33}
150 – 160	0.4	0.5	0.5	all except CLP_4, CLP_3, CLP_2, C_{44}, C_{33}, C_{42}, C_{32}
105 – 160	0.5	0.4	0.4	T_0, CLP_0, T_1, T_2, T_3
90 – 125	0.75	0.7	0.72	T_0, CLP_0, T_1, T_2, T_3
200	0.25	0.43	0.42	all except CLP_4, CLP_3, C_{44}, C_{43}, C_{33}
200	0.325	0.25	0.25	T_0, CLP_0, T_1, T_2, T_3
200	0.4	0.24	0.25	T_0, CLP_0, T_1, T_2, T_3
200	0.5	0.35	0.35	T_0, CLP_0, T_1, T_2
200	0.75	0.54	0.56	T_0, CLP_0, T_1

[a] See note to Table 1.

contain alien fragments. Experiments confirmed the correctness of this model.

Entelis *et al.*[5] developed the so-called kinetic fragmental model, which allowed the effect of the MMD and FTD of oligomers on the final structure of the polymer network to be analysed. A linear prepolymer A∿∿∿A containing multifunctional molecules of the type A∿∿∿T, a bifunctional oligomer BB and the branching agents A(A)−○−(A)A or A(A)−○−A (where ○ is a cross-link point of the network) were considered as initial reactants.

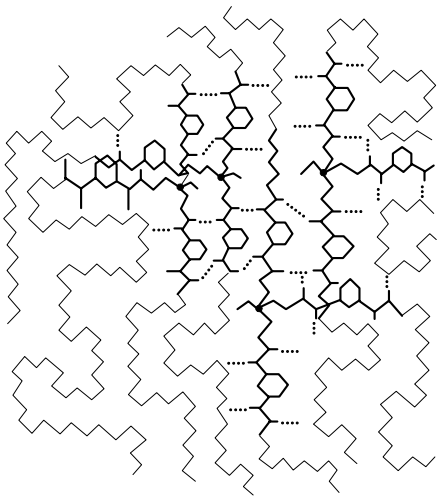


Figure 4. Schematic representation of polyurethane network.[53] Rigid-chain blocks are given in bold.

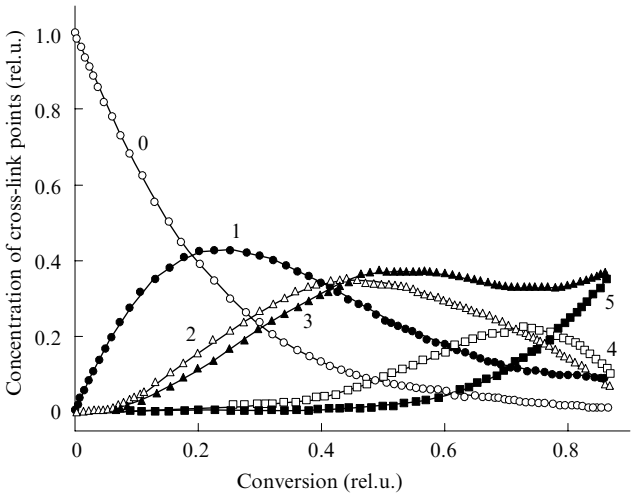


Figure 5. Dependences characterising the topological structure of the system formed upon curing of ED-20 + propylene carbonate (PC, 10 mass %) mixture with diethylenetriamine (DETA).
Figures near the curves correspond to functionalities of cross-link points n_i.

Reactions between the functional groups A and B result in fragments of the following structural types:

A~~A, ○–A, A–T,

B~~A, ○~~A, A~~T,

B~~B, ○~~B, B~~T,

BB, ○~~○, ○~~T.

For each structural type, expressions for the total concentrations and for the length distribution were derived. This allowed the MMD functions of linear molecules, side chains and chains between cross-link points to be calculated as functions of the MMD of the initial components. Results of calculations of some syntheses of various polyurethanes based on oligodiols, triols or tetraols and diisocyanates in the presence of monofunctional additives with allowance for their MMD and FTD (see monograph [5]) were checked experimentally and reasonable agreement was obtained.

To analyse the topologies of network structures formed upon polycondensation of reactive oligomers, a concept of bond blocks (BB), which combined kinetic and statistical methods, was proposed.[54–58] It is this concept that allows a generalised approach to, *e.g.*, the determination of the gel point to be developed.

A bond block is a structure, which can belong to any macromolecule or a polymer network. It can be represented by a subgraph whose vertices and edges denote bonds and units. A complete set of concentrations for all BBs unambiguously characterises the composition and structure of a system under study. Informationally, this data array is analogous to the MMD function for a linear polymer. But actually it contains a greater body of information, being a characteristic of both the molecular and topological structure of the polymer.

For any macromolecule, there are BBs whose formation obeys some kinetic equations. Statistical methods make it possible to build a desired structure using a number of BBs. For instance, kinetic calculations were used to determine the running concentration of amino groups of different connectivity (Fig. 5) in epoxyamine polymers. The amino groups were randomly linked by epoxide chains and the bonding probability was specified by the corresponding conversion value. This procedure was used to determine the parameters of the gel point and the topological structure of the polymer network.[31, 32, 59, 60]

According to theory of branching processes,[2, 21] the network structure is governed by the chain termination parameter v, which is determined by solving the equation

$$u(x) = x\left(1 - \alpha + \alpha \sum n_i u^{i-1}(x)\right), \tag{2}$$

where x is an arbitrary variable, α is the degree of conversion and i is the functionality of the cross-link point,

$$n_i = \frac{iA_i}{\sum_i iA_i},$$

A_i is the concentration of cross-link points of the functionality (connectivity) i. Assuming that $u(1) = v$, one gets

$$v = 1 - \alpha + \alpha \sum n_i v^{i-1}. \tag{3}$$

Simplification for, *e.g.*, a pentafunctional amine, gives

$$n_{a5}v^3 + (n_{a5} + n_{a4})v^2 + (n_{a5} + n_{a4} + n_{a3})v + 1 - n_{a1} - \alpha^{-1} = 0. \tag{4}$$

Solution to this cubic equation makes it possible not only to express v as a function of the degree of conversion α, but also to obtain the condition for the determination of the gel point.[58, 61]

The yields of the sol (S) and gel (G) fractions and the concentration of pendant chains (X) are given by

$$S = (1 - \alpha + \alpha v)^2, \tag{5}$$

$$G = \alpha^2(1 - v)^2, \tag{6}$$

$$X = 2\alpha(1 - v)(1 - \alpha + \alpha v), \tag{7}$$

where v is the root of Eqn (4) other than unity.

The proportion of elastic active chains (p) is determined from the equation

$$p = \alpha^2(1 - n_0 - n_1)^2. \quad (8)$$

The relations derived were used [62] to calculate the parameters of the topological structure of a ternary system containing an epoxy oligomer (ED-20), a modifier (propylene carbonate, PC) and a curing agent (diethylenetriamine, DETA).

To validate the model considered, we compared the calculated and experimental values of the conversion of functional groups and the gel fraction (Figs 6 and 7). Differences between the calculated and experimental values can be explained by an increase in viscosity and by the fact that the interaction of cyclocarbonate and amino groups results in urethane groups characterised by strong intermolecular interaction. In addition, ring formation was ignored in the calculations.

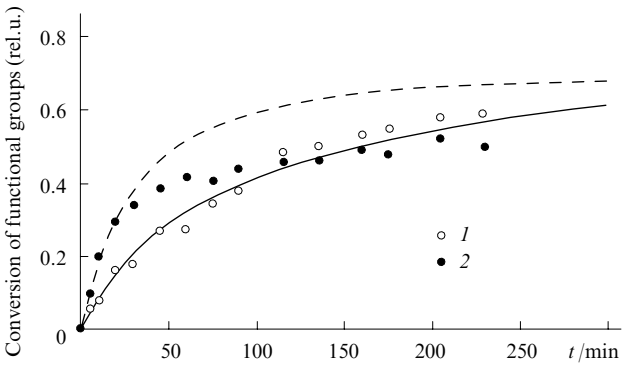


Figure 6. Calculated (curves) and experimental (points) conversions of epoxide (solid line and *1*) and cyclocarbonate (dashed line and *2*) groups in curing of a blend of ED-20 with PC (10 mass %) and DETA. Experimental values of conversion of epoxy groups (*1*), experimental values of conversion of cyclocarbonate groups (*2*); t is the running time.

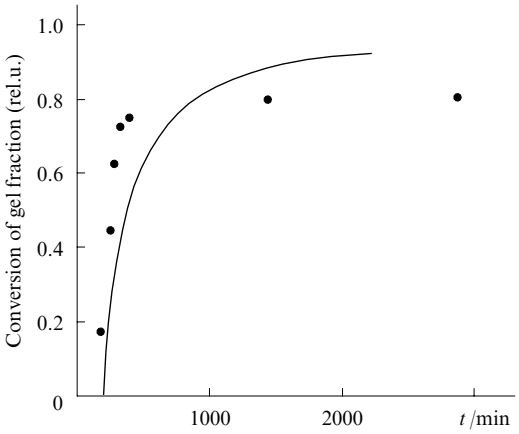


Figure 7. Calculated (solid line) and experimental (points) conversions of gel fraction in curing of a blend of ED-20 with PC (10 mass %) and DETA.

Concluding our consideration of the topological structure of polymer networks, mention may be made of a conclusion drawn at the Conference 'Growing Networks and Graphs in Statistical Physics, Financial, Biological and Social Systems' held in 2003.[63] This is as follows.

Recently, numerous network models were proposed and empirically studied by numerical simulation methods or approximate analytical methods. However, in spite of this, these models have not been completely and rigorously understood as yet. As a rule, networks have a hierarchical organisation, which implies a block architecture. In other words, all networks can be divided into a variety of interconnected blocks, each of them having a particular function or contributing to the properties of the entire network.

3. Supramolecular level

In spite of significant differences between the kinetics of polymerisation and polycondensation,[25] oligomeric systems cured following these mechanisms have much in common. In any case the final curing products can be represented as blends of polymer networks and oligomer molecules; polymer networks and branched molecules; polymer networks of different cyclic structure; polymer networks and linear polymers and their combinations. Such blends are, as a rule, thermodynamically incompatible, and their components seem to undergo separation on the molecular level. But owing to almost complete suppression of translational mobility during network formation the structures of such blends remain unchanged with time ('frozen' fluctuations [64]). These structures can schematically be divided into three types, namely, spatial and topological inhomogeneities, as well as the connectivity inhomogeneities (Fig. 8).

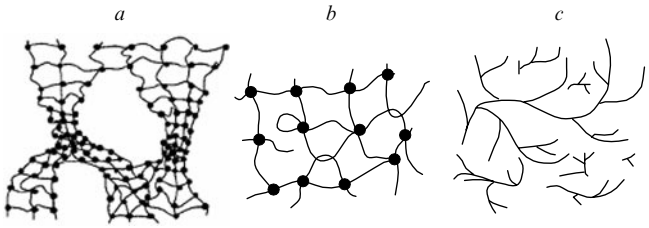


Figure 8. Schematic representation of supramolecular structures of curing products of oligomer systems: spatial (*a*) and topological (*b*) inhomogeneities and the connectivity inhomogeneities (*c*).

The degree of 'mixing' of different components is determined by the degree of incompleteness of component separation or by its reciprocal, the degree of segregation α (it should not be confused with the degree of conversion, which is also denoted by α, see above). The degree of segregation can be calculated from, *e.g.*, small-angle X-ray scattering (SAXS) data [53] using the relation

$$\alpha = \frac{\Delta\eta^2}{\Delta\rho_e^2},$$

where $\Delta\eta^2$ is the experimental value of the mean square of the electron density fluctuation and $\Delta\rho_e^2$ is the mean square of the electron density fluctuation calculated assuming a complete separation of the components. The α value depends on the ratio of the rate of network formation to the rate of phase separation, *i.e.*, in which stage of curing

the components of the system under study lose translational mobility and the ability to undergo microsyneresis.

In the macroscopic volume of a cured system the attainment of molecular mixing ($\alpha \to 0$) is unlikely, but in some local microdomains the components can be even more highly (macromolecularly or submolecularly) dispersed. The macroscopic structure of cured oligomer systems is always characterised by nonuniform distributions of the components over the volume, different degrees of mixing of different components and by concentration gradients of the components within local microdomains, which occurs even in the primary solid particles. Their composition differs from the average composition of the system and the α value can vary over a very wide range (1% to 75%).[6]

This can also be described in another manner using, *e.g.*, an analogy with the concept of sinusoidal character of the amplitude of composition fluctuations in spinodal decomposition (see below), as was done earlier.[65] In this case one can determine how the molecular compositions of constituent phases depend on the duration of the chemical reaction.

A remark is appropriate at this point. Lipatov mentioned[6] that the notion 'concentration fluctuation' in the context of, *e.g.*, Ref. 65 is applicable to single-phase systems only. But curing of oligomeric systems, even initially single-phase ones, is accompanied by the appearance of inhomogeneities as the chemical reaction develops. These inhomogeneities have certain necessary features of a phase; however, from the classical point of view[66] they cannot be considered as phases because of the lack of some sufficient features of the phase. Therefore, the cured oligomeric systems are no longer single-phase but do not undergo transitions to the two- or multiphase states. Shilov and Lipatov[67] called such nonequilibrium structures 'phasones'. Phasone structures are only formed in spinodal decomposition. Nevertheless, kinetically stable, but thermodynamically nonequilibrium structures characterised by incomplete separation of components and phases are also formed by the nucleation mechanism of phase separation.[68–70] Therefore, the presence of structures with incomplete component separation is a characteristic feature of all mechanisms of phase separation in all polymer networks. Figure 9 presents micrographs obtained in a study of poly(methyl methacrylate) samples by near-field scanning optical microscopy.[70] Optically transparent poly(methyl methacrylate) contained fluorescent labels, which made it possible to visualise the spatial distribution of segments. As can be seen, the polymer network, unlike non-cross-linked samples, is inhomogeneous on the submicrometre level.

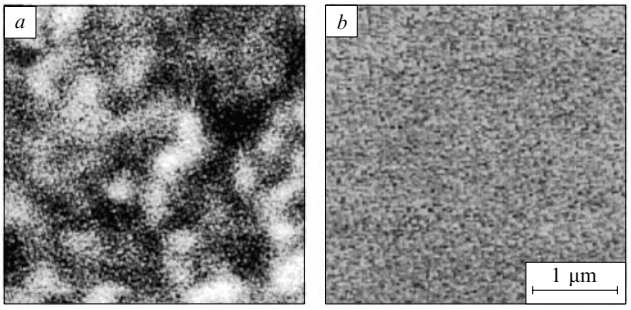


Figure 9. Micrographs of cross-linked (*a*) and non-cross-linked (*b*) poly(methyl methacrylate).[70]
Light source wavelength 442 nm.

All things considered, the formation of inter-chain chemical bonds should result in a closer packing because covalent bonds are much shorter than the van der Waals bonds. However, closer packing in the whole volume is only possible if the chemical interaction between components does not violate the arrangement of other close-packed chain fragments. This is not always the case. A chemical event can give rise to competition between the gain in packing due to shortening of bonds and the loss of ordering of chains between cross-link points; therefore, the total contribution of these mutually exclusive trends to the change in the free volume of the system can either be positive or negative.

Experiments give both types of results.[71–75] The final results are to a great extent dependent on the length of oligomer blocks. Flexible blocks can more readily be packed in a regular fashion. The result also depends on the energies of intermolecular interaction between rigid molecular fragments[72] and on the degree of their cross-linking[76] (the higher the degree of cross-linking the smaller the number of possible conformations), on the temperature at which curing was done (relaxation processes are suppressed below the glass transition temperature T_g), *etc*. But even if the reaction temperature was higher than T_g, the free volume is determined by the cooling (annealing) conditions.[77,78]

Yet another approach[4] describes the supramolecular structure of cured oligomeric systems in terms of 'physical' and 'chemical' clusters.

The degree of ordering in a cured system is to a great extent determined by the level of supramolecular structural organisation in the initial liquid oligomeric system. Experimental detection of both short-range and long-range order upon curing, as well as disordering of the supramolecular structure in the course of curing have been reported.[25] A possible explanation for these seemingly contradictory data is based on the consequences from the Arinshtein theory,[79] according to which chemical reactions of anisotropic molecules can lead to both higher and lower structural organisation of the system (higher and lower orientation order of reactant molecules) depending on the ratio of the kinetic constants for the reaction; this was confirmed in Ref. 80.

The formation of anisotropic structures in oligomer systems in the initial state or under curing conditions can occur not only spontaneously due to thermodynamic reasons[81] or be initiated by the chemical reaction,[79,80] but also under the action of various force fields on the system being cured (see, *e.g.*, Refs 20, 82–86).

The structure of films, which were prepared from blends of high-molecular-mass polystyrene (PS) (MM > 10^6, $M_w/M_n = 1.1$) with oxyethylene dimethacrylates and preliminarily exposed to uniaxial tension (relative elongation λ varied from 0 to 1000%), was studied by birefringence, IR dichroism and X-ray diffraction methods.[83]

The degree of molecular orientation (Δn) calculated from birefringence data using an approved procedure[87] for some systems before and after irradiation with accelerated electrons (irradiation doses varied from 0 to 200 kGy) at different λ values are listed in Table 3. Since a preliminary study[83] showed that irradiation of the initial PS in both oriented and free states causes no changes in Δn, from the data of Table 3 it follows that all the changes observed are due to an increase in orientation order of the oligomer molecules. The system can become more ordered both under tension and (additionally) during subsequent polymerisa-

Table 3. Changes in the degree of molecular orientation of polymer-oligomer systems upon tension before (in the numerator) and after (in the denominator) irradiation.[83]

System	λ (%)	Dose /kGy	$-\Delta n \times 10^3$	System	λ (%)	Dose /kGy	$-\Delta n \times 10^3$
PS + DMOE-1 (50%)	200	0/90	3.1/4.3	PS + DMOE-3 (50%)	800	0/62	26.3/64.4
	400	0/90	7.2/11.4		1000	0/62	42.9/149.8
	600	0/90	10.4/16.8	PS + DMOE-3 (80%)	200	0/100	0.9/1.7
	800	0/90	30.5/44.8		400	0/100	3.2/4.5
PS + DMOE-3 (20%)	200	0/38	4.1/3.0		600	0/100	3.1/4.9
	400	0/38	9.8/11.0		800	0/100	3.9/5.6
	600	0/38	24.9/38.6		1000	0/100	6.9/21.6
	800	0/38	50.2/52.2	PS + DMOE-13 (50%)	200	0/51	1.6/1.1
	1000	0/38	36.1/54.6		400	0/51	4.4/5.3
PS + DMOE-3 (50%)	200	0/62	5.8/11.0		600	0/51	9.8/14.5
	400	0/62	8.7/30.4		800	0/51	15.8/22.7
	600	0/62	13.5/32.2				

Note. DMOE-1 is $CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CO_2(CH_2)_2O_2C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$; DMOE-3 is $CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CO(OCH_2CH_2)_3O_2C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$;

DMOE-13 is $CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CO(OCH_2CH_2)_{13}O_2C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$.

tion of the films, the effects being significant, namely, Δn increases by a factor of 1.5 to 3.

Interpretation of these results remains to a great extent unclear. However, the increase in the molecular orientation of the oligomeric component in these systems under the action of mechanical force field and fixation (even an increase) of this orientation order as a result of radiation-induced curing have been demonstrated with certainty.

Yet another example is as follows. In his monograph [20] Khosin reported the dependences of the aggregate sizes and densities of the epoxide oligomer ED-20 on the duration of sonication of samples (Table 4). As can be seen, sonication leads to rearrangement of the aggregate structure of the liquid oligomer. The character of this rearrangement is ambiguous. First, the effective aggregate size and the density of molecular packing increase. However, at a particular instant these characteristics begin to decrease as sonication continues. This extremal behaviour was logically explained by the fact that initial structural ordering (the possibility of formation of regular aggregates is facilitated) is followed by destruction of aggregates and disordering when the excess energy exceeds a particular limiting value. It was pointed out that the optimal energy of structural rearrangement depends on the chemical structure and molecular mass of oligomer and on the treatment temperature.

Table 4. Effect of sonication on the size of aggregates (r) and the density (ρ) of ED-20 oligomer.[20]

Parameter	Duration of sonication /min				
	0	15	30	45	60
r /μm	0.05	0.15	0.98	0.62	0.01
ρ /kg m^{-3}	1163.1	1165.3	1169.9	1166.7	1162.8

Comparison of these properties of the initial systems with those of cured polymers (Fig. 10) reveals a full correlation, namely, changes in r and ρ for the initial systems occur in parallel to the changes in T_g, proportion of the extracted fraction S, and the compressive strength and bending strength of polyepoxides. Although an indirect proof, this is a strong argument in favour of fixation of ordered structural elements in the liquid system during polycondensation.

The effect of the supramolecular structure on the morphology of polymer networks based on oligomers cannot be revealed with certainty ignoring the phase structure of the system. Inhomogeneities observed in the electron microscopy, optical and other experiments are most often due to the presence of thermodynamically nonequilibrium phase inclusions, which in some cases contain fragments of certain supramolecular structures. Therefore, one can say about different degree of packing within such particles, about one or another degree of packing in the 'inter-grain space', about periodical distribution of such microinhomogeneities over the volume of the polymerising system, *etc*. Taking account of these considerations, mention may be made that

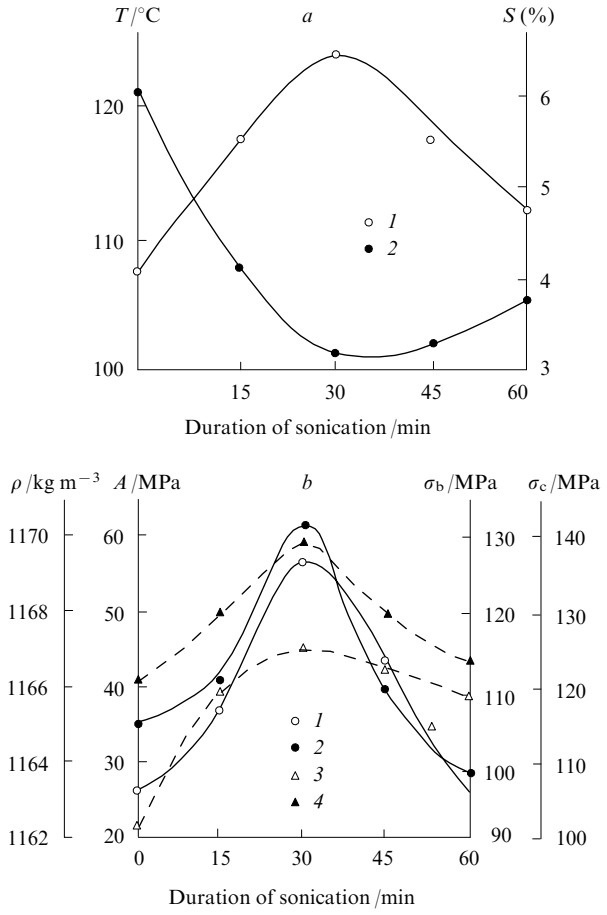


Figure 10. Effect of the duration of preliminary sonication of oligomer on the properties of epoxyamine polymer .[20]
(*a*) glass transition temperature T_g (*1*); content of sol fraction *S* (*2*); (*b*) density (*1*) and the compressive strength (σ_c, *2*), bending strength (σ_b, *3*) and adhesive strength normal to steel surface (*A*, *4*), respectively.

the morphology of the supramolecular structure of cured oligomer systems first of all depends on the density of cross-linking (coalescence of grains) in the macroscopic volume of the system. In principle, morphologic forms known for amorphous and crystalline polymers (*i.e.*, stacks, globules, lamellae, fibrils, spherolites, *etc.*) are possible for loose networks. All these morphological forms were observed in experiments with cured oligomer systems,[68, 72, 73, 88–90] in any case, it is this interpretation of experimental results that was given by the authors of those studies.

As the concentration of cross-link points increases, the formation of close-packed structures becomes progressively more difficult. Chemical cross-linking points disturb the structural organisation of network systems on both short- and long-range levels. Experiments with highly cross-linked systems ($> 10^{21}$ cross-link points per cm^3) led to observation of only the simplest morphological forms, namely, globular formations. By varying the curing regimes, component ratios, *etc.* one can only control the size and mutual arrangement of such aggregates.

4. The colloid-dispersion level

The presence of inhomogeneities in solutions does not mean heterogeneity of the solutions (in the sense that the phase transition is completed). This also does not indicate micro-phase separation, as is sometimes reported. Leaving other points of view[17, 24] out of consideration, we will only emphasise that, according to Gibbs' classical definition, 'a phase is a totality of homogeneous parts, uniform throughout the system in chemical composition and physical properties, which do not depend on the amount of matter, and separated from other parts of the system by boundary surfaces'.[66] Even if we take into account the remark by Rakovskii[91] ['not all physical properties are thermodynamical ones; rather, only those which can be represented as functions of the state parameters (volume, pressure, temperature, concentration) only belong to thermodynamical properties'],‡ the phase is also characterised by two essential features, namely, its properties are independent of the amount of matter (component ratio) and there is some boundary surface confining the phase. If this occurs simultaneously, then, according to Gibbs, we deal with the necessary and sufficient conditions for a phase to exist. Simultaneous meeting these conditions distinguishes the thermodynamic phase from other types of inhomogeneities in both liquid and cured network systems.

Without dwelling on arguments put forward by different authors (we believe they were logically and convincingly analysed by Lipatov[6]) we will (conditionally) assume that the primary fragments of structural inhomogeneity in cured oligomer systems are aggregates characterised by nonuniform compositions and different degrees of separation. These are structures characterised by incomplete component separation and phase separation and by different degree of segregation,[12] that is, 'phasones' (see above).[57] Morphologically, these can be globules, or grains, or microgels (names can be different).[68] As mentioned above, their structures can be represented as blends of polymer networks and oligomer molecules; polymer networks and branched molecules; polymer networks of different degree of cross-linking; polymer network fragments with different segmental flexibility; polymer networks and linear polymers, as well as combinations of such blends. This concerns the products of curing of all oligomers and all oligomer systems. Owing to 'chemical quenching' (term used in Refs 4 and 17), *i.e.*, due to the suppression of translational mobility of structural elements as a result of chemical transformations, the systems are no longer in thermodynamic equilibrium, but still remain kinetically stable.

Changes in the chemical composition along some spatial coordinate going into the interior of the particle (grain) and on going from one particle to another can be represented by a sinusoid (which can have a 'saw-like' or degenerate 'sigmoid' shape). In the framework of this approach, it is important to choose a criterion for the determination of the phase boundary and inter-phase layer.

In electron microscopy micrographs, the phase boundary seen at particular (small) magnification becomes diffuse as the magnification increases; small particles visible at larger magnification become invisible as the resolution decreases.[73] Therefore, generally the size of structural inhomogeneities in products of curing of oligomer systems should be estimated keeping in mind that in this case the notion 'phase boundary' is conditional (its extension and thickness depend on the experimental methods of determination), and so is the size of phase inclusions, which is

‡ More recently, this became a basis for classification of thermodynamic variables into 'field' and 'density-type' ones.[92]

determined in various experiments. Additionally, since there is a gradual transition from the highly cross-linked centre of a particle through a loose network in peripheral regions to the inter-grain (inter-globular) space, the notion 'transient layer' (or 'interphase region') also has no rigorous physical meaning.[93] Nevertheless, the spatial transition from one structural type to another does occur and quantitative determination of its parameters can be done using various models, *e.g.*, as a structure with an nearly average chemical compositions.§

The extension and volume fraction of the transient layer depend on the degree of segregation of the components. The volume fraction of the inter-phase region for the cured system 'poly(vinyl chloride) (PVC) + trioxyethylene dimethacrylate' evaluated from the data of relaxation studies[96] is 10% – 40%. The width of this interval depends on the component ratio and on the curing regimes. Similar estimates for the transition layers in the cured systems based on polyurethanes and poly(urethane acrylates) were obtained by SAXS.[53] The thickness of the interphase layer depends on the experimental techniques. Powder X-ray diffraction restricts the upper limit of the thickness of the interphase layer to 5 – 10 nm.[97]

The problem of distinguishing between the continuous and dispersion phases in a particular system is non-trivial. In the case of networks obtained by curing of 'pure' oligomers the answer is given by the schemes of the structures shown in Figs 11 and 4. In one case, the continuous phase comprises aggregated grains from the highly cross-linked network containing disperse microregions of imperfect (defect, loose, containing side products) network of 'inter-grain matter', whereas in the other case the dispersion medium is composed of flexible, loose-packed network fragments while the disperse phase is built of rigid network aggregates. The situation with blends, (*e.g.*, polymer – oligomer systems) is more complicated and becomes even more complicated when considering the curing of initially two-phase oligomer systems. The structure thus formed was called a 'phase-in-phase-in-phase'.[4, 17]

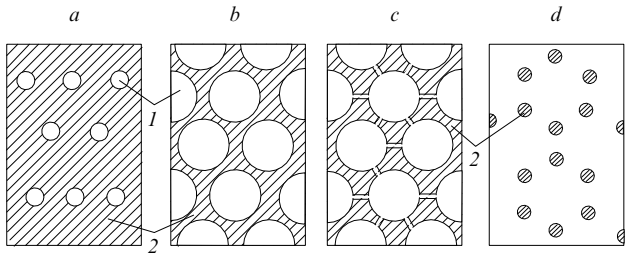


Figure 11. Scheme of structure evolution in the course of curing of reactive oligomers in different stages of post-gel curing.[23]
Nucleation (*a*), growth of grains (*b*), coalescence (*c*) and phase inversion (*d*); grain (*1*) and inter-grain space (*2*).

Prior to going to experimental substantiation of the concepts of hierarchical structure of oligomer-based polymer networks (see above), we will consider modern views of the reaction-induced phase separation of these systems.

§ Detailed consideration of models for transient layers can be found in Refs 94 and 95.

III. Phase separation under reaction conditions

Recently, the kinetics and thermodynamics of phase separation during formation of networks have been studied very intensively, but this research is still far from completion.[98 – 131]

Phase separation in the course of chemical curing of oligomers is more complicated than the liquid → solid phase transition, which occurs, *e.g.*, on cooling of polymer solutions or melts. The reason is that not only the concentration (φ), but also the molecular compositions of the components of the system change. Therefore, the classical condition for instability

$$\frac{\partial^2 \Delta G}{\partial \varphi^2} < 0$$

is transformed to

$$\frac{\partial^2 \Delta G}{\partial \varphi^2} + Y < 0, \qquad (9)$$

where ΔG is the change in the Gibbs free energy of mixing, Y depends on the reaction parameters (duration, temperature, degree of conversion, degree of segregation of components, *etc.*).

As the chemical reaction develops, the structural characteristics of the system also change and, correspondingly, so do the thermodynamic conditions. As an example, Fig. 12 presents the phase diagrams constructed at different conversions of a blend of a butadiene-*co*-acrylonitrile (8%) copolymer having terminal CO_2H groups (SKN-8-KKG) and an epoxy oligomer ED-20 cured with *m*-phenylenediamine.[112, 131] Initially, this is a single-phase blend at all

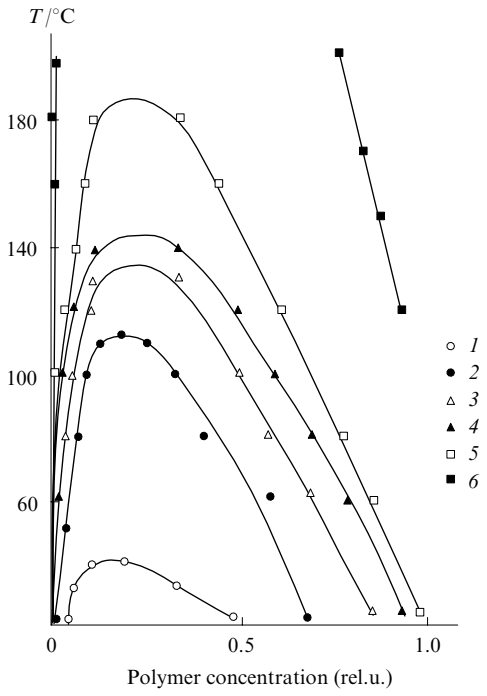


Figure 12. Phase diagrams of the system ED-20 – SKN-8-KKG under curing conditions at a conversion of 31 (*1*), 37 (*2*), 40 (*3*), 42 (*4*), 44 (*5*) and 53% (*6*).[131]

component ratios. As the chemical reaction develops, the thermodynamic affinity of the reaction products becomes poorer and at conversions higher than 30% the blend shows a limited compatibility (*i.e.*, phase separation becomes possible). Further increase in the conversion causes the compatibility range to narrow even more. At conversions higher than 55%, the branches of the binodal lines pass near the temperature axis, which indicates a complete incompatibility of curing products at all component ratios. The cross sections of such phase diagrams normal to the temperature axis give the conversion diagram similar to that shown in Fig. 13.

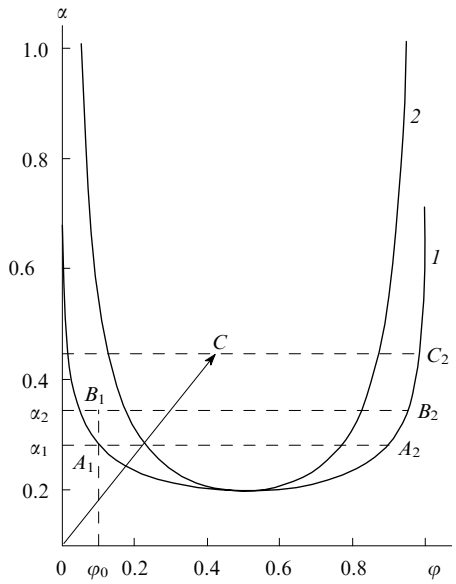


Figure 13. Phase diagram plotted in the composition–conversion coordinates.
T = const; binodal (*1*) spinodal (*2*). For details, see text.

At a low rate of the chemical reaction, phase separation by the nucleation mechanism in (initially) homogeneous system will begin at the conversion α_1; the composition of the newly forming phase will be determined by the points A_1 and A_2 in the binodal. At high reaction rates, the system will pass through the binodal until, *e.g.*, the conversion α_2 before start of the formation of a new phase, and the phase compositions will be determined by the points B_1 and B_2. But since the reaction continues and the system does not leave the metastable region, phase separation will lead to formation of particles of variable composition. This will occur until the gel point.

Even the simplest processes of network formation (ignoring cyclisation, effect of the free volume and suppression of mobility, *etc.*) in the course of chemical interaction between polyfunctional monomers both under solvent-free conditions and in good (athermal) solvent reported by de Gennes in his famous monograph [113] provide good illustrations of the complexity of phase transformations in reaction systems. The author, in particular, showed that the classical theory of gelation,[114,115] which uses the 'branching tree' concept, fails in the framework of the percolation model, being limited to the self-consistent field approximation. In any case, calculations performed using this theory and the scaling approximation give different results.

In particular, near the gelation threshold one has

$$\Delta p = p_c - p \to 0,$$

where p_c is the percentage of cross-links corresponding to the sol–gel transition; p is the running percentage of cross-links and the coefficient δ in the equation for the average degree of polymerisation

$$N_w \cong \Delta p^{-\delta},$$

is equal to 1 in the classical case and 1.8 in the scaling approximation.

For solution polymerisation, the lattice model assumes that each lattice site (i) can be occupied by either the monomer (occupation number $n_i = 1$) or the solvent molecule ($n_i = 0$). If two neighbouring sites (i, j) are occupied by the monomers (n_i and $n_j = 1$) and the attractive energy between them is E, a chemical bond is formed between them.

The number of reacted bonds is given by

$$R = \frac{\partial \log \Theta}{\partial \beta},$$

where Θ is the large statistical sum

$$\Theta = \sum \exp\left(\alpha \sum n_i + \beta \sum{}' n_i n_j\right).$$

Here α is the logarithm of the activity of monomers, β is the logarithm of the activity of the bonds forming the gel. The prime at the sum denotes that summation is performed over the nearest-neighbour pairs. The proportion of reacted bonds is

$$p = \frac{R}{R_{max}}.$$

The maximum degree of cross-linking equal to

$$R_{max} = \frac{N_s z \varphi^2}{2}$$

is attained when each monomer molecule is bonded to z other molecules. Here, N_s is the number of lattice sites.

If the positions of the reacting molecules are uncorrelated, one has $\beta = 0$ and

$$R|_{\beta=0} \equiv R_0 = \frac{N_s z \varphi^2}{2}.$$

As the reaction develops, the R and β values increase. In the course of network formation, $R \to R_{max}$, and the parameter β^{-1} changes from $+\infty$ to 0.

This situation is shown in Fig. 14, which presents the phase diagram constructed in the $\varphi - T_{eq}$ coordinates, where $T_{eq} \equiv E/\beta$ is the equivalent temperature of the corresponding lattice gas (T_{eq} decreases in the course of the reaction). The single-phase region in Fig. 14 is confined by the binodal (above the curve Γ). In turn, the curve Δ is the boundary of the sol–gel transition in the single-phase region and C is the critical point.

At high equivalent temperatures, the line Δ approaches the vertical asymptote $\varphi = \varphi_{cs}$. At lower temperatures T_{eq}

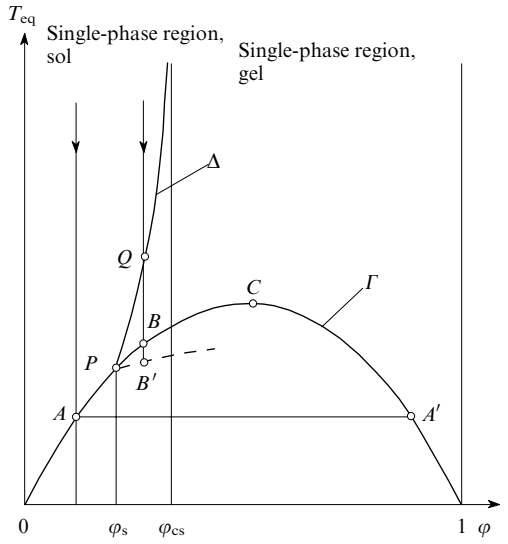


Figure 14. Phase diagram plotted in the coordinates 'equivalent temperature–concentration of polyfunctional oligomer' for a gel-forming system in semi-dilute solution in a good solvent (for details, see text).[113]

and a fixed φ value, the probability of bond formation increases, and the gel phase dominates, *i.e.*, a decrease in T_{eq} causes the line Δ to deviate towards lower concentrations and to arrive at the binodal at the point P, which does not match the critical point C.

Depending on the oligomer concentration, de Gennes considered three situations.

1. If $\varphi < \varphi_s$, the system is in the sol state up to the point A at which the gel fraction appears (the concentration of the gel fraction is described by the point A').

2. In the concentration range $\varphi_s < \varphi < \varphi_{cs}$, the system is in the sol state up to the point Q and undergoes a transition to homogeneous gel after this point. As the point B is reached, phase separation into two gel phases should occur, but usually this takes place at a lower temperature (at the point B') and manifests itself as microphase separation.

3. At $\varphi > \varphi_{cs}$, network formation occurs in the regime of continuous gel formation and the microphase separation is governed by the initial reaction conditions.¶

For three-dimensional polymerisation, the very early stages of the process involve the formation of microgel particles, *i.e.*, there are local regions characterised by high conversions and polymer concentrations. This means that, locally, the system passes through the spinodal (*i.e.* in the region of unstable state) at, *e.g.*, the point C (see Fig. 13). Therefore, phase formation by the mechanism of spinodal decomposition involves enhancement of concentration contrast of fluctuations. As time passes, the concentration contrast will increase until the glass transition of the polymer-enriched phase. Clearly, this depends on the reaction temperature and can occur far before arriving at the point C_2 (see Fig. 13).

¶ This consideration does not point to a particular mechanism of phase separation. Clearly, this is in essence a polycondensation process with respect to the mechanism of network formation. The phase formation occurs by nucleation followed by the growth of particles.

Manevich and Shaginyan[101] reported a detailed consideration of the kinetics of spinodal decomposition with allowance for chemical transformations in the framework of the phase separation model using the scenario with slowing down the process at a low reaction rate. Changes in the composition during the chemical reaction lead to complication of the known balance equation for the blend of linear polymers[116,117]

$$\frac{\partial u(r,t)}{\partial t} = -\operatorname{div} I + J_x, \tag{10}$$

where u is the concentration with respect to a single component of the blend at the point r in the spatial coordinate x at the instant t and I is the diffusion flux density; the last term determines the rate of the chemical reaction; it is calculated assuming that, at least in the initial stage, it can be approximated by the Onsager linear expansion

$$J_x(r,t) = \Lambda_x u(r,t), \tag{11}$$

where Λ_x is the Onsager diffusion coefficient. The model also assumes a positive rate constant for the chemical reaction ($\kappa > 0$) and that the reaction is slow compared to diffusion transfer. Then one has

$$\frac{\partial u(x,t)}{\partial t} = \frac{\partial[A(u)\partial u/\partial x]}{\partial x} - b_0\frac{\partial^4 u}{\partial x^4} - \kappa u, \tag{12}$$

where

$$A(u) = a_0 + a_1 u + a_2 u^2,$$

b_0 is a constant.

In solving Eqn (12) the rate constant for the chemical reaction was assumed to be in the interval 10^{-4}–10^{-6}. Even in this relatively narrow range the effect of the reaction rate on the character of phase separation manifests itself in different manner. At $\kappa < 10^{-5}$, the effect of the chemical reaction on the initial stage of phase separation characterised by exponential enhancement of the mode of the maximum increase in concentration does not cause qualitative changes in the character of the process. This manifests itself only in an increase in the lifetimes of kinetically stable species, while the kinetics of phase separation remains the same as in the case of spinodal decomposition of the polymer blend.[116,117] At $\kappa \geqslant 10^{-5}$, the role of the chemical reaction manifests itself not only in an increase in the lifetimes of the kinetically stable species, but also in suppression of some stages of slowing down the phase separation process. For instance, if a chemical reaction is characterised by $\kappa \geqslant 10^{-5}$, the temporal evolution of the structure no longer includes the trimodal stage known for the decomposition of polymer blend;[116,117] only two slowdown regions are retained. Further acceleration of the chemical reaction makes the role of the last term in Eqn (12) so important that analogies with spinodal decomposition become incorrect. In this case all intermediate stages of phase separation found[116,117] for retarded decomposition of linear polymer blends are absent and the completion of the linear stage is immediately followed by the formation of a heterogeneous structure.

Simulation of the formation of microinhomogeneities in epoxy oligomer blends cured in the presence of a linear

polymer [110] and in acrylic oligomer blends cured in the presence of polyisoprene [111] performed in terms of interconnected changes in the free energy and diffusion in the course of curing of these systems led to an analytical solution to the diffusion equation

$$u_k(t) = C_k(1+4A_0k_x\mathrm{t})^{-\beta}\exp(R^*t), \tag{13}$$

which implicitly includes the temporal dependence of the Onsager coefficient on the degree of polymerisation (polycondensation) of the first component (N_1). Here C_k is the Fourier component of the initial concentration inhomogeneity, k_x is a dimensionless parameter relating the rate of diffusion relaxation of the kth mode (numerator) to the rate of the chemical reaction (denominator) in the dependence of A_0 on the degree of conversion $\alpha(t)$

$$\alpha(t) = \frac{4A_0k_xt}{1+4A_0k_xt},$$

$$\beta = \frac{\Lambda_0k^2}{3(1-\varphi_0)A_0},$$

the enhancement coefficient

$$R^*(k) = \Lambda_0L_{s0}^2k^2\left[(k^*)^2 - k^2\right],$$

where

$$(k^*)^2 = \frac{2}{L_{s0}^2}\left[\left(\chi - \frac{1}{N_1\varphi_0}\right)+\left(\frac{1}{6}-6\varphi_0\right)\right]$$

(χ is the Flory–Huggins interaction parameter),

$$L_{s0}^2 = a^2\left[2\chi + \frac{1}{18}\varphi_0(1-\varphi_0)\right],$$

a is the size of identical monomer units; φ_0 and φ are the initial and running volume concentrations, respectively; the asterisk (*) refers to the threshold values.

Analysis of Eqn (13) leads to some interesting conclusions. First, depending on the $R^*(k)$ value, the $\chi-\varphi$ thermodynamic plane of the cured system includes regions of both thermodynamically stable (spatially homogeneous 'solid solutions') and unstable states divided by the curve

$$\chi^*(\varphi_0) = 0.5\,N_1\varphi_0 - \left(\frac{1}{6}-6\varphi_0\right).$$

Having projected this boundary line on the phase diagram of the initial system and chosen the φ and T values corresponding to the region of 'solid solutions', one gets that at the concentrations

$$\varphi < \varphi^*(N_1) = \frac{3}{3+N_1}$$

and at $\chi < \chi^*(\varphi_0)$ the reacting blend always (from the initial to the cured state) remains spatially homogeneous for all k such that $R^*(k) < 0$. Therefore, an equilibrium microheterogeneous structure can form in this very narrow region of the parameters φ, T, N_1 and χ. Curing of the systems corresponding to other regions of the phase diagram leads to nonequilibrium situations and is predetermined by the size of concentration fluctuations, which in turn depend on how close is the state of the system to the spinodal line.

Second, from analysis of Eqn (13) it follows that the formation of the mode of maximum increase in the inhomogeneity depends on time. If the initial state of a curing system is located below the spinodal and $\chi < \chi_s(\varphi_0)$, the most rapidly increasing mode of the increase in the concentration inhomogeneity spontaneously separates after some time (time delay at which the system remains stable) and its wavenumber rapidly attains the limiting value $k^*/\sqrt{2}$. Both the time delay and the limiting wave number are determined by how close to (far from) the boundary of thermodynamic stability of the initial (or cured) system is the system in question.

Thus, the formation of the structure of chemically cured reactive oligomer systems can show large differences in periodicity of appearance and in lifetimes of critical-size of concentration fluctuations and, therefore, in the size and composition distributions of microheterogeneous inclusions in the final structure of the cured oligomer system compared to the periodicity observed usually for both 'pure' spinodal decomposition [118–120] of curing oligomers and spinodal decomposition of linear polymers.

Indeed, thermodynamics only indicates the direction of the process whose occurrence is an essentially kinetic problem; figuratively speaking, in this case also 'thermodynamics proposes but the kinetics disposes'. It is the kinetic features that are responsible for the phase structure of the system. This is illustrated by Fig. 15. Here, depending on the concentration of the catalyst [2,4,6-tris(dimethylaminomethyl)phenol], which determines the rate of polymerisation of diglycidyl resorcinol ether (DRE), the phase structure of PEF-3A (oligotetrahydrofuran with terminal urethane epoxy groups) is changed basically.[102, 112, 131] Namely, acceleration of the reaction leads to a decrease in the mean particle size and to an increase in modality of the distribution function. The proportion of rubber separation also considerably decreases.

Numerous experimental and theoretical studies of phase separation proceeding by various mechanisms in the course of network formation (see, *e.g.*, Refs 4, 17, 24) were carried out in connection with research on interpenetrating polymer networks.

Detailed studies of curing of epoxy oligomers in the presence of liquid rubber additives [102, 112, 121] led to formulation of the mechanism of the Cure Reaction Induced Microphase Separation (CRIMPS).[98, 122]

Experiments showed high probability of nucleation mechanism in this case. Indeed, an X-ray scattering study [123] revealed the formation of $\sim$3–50 nm particles long before the cloud point indicating the beginning of phase separation. Near the cloud point, these particles grow, while the particle size in the past-cloud-point region reaches a few micrometres.

A scenario of nucleation induced phase formation was considered in Refs 106 and 122.

Assume a quasi-equilibrium case. At the conversion α_1, particles with the core radius r (core composition is φ_2) and the shell radius R (shell composition is φ_1) are formed. From the balance conditions it follows:

$$\omega \equiv \frac{r^3}{R^3} = \frac{\varphi_0-\varphi_1}{\varphi_2-\varphi_0}.$$

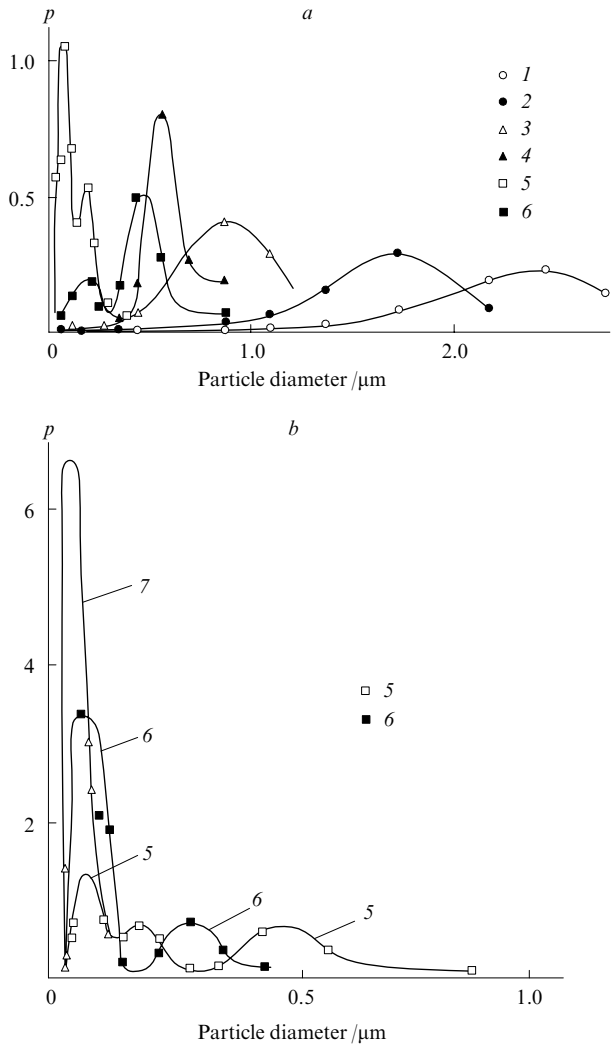


Figure 15. Phase structure of PEF-3A plotted *vs.* polymerisation rate of diglycidyl resorcinol ether;[102]
p is numerical proportion of particles; catalyst concentration (%): 0.8 (*1*), 1.0 (*2*), 2.0 (*3*), 3.0 (*4*), 3.4 (*5*), 4.6 (*6*) and 5.0 (*7*).

The change in the Gibbs free energy upon formation of a particle is given by

$$\Delta G = \frac{4}{3}\pi R^3\Big[g(\varphi_1)\omega + g(\varphi_2)(1-\omega) - g(\varphi_0) + \\ + 4\pi R^2\left(\omega^{2/3}\sigma_1 + \sigma_2\right) = -\frac{4\pi r^3\varepsilon}{3\omega} + 4\pi r^2\sigma,$$

where

$$\varepsilon = g(\varphi_0) - g(\varphi_2) + \omega\big[g(\varphi_2) - g(\varphi_1)\big],$$

$$\sigma = \sigma_1 + \omega^{-2/3}\sigma_2,$$

σ_1 and σ_2 are the surface energies at the core–shell and shell–medium boundaries, respectively .

Using the condition for maximum free energy

$$\frac{\partial\Delta G}{\partial r} = 0,$$

one gets the radius of the critical nucleus †

$$r_c = \frac{2\sigma\omega}{\varepsilon},$$

$$R_c = \frac{2\sigma\omega^{2/3}}{\varepsilon}.$$

The nucleation probability (p) is

$$p = A\exp\left(-\frac{\Delta G_c}{RT}\right),$$

where A is the pre-exponent,

$$\Delta G_c = \frac{16\pi\sigma^3\omega^2}{3\varepsilon^2}.$$

According to calculations,[106] p increases with the conversion.

Further evolution of nuclei is governed by two processes, namely, diffusion of the components of the system, which ensures the growth of particles, and the Ostwald maturing,[125–127] *i.e.*, redistribution of matter between particles, which leads to an increase in the mean particle size. The viscosity of the medium increases in the course of the reaction, while the diffusion coefficient decreases. In addition to the increase in the nucleation probability this leads to a decrease in the size of the newly forming particles. As a result, the particle size distribution is broadened and can become polymodal. Further growth of particles by both coalescence [126, 127] and Ostwald ripening [125] is slowed down. But if the reaction is sufficiently slow, the second process can lead to narrowing of the distribution.

The formation of periodic structures is possible not only during spinodal decomposition of curing oligomers, but also when phase formation proceeds by the nucleation mechanism.

Structurally, the problem of nucleation of heterogeneity centres can be reduced to analysis of the changes in the number and size of disperse particles that are formed during oligomer curing. Indeed, if the phase-formation centres appear randomly in the intially single-phase systems, the size distribution of the growing solid particles should be unimodal. This is predicted by the nucleation theory [102, 106] and was detected experimentally.[96, 128, 129] If curing is accompanied by additional nucleation, the final distribution can differ from the unimodal Poisson function. In particular, bi- and even trimodal distributions (see Fig. 15) have been reported.[112, 121, 130, 131]

The reasons for possible variety of the distribution functions in cured oligomer systems and of the mechanisms of discrete (in time) and spatially localised successive nucleation were considered, in particular, by Rozenberg *et al.*[102, 106, 129]

The re-nucleation condition is governed [102] by some supersaturation of the solution

† According to the classical theory (see, *e.g.*, Ref. 124), an equilibrium particle ($\partial\Delta G/\partial r < 0$) of a new phase is formed as a result of the growth of nonequilibrium ($\partial\Delta G/\partial r > 0$) critical nucleus.

$$\Psi = \frac{c}{c_b}$$

at a given instant t, at which one has

$$\frac{d\Psi}{dt} > 0.$$

Here c and c_b are the running and equilibrium oligomer concentrations, respectively. In other words, nucleation of a new particle is possible if the first derivative of supersaturation is positive. In conventional chemical polyreactions after primary nucleation the ratio c/c_b remains less than unity and, therefore, one has $d\Psi/dt < 0$. In the network formation reactions, the situation is more complicated. After substantiation of the fulfillment of the Prigogine–Defey criterion in these processes,[132] it was accepted [98] that fundamental forbiddenness of changes in the sign of the derivative $d\Psi/dt$ is removed, because for the reactions accompanied by phase separation of the system the rate, at which the concentration decreases, is proportional to the interdiffusion coefficient (D) and given by

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2},$$

$$\frac{dc}{dt} = \beta\Gamma W,$$

where β is a coefficient depending on the degree of polymerisation (Γ) and the polymerisation rate (W) and x is the spatial coordinate of the concentration of matter near the growing particle.

It was theoretically proved [102] that the rate constants for chemical reactions of anisotropic liquids with aligned reacting molecules can change in a cyclic manner. Moreover, the reaction can even stop and 'reanimate' itself after some time.

The nucleation probabilities for different instants of the chemical reaction were calculated for some oligomer systems [102] based on the classical concepts [133, 134] with inclusion of prerequisites for re-nucleation (see above). This was done using experimental dependences of W, D and c_b on the degree of curing of RDE blends with oligomeric rubbers SKN-8-KKG and SKN-14-KKG, and with PEF-3A. According to calculations, the probability of secondary nucleation at a distance of $(1/2)L$ between two growing particles (products of primary nucleation occurred at t_1) abruptly (by a few orders of magnitude) decreases due to the motion of the reaction component towards the surface of the growing particle and, therefore, a decrease in the concentration at the possible nucleation point. However, after some time at instant t_2 a simultaneous decrease in D and c_b, occurring with an increase in α in the time interval from t_1 to t_2, causes the derivative $d\Psi/dt$ to change its sign; correspondingly, the probability of nucleation at the instant t_2 increases. If a new second-generation particle appears, the probability of nucleation of other particles in the vicinity of this particle again decreases for some time but at instant t_3 the situation again meets the conditions for nucleation of next-generation particles (for the reasons, see above). The limiting cases of this self-oscillating character of phase formation correspond to complete suppression of molecular mobility ($D \to 0$ due to gel formation or isothermal glass transition) or to consumption of the unreacted oligomer ($c \to 0$).

The character of the distribution of inclusions formed under actual oligomer curing conditions depends on many factors. The dependence of the distribution function on the curing rate is illustrated by the data of Table 5. As W increases, the distribution function transforms from unimodal to a bi- and then trimodal one and then again degenerates to a unimodal function.[129]

Table 5. Distribution types of phase inclusions in cured blend RDE + PEF-3A at different curing rates.[129]

$10^4 W/s^{-1}$	Volume fraction (%)	Distribution type
0.8	3.0	Unimodal
1.2	2.7	"
4.1	1.5	"
6.4	0.6	Bimodal
8.3	0.5	Trimodal
12.1	0.3	Bimodal
14.8	0.2	Unimodal

Note. $T = 120$ °C, the curing rate was controlled by varying the catalyst concentration.

In most cases, analysis of experimental data on the kinetics of phase separation during curing of oligomer systems (see above) is based on either the spinodal or nucleation mechanism of phase separation. Some authors (see, *e.g.*, Refs 6, 88, 109, 135) assumed the possibility for both mechanisms to alternate in different stages of curing of oligomer systems as well as to operate concurrently in different phases (this was shown theoretically).[110, 111, 136]

It should be emphasised that, irrespective of the phase separation mechanism, the final structure formed on curing of oligomer systems is always (except some hypothetical cases [110, 111]) characterised by incomplete component and phase separations. Phase separation (moreover, phase stratification) expected for thermodynamic reasons always does not reach an equilibrium due to suppression of translational and rotational mobility of structural fragments in the system being formed during the chemical reaction.

Yet another aspect of the phase formation problem is microsyneresis, *i.e.*, displacement of unreacted oligomer molecules, β-polymer fragments, partially cyclised products (in principle, all of them are reactive species) from the zone of the reaction in microgel towards grain periphery and to the inter-grain space. Because of this, the chemical reaction moves to the near-surface zone of a grain and to inter-grain space. This explicitly illustrates the complexity of the mutual influence of thermodynamic and kinetic factors on phase separation processes.

Dušek seems to be the first who paid attention to microsyneresis in three-dimensional polymerisation and proposed a semiquantitative description.[137–139] The thermodynamic criterion for phase separation of a polymer network swollen in a solvent (in this case, in its own oligomer) is given by the equation relating the change in the free energy of the polymer interacting with the solvent (ΔG) to the degree of cross-linking (v) and by the Flory–Huggins interaction parameter,

$$\Delta G = \frac{RT}{V}\left(\frac{\varphi_1}{z_1}\ln\varphi_1 + \frac{\varphi_2}{z_2}\ln\varphi_2 + \chi\varphi_1\varphi_2\right) + \qquad (14)$$

$$+ RTV\nu\left(\varphi_2^{1/3}\frac{\langle r^2\rangle_d}{\langle r^2\rangle_0} - \frac{\varphi_2}{2}\right).$$

Here V is the partial molar volume of the solvent, φ_1 and φ_2 are the volume fractions of the components 1 (in this case, oligomer) and 2 (polymer) in the system, z_1 and z_2 are the relative molar volumes of the components and $\langle r^2\rangle_d$ and $\langle r^2\rangle_0$ are the root-mean-square chain lengths in the network in the unswollen and swollen states, respectively.

Of course, Eqn (14) is simplified compared to real situations. This concerns both the free energy of mixing (first term) and the expression for the elastic potential (second term). Clearly, even in an ideal case the parameters φ, ν and, possibly, χ depend on conversion. Depending on which factor governs the separation process, the ν- and χ-syneresis are conditionally distinguished. The former usually occurs in three-dimensional polymerisation, while the latter in polycondensation.

IV. Formation of network structures upon curing of oligomers

Network formation from reactive oligomers by the polymerisation and polycondensation mechanisms has both common and distinctive features.[25] A general proposition is as follows.

Polymerisation is the process of successive addition of oligomer molecules to a growing chain, which obeys the following scheme:

$$R_n + M \longrightarrow R_{n+1}.$$

Polycondensation is the process of joining chain fragments having reactive terminal groups, which obeys the scheme

$$R_n + R_m \longrightarrow R_{n+m}.$$

Clearly, differences between the growth mechanisms of polymer chains and fragments of network structures cause the molecular and all other levels of structural organisation of the curing products formed by the polymerisation and polycondensation mechanisms to be different.

However, on the one hand, experimental data indicate that both the formation processes and the final structures of polymer networks obtained by the same mechanism show significant differences if the curing was performed in different regimes. On the other hand, the structures of polymer networks obtained by oligomer curing following different mechanisms have common features.

In the text below we will discuss these features with allowance for the hierarchical level of structural organisation at which the experimental data are analysed, the criterion chosen for analysis of the common features and differences and also taking into account (or ignoring) the potential (resolution, informativity, *etc*.) of the methods used to obtain the experimental results under examination.

Now we will present some examples illustrating specific differences and common features of the curing of reactive oligomers by different mechanisms, which determine the similarity and distinctions between the final network structures.

1. Structural information from NMR data

The kinetic dependences of the characteristic times of spin–spin proton relaxation (T_2) determined in a pulsed NMR study of curing of diphenylolpropane diglycidyl ether (DPPDGE) by the polycondensation and polymerisation mechanisms are shown in Fig. 16. The plots were constructed using experimental data obtained in a comprehensive study[33] of the relaxation behaviour of oligomer systems. Leaving the chemical aspects of polycondensation and ionic polymerisation of epoxy oligomers out of consideration (they are well documented in, *e.g*., Refs 2, 25, 140), we will only dwell on the character of changes in rotational diffusion in oligomer systems, which characterises the evolution of structural transformations.

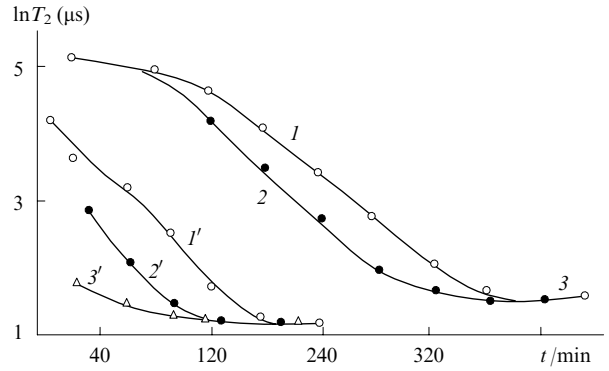


Figure 16. Temporal dependence of relaxation times T_{2a} (*1*, *1′*), T_{2b} (*2*, *2′*) and T_{2c} (*3*, *3′*) in the course of curing of diphenylolpropane diglycidyl ether by polycondensation with dichlorodiaminophenylmethane at 140 °C (*1*, *2*) and by polymerisation in the presence of catalyst 2,4,6-tris(dimethylaminomethyl)phenol at 60 °C (*1′*, *2′*, *3′*).[33]

A liquid initial system is characterised by a single relaxation time T_2, which is slowly shortened during polycondensation; after some time (80–90 min for a given regime), the system is characterised by two relaxation times, T_{2a} and T_{2b} (see Fig. 16, curves *1* and *2*). This indicates the formation of topological structures characterised by different mobilities (*i.e*., different degrees of connectivity of particular structural fragments) in the system. In this case, the differences between T_{2a} and T_{2b} in absolute values are small (at most a decimal order). The relaxation times T_{2a} and T_{2b} decrease in parallel in the course of curing, even after the gel point.‡

Calculations of the kinetics of formation of chemical cross-link points of different functionality[62] showed that in this system an increase in conversion causes the proportion of cross-link points of higher connectivity to increase due to a decrease in the proportion of the fractions of linear molecules and network fragments with mono- and bifunctional cross-link points. The cross-link points of higher connectivity (tetra- and pentafunctional) begin to form only near the gel point.

Now we return to Fig. 16 and emphasise that the relaxation times T_{2a} and T_{2b} eventually become equal to

‡ A SAXS study[67] of curing of bisphenol A diglycidyl ether with oligo(isoprene hydrazide) (taken in equimolar ratios) revealed changes in the rate of the increase in the scattering intensity and the mean square of the electron density fluctuations after the gel point.

the relaxation time characteristic of a rigid lattice (T_{2c}). The temporal dependences of T_{2a} and T_{2b} (up to their transformation to T_{2c}) are similar in shape to the temperature dependences of the characteristic times of liquid epoxy oligomers with various fractional compositions.[33]

Thus, experiments on polycondensation curing of epoxy oligomers revealed, on the sensitivity scale of NMR spectroscopy, only two types of evolutioning structures, which seem to differ in MMD parameters, degree of branching and degree of cyclisation, which eventually form rigid networks characterised by a single time of structural relaxation. However, raising the curing temperature of epoxy oligomers or modifying the network structure using monofunctional reactants leads to detection, by NMR spectroscopy, of a structure with two characteristic times of nuclear relaxation in the final stage of polycondensation.[33]

Curing of DPPDGE by the polymerisation mechanism (Fig. 16, curves $1'-3'$) occurs differently compared to polycondensation curing. Immediately after the induction period, structures characterised by the spin-spin relaxation time T_{2c} typical of rigid networks (curve $3'$) appear in the liquid system, which is characterised by the relaxation time T_{2a}. In the case of polycondensation mechanism, they are formed only in the final stage of the process. In the course of polymerisation, the proportion of the structures characterised by the relaxation time T_{2c} increases owing to fast transformation of the component with the characteristic time T_{2b}, which is formed in the system somewhat later, to the component characterised by the relaxation time T_{2c} (curve $2'$) and to gradual shortening of T_{2a} to about T_{2c} (curve $1'$). Detailed assignment of these relaxation times to particular structural fragments will be presented in the text below when we will analyse the formation of structural fragments during radical polymerisation of oligoether acrylates. Here mention may be made that, in contrast to polycondensation, in the case of polymerisation of epoxy oligomers there are three rather than two structural types, which co-exist in some steps of the evolution of the system, but as in the case of polycondensation, DPPDGE in the presence of dichlorodiaminophenylmethane (DC) in the final stage of polymerisation is transformed to a structure characterised by the relaxation time T_{2c} typical of rigid (highly cross-linked) networks.

Different characters of the formation of polymer structures upon curing of oligomers by the polymerisation and polycondensation mechanisms are also indicated by the results obtained in studies of not only rotational, but also translational mobility. At the same time, it was established that the interdiffusion and self-diffusion coefficients decrease with conversion for both polymerisation and polycondensation mechanisms.[1, 33, 67, 102]

Valuable information on the formation of the topological and phase structures in the course of radical-induced polymerisation of unsaturated oligomers was obtained in studies.[141–144]

As a typical example, Fig. 17 presents the temporal dependences of the relaxation times T_2 and the corresponding populations of proton ensembles (P) determined in the course of polymerisation of trioxyethylene α,ω-dimethacrylate.[141] During the induction period, the transverse magnetisation decays exponentially with a single relaxation time T_2^0. Then, the shape of the transverse magnetisation decay curves irreversibly changes. In different stages of curing, these curves are described by a superposition of several (two

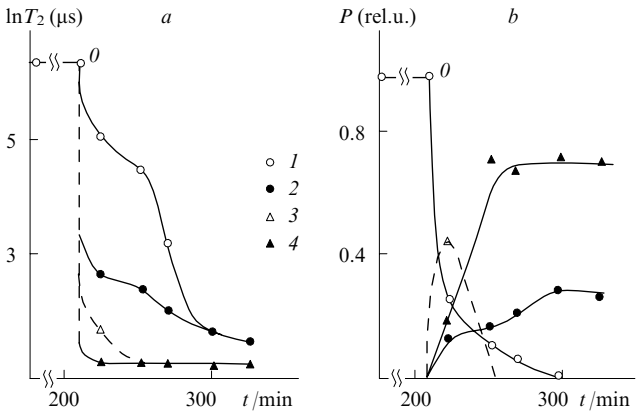


Figure 17. Temporal dependence of relaxation times T_2^0 (0), T_{2a} (*1*), T_{2b} (*2*), T'_{2c} (*3*), T_{2c} (*4*) (*a*) and populations P^0 (*0*), P_a (*1*), P_b (*2*), P'_c (*3*), P_c (*4*) (*b*) in the course of radical polymerisation of trioxyethylene α,ω-dimethacrylate at 110 °C in the presence of dicumene peroxide (0.5%) and hydroquinone (0.007%).[141]

to four) Lorentzian and Gaussian components with the characteristic relaxation times T_{2a}, T_{2b}, T'_{2c} and T_{2c}.

Here, a methodological remark is necessary. Each structural type in the samples under study is characterised by its own spectrum of correlation frequencies.[31] These spectra can overlap.[33, 141] Therefore, the experimentally measured T_2 and P values are averaged relaxation parameters. This concerns all the results obtained by pulsed NMR spectroscopy including those mentioned above as well as those listed below.

After start of radical polymerisation of an oligoether acrylate, the reaction system is characterised by not only T_{2a}, but also three additional relaxation times, *viz.*, T_{2b}, T'_{2c} and T_{2c} (see Fig. 17 *a*). They differ from T_{2a} by 2–3 orders of magnitude (*cf.* at most an order of magnitude in the case of polycondensation, see Fig. 16). These relaxation times characterise the changes in the fragmental mobilities of network structures with the increase in the concentration and functionality of cross-link points. It is accepted that T_{2c} (curve *4*) is the relaxation time of highly cross-linked poly(ether acrylate) with the density of cross-linking similar to the topological limit (T_{2c} remains constant). The formation of these structures is accompanied by local microphase separation. The time T'_{2c} (curve *3*) is the characteristic relaxation time of the network structures in which the degree of cross-linking did not reach the topological limit at the instant t, but $T'_{2c} \to T_{2c}$. The time T_{2b} (curve *2*) is the relaxation time of the structures with incomplete microphase separation. These are loose networks characterised by incomplete cross-linking and cyclisation; their swelling occurred in the free oligomer, in defective (0-functional) molecules and in the β-polymer. After completion of radical polymerisation of oligoether acrylates, the fragments characterised by the relaxation time T_{2b} are retained in the final structure. In the case of ionic polymerisation of epoxy oligomers such fragments cannot be identified by pulsed NMR spectroscopy (see Fig. 16). It is believed[141] that the time T_{2b} in the final stage of curing characterises the mobility of structural fragments in the interphase region (intergrain space, interlayer space).

Information on changes in the proportions of the structures characterised by the relaxation times T_{2a}, T_{2b}, T'_{2c} and T_{2c}, which occur in the course of curing of trioxy-

ethylene α,ω-dimethacrylate, is presented in Fig. 17*b*. On the whole, the changes detected by pulsed NMR spectroscopy obey the schemes of formation of heterogeneous poly(ether acrylate) structure proposed [3] based on analysis of the polymerisation kinetics of oligoether acrylates. As applied to the analysis of the experimental results in question, the formation of a poly(ether acrylate) network structure can conditionally be divided into two steps.

The first step is completed with the formation of particles comprising a highly cross-linked polymer with the limiting topological structure ($P_c \to$ const). Here, the content of the highly cross-linked product characterised by T_{2c} increases linearly with time (see Fig. 17*b*, curve *4*) and occurs in different manner. First, a rigid network is formed due to polymerisation, which begins in the sybotaxes, where the 'kinetically favourable order' enables rapid formation of a rigid structure (transition $T_{2a} \to T_{2c}$). A 'loose' network ($T_{2b} \to T'_{2c}$) is formed simultaneously. Then, owing to the intramolecular cyclisation reactions in the structures characterised by T'_{2c} ($T'_{2c} \to T_{2c}$) and with T_{2b} (partial transition $T_{2b} \to T'_{2c} \to T_{2c}$ or $T_{2b} \to T_{2c}$) and to the addition of free oligomer (unreacted at the instant *t*) to the 'pendant' bonds of neighbouring fragments of the loose network, fragments of rigid network are formed in the interphase region (transition $T_{2a} \to T_{2b} \to T_{2c}$, probably, *via* the transition state c T'_{2c}).

In the second step of curing, one has T_{2c} and P_{2c} = const and $P_a \to 0$ and $P_b \to$ const. The mobilities of the components in the structures characterised by T_{2a} and T_{2b} become significantly lower, which can be interpreted as a result of phase inversion in the reaction system (monolithisation). In the final stages of polymerisation, the formation of the topological structure of the network is governed by the reactions in the intergrain space (interlayer space), *i.e.*, intramolecular cyclisation and cross-linking by the unreacted oligomer molecules. The decrease in P_a is exactly equal to the increase in P_b. The relaxation time T_{2b} is noticeably shortened, but never approaches the T_{2c} values, which points to high defectness of packing in this phase of the polymerisation product.

2. Structural information from EPR data

Information on the complexity of the supramolecular structure of polymer networks was obtained by Korolev *et al.* in EPR studies of polymerisation of oligo(ether acrylates) using the spin probe technique.[23, 145–149]

A paramagnetic probe 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was introduced into the system in two ways, (i) into the final poly(ether acrylate) network structure by sorption of TEMPO vapours or (ii) into the initial oligomer with subsequent curing and regeneration of the probe.

In the former case, the sorption of TEMPO molecules occurs selectively. The probe penetrates only into the zone of the loosely cross-linked (loose) intergrain space, whereas the highly cross-linked domains are inaccessible to the probe.§ The experimentally detected probe signal is characterised by the single spectrum, which characterises the molecular mobility of the structural elements located in the intergrain space.

§ This was proved in elegant experiments on irradiation of ultimately cured poly(ether acrylate) containing absorbed spin probe.

In the latter case (regeneration), two types of microvolumes with different mobilities of structural fragments are identified.

The spectrum of a regenerated spin probe in a polymer based on trioxyethylene α,ω-dimethacrylate is a superposition of two spectra, a narrow (3600 A m^{-1}) and a broad one (5400 A m^{-1}). The narrow spectrum is characterised by a correlation time t_c of 1×10^{-9} s (*cf.* 1×10^{-7} s for the broad spectrum). One spectrum characterises the molecular mobility of fragments of the grain structure (highly cross-linked polymer) while the other spectrum characterises the intergrain space (loosely cross-linked polymer). These data prove structural inhomogeneity of poly(ether acrylate) networks on the 'grain–intergrain space' level. Yet another series of EPR experiments revealed that the intergrain space is also nonuniform. Figure 18 presents the temperature dependences of the width of the spectrum of the paramagnetic probe sorbed into polymers with different degree of polymerisation. In all cases, three characteristic intervals of changes in the width of the EPR spectrum were observed

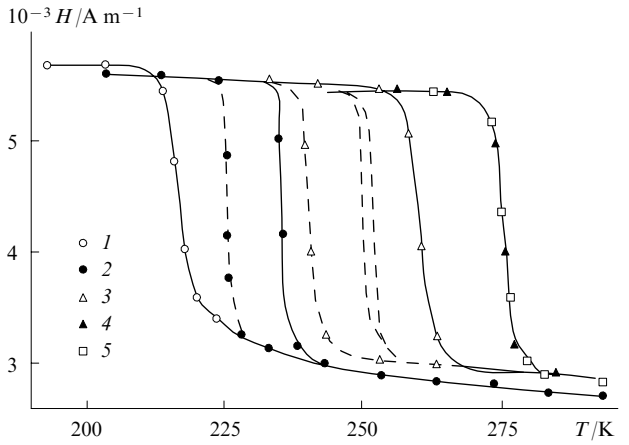


Figure 18. Temperature dependences of the widths of EPR spectra of TEMPO in TGM-3 polymer at a degree of conversion of 0 (*1*), 26 (*2*), 51 (*3*), 58 (*4*) and 73% (*5*).[148]
Transient regions ($\Delta T_{1,2}$) are confined by solid lines from the T_1 side and by dashed lines from the T_2 side.

irrespective of the degree of conversion as the temperature changes in the range 193 to 293 K. In the high-temperature region, a narrow spectrum (2945–3025 A m^{-1}), whereas in the low-temperature region, a broad spectrum (5413–5650 A m^{-1}) was detected. The temperature interval

$$\Delta T_{1,2} = T_2 - T_1,$$

corresponds to a transient region in which with arising the temperature causes the intensity of the narrow signal to increase at the expense of the intensity of the broad signal up to complete disappearance of the latter at T_2. The width of this transient region depends on the degree of conversion α, which is determined from calorimetric data. For the initial oligomer, the transient region is not observed, whereas for the oligomer being cured the interval $\Delta T_{1,2}$ increases as α increases (Table 6).

These data are interpreted as follows. The intergrain space (interlayers) includes numerous microvolumes with

Table 6. Dependences of $\Delta T_{1,2}$ and T_g on α.[149]

α (%)	$\Delta T_{1,2}$ /deg	T_g/K
0	0	218
26	7	231
51	20	253
58	23	265
73	25	269

different degrees of completion of the network structure (degree of cross-linking), degree of cyclisation and connectivity of cross-link points. Correspondingly, each microvolume is characterised by its own glass transition temperature due to different mobilities of structural fragments in the own structure. Experimentally, in the course of temperature scaning the glass transition first of all leads to 'freezing' of the mobility of those microvolumes whose T_g values are lower than the running temperature T. As α increases, the number of such microvolumes increases and, correspondingly, the interval $\Delta T_{1,2}$ also increases and the integrated T_g value simultaneously increases (see Table 6). The intensity ratio of the narrow and broad signals in the superposition region ($\Delta T_{1,2}$) characterises the proportions of the local structures, which are formed in the intergrain space and have different degrees of completeness of polymerisation (the limiting case is the grain structure).

These results are in agreement with the NMR data (see above), according to which the final polymer network structure is characterised by a spectrum of spin–spin relaxation times.

The fact that only one glass transition temperature is determined for all polymers deserves attention. This means that the size of inhomogeneities detected by EPR spectroscopy is very small. This regularity is typical of all types of polymer networks.[150]

3. Structural information from light scattering data

Analysis of the results obtained in Refs 1 and 151 made it possible to conclude[25] that in the first step of polymerisation of unsaturated oligomers the number of particles remains almost unchanged or even somewhat decreases, but the particle size considerably increases, and that the growth of particles sharply slows down in the second step. As to the polycondensation (urethane formation) reactions, the particle size remains almost unchanged up to the gel point and then decreases.

The aim of a light scattering study[135] was to investigate the effect of the phase structure of a system on the kinetics of changes in the size of particles formed in the course of polymerisation and polycondensation of epoxy oligomers. The phase structure was controlled by introducing additives (polyoxypropylene glycol dimethacrylates, acrylonitrile copolymers, *etc*.). It was found that, irrespective of the curing mechanism, the shape of the light scattering curve depends only on the concentration of the additive (φ), *viz*., an increase in φ causes the curve to transform from S-shaped at $\varphi < 0.05$ to a curve with a maximum. This was associated with the occurrence of secondary processes, namely, reorganisation of particles by the coalescence and Slezov–Lifshits mechanisms.

Depending on the curing rate, three mechanisms of phase formation were distinguished. Namely, phase separation proceeds by the mechanism of nucleation and growth far from the critical point (this was specified by the concentration of the additive) at low curing rate; by the spinodal decomposition mechanism at high reaction rates; and by a mixed mechanism at moderate reaction rates. Near the gel point, the spinodal mechanism is always in operation.

The data listed in Table 7 allow one to monitor the size of inhomogeneities in the course of polycondensation of the systems 'diglycidyl resorcinol ether (DRE) + 4,4′-diaminodiphenyl sulfone (DADPhS)', 'diethylene glycol diglycidyl ether (DDE) + DADPhS' and 'DRE + *m*-phenylenediamine (PDA)' at different curing temperatures. As can be seen, in all cases such inhomogeneities appear far from the gel point (*i.e*., the process is inhomogeneous at relatively low conversions), but in some cases polycondensation is accompanied by an increase in the size of these inhomogeneities, whereas in other cases the process does not involve significant changes in particle size.

Table 7. Changes in the size of inhomogeneities in the course of polycondensation.[150]

System	T/°C	Size of inhomogeneities /nm	
		before gel point	after gel point
DRE + PDA	70	127–336	272
DRE + DADPhS	70	103–336	136
DDE + DADPhS	138	110	120
DDE + DADPhS	120	190	200

One should keep in mind that light scattering during three-dimensional radical polymerisation occurs from microgel particles, whereas in the epoxide systems the scattering centres are density fluctuations typical of all liquids capable of undergoing transition to the glassy state.[74, 152, 153]

4. Structural information from electron microscopy data

The morphology of polymer networks formed upon curing of liquid oligomers is strongly affected by the length and flexibility of oligomer block and by the additive (plasticiser).

Curing of short-chain oligomers and rigid-chain oligomers, irrespective of the nature of initial components and curing mechanism, almost always leads to globular structures, as indicated by electron micrographs. Globules can be arranged in space with different periodicity and their size and shape distributions can also be different (this depends on curing regimes).[20, 56, 72, 96] Lengthening of the oligomer block in the initial molecules can lead to formation of network structures with elements of short-range and even long-range order.

Figure 19 presents micrographs of the initial oligomers of bis(4-methacryloxyethyl carbamate toluylene-2-carbamic) esters of oligo(ethylene glycols) with different length of the oligomer block ($M_n = 6 \times 10^2 - 10^4$) and cured systems. As can be seen, all oligomers with $M_n \leqslant 1200$ contain 20–50-nm globules in both the initial and cured state, but the shape of the globules is somewhat distorted as a result of network formation (see Fig. 19 *a*,*b*). As the length of the oligomer block increases, the supramolecular structure of polymer networks becomes more complicated. The supramolecular structures of the initial oligomers with $M_n = 1600$ and 2250 (Fig. 19 *c*,*d*) and the polymer networks based on them are almost identical. Both of them are characterised by the presence of lamellae 10–18 nm

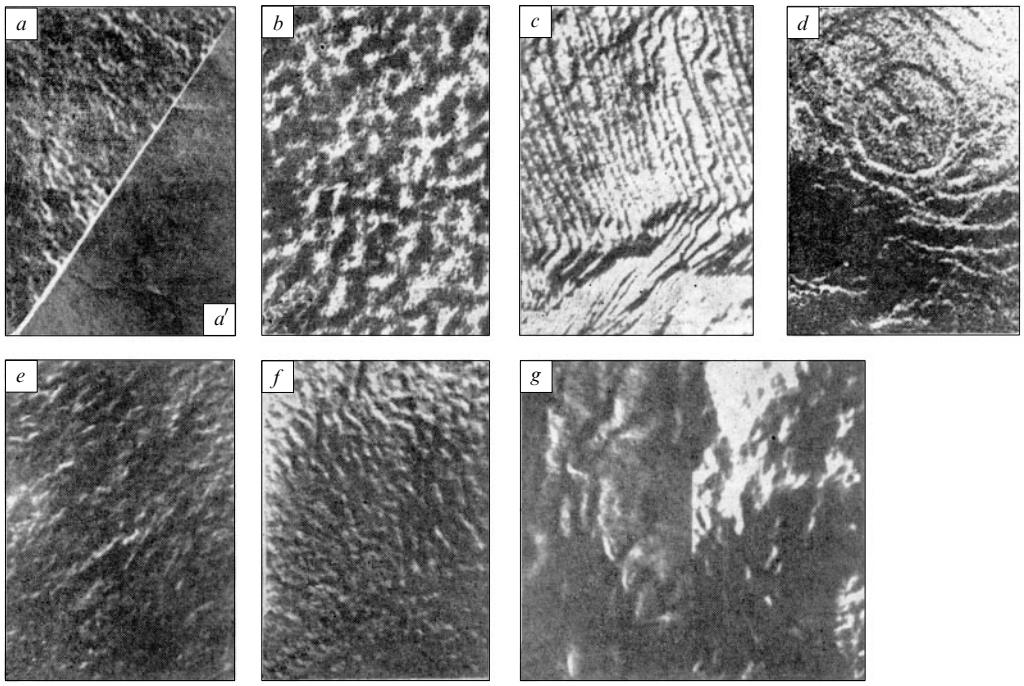


Figure 19. Micrographs (magnification 30 000) of replicas of cleavages of vitrified oligomers (*a*, *c*, *d*, *e*) and polymer networks based on them (*a*′, *b*, *f*, *g*) with M_n = 1200 (*a*, *b*), 1600 (*c*), 2250 (*d*), 3600 (*e*, *f*) and 6900 (*g*).[72]

thick, which is consistent with the oligomer block lengths calculated for planar oligomer chains. Based on this, it was concluded [73] that the network structure formed in the polymerisation at terminal functional groups almost perfectly inherits the supramolecular structure of the liquid oligomers. Additionally, the packing of macromolecules both in the network structure and in the liquid state is governed by the intermolecular interaction between anisodiametric molecules. Further increase in the length of oligomer blocks (M_n = 3600 and 6900) leads to formation of fibril-like structures (Fig. 18 *e*, *f*, *g*). Note that lamellar supramolecular structures were also found in a study of polycondensation curing of epoxy oligomers with oligoisoprene dihydrazides of different molecular mass.[67, 154]

Not only globules, but also fibril-like structures were revealed in a curing study [12] of short-chain oligoether acrylates (the process was carried out in an elastic matrix, which acted as a kind of plasticiser).

The following should be noted. First, the experiments involved a specific sample preparation technique (oxygen plasma etching over different time intervals) and showed that these structural fragments were formed by the poly(ether acrylate) network 'penetrated' by a small amount of rubber molecules. Second, the formation of such structures depends on the curing conditions.

5. Structural information from X-ray diffraction data

X-Ray powder diffraction studies of α,ω-dimethacrylate(tetramenthylene) glycols [155] showed that the X-ray powder diffraction patterns of the oligomers having less than ten methylene units ($n < 10$) and the network products of their curing are characterised by diffusive reflection typical of amorphous systems, whereas the X-ray powder diffraction patterns of the polymers prepared by curing of oligomers with $n > 17$ show clearly seen reflections characteristic of crystalline folded-chain polymers.

In the course of polymerisation of crystallisable oligomers, the degree of crystallinity naturally decreases (due to distortions caused by the appearance of terminal cross-link points), but, nevertheless, remains rather high for the networks based on long-chain oligomers. This, in particular, follows from the data of Table 8, which lists the degrees of crystallinity of long-chain oligomers before and after curing.

Table 8. Degrees of crystallinity of dimethacrylic oligomers of different molecular mass and polymer networks based on them.[73]

Oligomer	Molecular mass of oligomer	Degree of crystallinity (%)	
		of oligomer	of polymer
OTMDA	3400	57	0
	4700	60	38
	10 800	74	48
	17 000	76	43
OEFDA	1900	53	0
	2900	75	26
	6000	80	48
	7600	83	53

Note. OTMDA is oligo(tetramethyleneglycol dimethacrylate) and OEFDA is oligo(ethylene glycol formal dimethacrylate).

The structures of polyurethane networks based on adducts of trimethylthiolpropane with 2,4-toluylene diisocyanate and oligo(propylene glycol) (OPG) or oligo(ethylene glycol adipinate) (OEGA), which are characterised by the presence of fragments of different flexibility (rigidity), were studied by powder X-ray diffraction.[53] This made it possible not only to evaluate the degree of ordering of microheterogeneous domains in the bulk of the amorphous

system, but also to calculate the ratios of the rigid (urethane) and flexible (glycol) segments in the rigid and flexible phase aggregates.[53]

Based on analysis of the intensity profiles (Fig. 20) and correlation functions of small-angle scattering in these systems, a model for lattice scattering centres was proposed.[53] Here, the lattice is comprised of polydisperse rigid aggregates (dispersion phase) dispersed in flexible microdomains (continuous phase) (see Fig. 4 and 21 *a*).

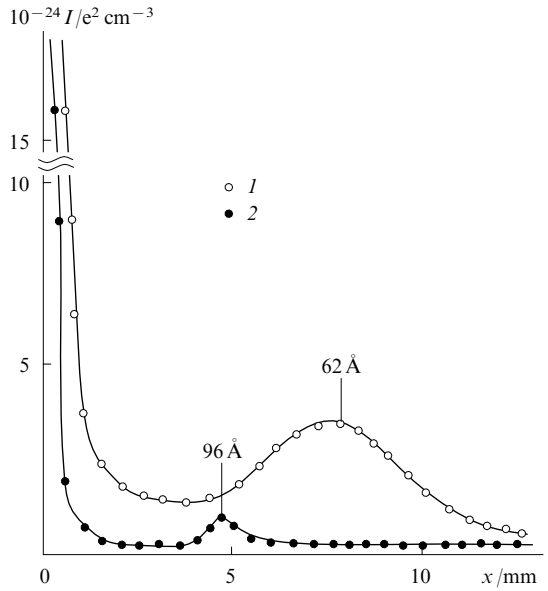


Figure 20. SAXS intensities (*I*) from polyurethane polymer networks based on OPG (*1*) and OEGA (*2*).[53]
x is the spatial coordinate; figures near curves denote the size of scattering centres.

This model differs from the idealised (Fig. 21 *b*) and paracrystalline monodisperse (Fig. 21 *c*) models. It is important that each phase of the model in question contains both urethane and glycol segments. Calculations of the mean square of electron density fluctuations $\Delta\rho_e^2$ (parameter characterising the degree of intermixing of these segments) using the expression

$$\Delta\rho_e^2 = \varphi(1-\varphi)(\rho_1-\rho_2)^2$$

(here ρ_1 and ρ_2 are the electron densities in the microdomains of the urethane and glycol segments, respectively, and φ is the volume fraction of urethane segments) made it possible not only to determine the degree of their segregation (α) and degree of mixing on the molecular level (γ), but also the total volume of the dispersion phase (φ_d) and the concentration of rigid (urethane) segments in both rigid-chain aggregates in the dispersion phase (φ_{dr}) and flexible-chain microdomains in the continuous phase (φ_{fd}). These data taken from Ref. 53 are listed in Table 9.

Table 9. Parameters of polyurethane network structures based on OPG and OEGA.[53]

$10^5\Delta\rho_e^2$ /e^2 Å^{-6}	α	γ	φ_d	φ_{dr}	φ_{fd}
Network based on OPG					
340	0.22	0.77	0.29 – 0.54	0.42 – 0.56	0 – 0.11
Network based on OEGA					
117	0.01	0.99	0.29 – 0.71	0.30 – 0.33	0.20 – 0.23

Among numerous curves $\varphi_d = f(\varphi_{dr}, \varphi_{fd})$, those meeting the condition for the existence of interference maxima in the scattering curves were chosen and used to determine the intervals of the values of the heterogeneity parameters for particular experiments (see Table 9). As can be seen, there exists a broad interval of φ_d values that do not contradict experimental data (0.29 – 0.54 for the OPG-based networks and 0.29 – 0.71 for the OEGA-based networks), whereas the φ_{dr} and φ_{fd} parameters vary within relatively narrow intervals of admissible values. For the OEGA-based networks, these intervals are particularly narrow. It is believed [53] that this is a consequence of much lower degree of segregation of these networks compared to the OPG-based networks (α = 1% and 22%, respectively), which in turn is due to the ability of the electron-donor groups of OEGA to form hydrogen bonds with electron-acceptor groups of urethane segments.

The scheme of the heterogeneous structure of the polyurethane network (see Fig. 21) and the scheme of the structure of poly(ether acrylate) network [151] (see also Fig. 11) are significantly different. In contrast to radical polymerisation, in the case of urethane formation coalescence of rigid aggregates (grains) is impossible and, therefore, the structure comprising flexible glycol segments with

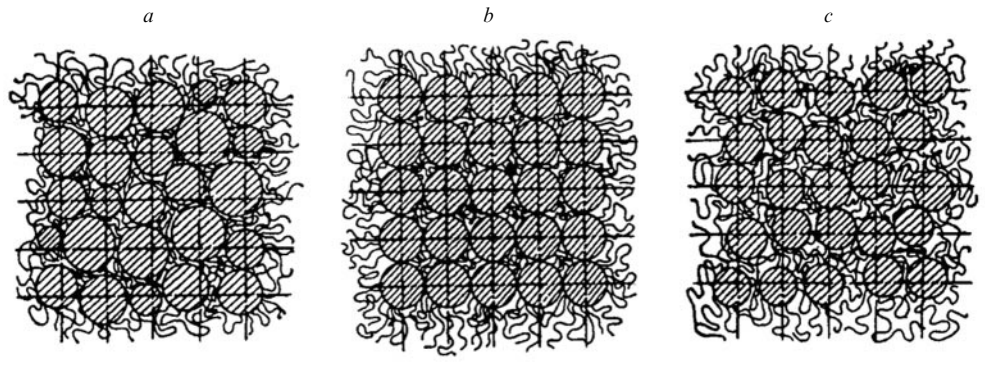


Figure 21. Models of heterogeneous structure of polyurethane polymer networks: polydisperse (*a*), ideal (*b*) and paracrystalline monodisperse (*c*).[53]

inclusions of rigid urethane fragments is the continuous phase, whereas the scheme from Ref. 151 prescribes that highly cross-linked structures represent the continuous phase and the defect regions represent the dispersion phase.

6. Limitations of structural methods used in curing studies of oligomer systems

When analysing the processes of formation of a polymer structure in the course of curing of oligomer systems, one should account for the sensitivity of the methods used for characterisation of structural transformations and of the procedures for sample preparation.

Methods of investigation of oligomer systems have their advantages and drawbacks. Some of them were mentioned above. Now we will consider a number of methodological aspects.

Measuring the optical density (scattering, refractive index, light transmission, *etc.*) of solid or liquid systems, one should keep in mind that structural fragments less than 100 nm in size cannot be detected in principle. Contrary to this, the SAXS technique is inapplicable to detection of structures larger than 100 nm in size. The rules of optics also preclude discrimination between phase fragments if the dispersion medium and the disperse phase have similar refractive indices. As a consequence, such experiments with some *a priori* heterogeneous systems give erroneous results (*i.e.*, optical transparency).

In electron microscopy studies of the structure of polymer networks, one should include the magnification when evaluating the morphology of certain structural fragments. For instance, at a magnification of 12 000, one can conclude that, structurally, the system under study represents homogeneous phase inclusions dispersed in a continuous dispersion medium. However, micrographs of the dispersion medium and dispersion phase obtained at a magnification of 100 000 indicate that each medium is microheterogeneous and comprises different-size globules. In this connection, it is appropriate to mention a remark:[156] 'main contradictions in data representation¶ are due to the interpretation and, strange to say, the aim of researchers to put the results obtained by other researchers aside rather than the experimental values of the measured parameters. The contradiction of experimental data is apparent because it characterises the complexity of the systems under study'. In addition, Lipatov[17] believes that electron microscopy is a kind of art rather than science and therefore the interpretation of the results obtained in the studies of amorphous polymers is usually ambiguous.

Kuleznev[95] seems to be the first who reported a typical error, which is very common to optical microscopy studies. Some authors relate all inhomogeneities observed by a microscope to phase formation. This is not always the case. Inhomogeneities in the field-of-vision of an eye lens (even excluding artifacts) cannot serve as a proof of the existence of the second phase in the system. The case in point is that a single-phase blend can also be inhomogeneous; some macromolecular coils and aggregates (associates, concentration fluctuations, *etc.*) of oligomer molecules can be comparable in size with the resolution of the instrument. In the microscopy studies, such structures can erroneously be treated as the heterophase particles. The error is that the thermodynamic properties of such inhomogeneities (even in the presence of a boundary surface) depend on the amount of matter in the system and, according to the Gibbs definition of phase, they cannot be a thermodynamic phase.

An objective limitation of dynamic methods consists in impossibility of evaluating the phase structure of a system in a wide temperature range. All temperature-induced transitions detected under dynamic test conditions characterise the sample structure, which corresponds to the sample preparation conditions and is 'fixed' by freezing. Contradictory experimental data reported by different authors can also be due to different sensitivity of experimental methods, which is related to the sample preparation techniques.

A number of experimental methods are objectively limited and so unsuitable for the detection of structural transformations in the system because they do not 'sense' them, being appropriate for the detection of different levels of transformations. Now we will provide some examples.

The kinetic curves obtained in the studies of polymerisation of trioxyethylene α,ω-dimethacrylate in *cis*-polyisoprene matrix by IR spectroscopy and dipolar polarisation relaxation are shown in Fig. 22. Curves *1* and *2* characterise the consumption of methacrylic bonds in the course of curing and the corresponding changes in the integrated mobility of methacrylic group dipoles. As can be seen, for a given system under particular curing conditions the conversion reaches a maximum value (~50%) after 20–30 min on the sensitivity scale of IR spectroscopy. According to dielectric measurements, the relaxation mobility of newly formed structural fragments remains almost unchanged. A large decrease in $\tan\delta$ begins later, about 40 min after the curing began. By measuring the dielectric characteristics of oligomer systems at different degrees of curing it was shown[88,157] that the structure whose dielectric properties are independent of the duration of subsequent curing can only be prepared after heating of the samples for 80–100 min. From this, in particular, it follows that, on the one hand, structural transformations occurring in the early stages of curing do not influence the character of system's response to the action of electric fields. On the other hand, it follows that the formation of structures responsible for

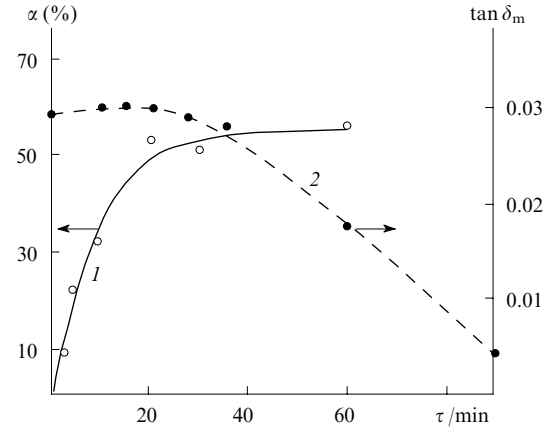


Figure 22. Degree of conversion of methacrylic bonds determined from IR spectroscopy data (*1*) and the dielectric loss tangent (*2*) plotted *vs.* duration of heating of the system *cis*-polyisoprene–trioxyethylene dimethacrylate at 150 °C.[88]
Oligomer content is 30 mass %, the concentration of dicumene peroxide is 2%.

¶ This particularly concerned the data on blend compatibility, but the remark is of general sense.

manifestation of the dielectric properties is completed at high conversions and small changes in α ($\Delta\alpha < 2\% - 3\%$), which goes beyond the sensitivity limits of IR spectroscopy. Similar results were obtained by Gorbunova [158] who studied curing of epoxy oligomers. A comparison of the informativity of various experimental methods showed that differential scanning calorimetry and IR spectroscopy describe the reaction kinetics up to the gel point and that the test characteristics remain unchanged in the post-gel region. However, such parameters, as the glass transition temperature and the elastic modulus also continue to change after the gel point.

Yet another example is as follows. Pulsed NMR spectroscopy usually fails to detect structural fragments characterised by T_{2b} (third phase) in the structure of epoxy-amine networks, although such fragments are always formed during polycondensation of epoxy oligomers [2, 25, 31] and significantly differ in mobility from rigid networks characterised by the limiting topological structure.[31] This seems to be due to low concentration of the structures characterised by the relaxation time T_{2b}. Pulsed NMR spectroscopy allows a correct differentiation of particular structures only if their concentrations are higher than 5%.[16, 159] Note that structural transformations in the course of curing of oligomer systems, which occur during the induction period (induction for spectral and relaxation methods) can be detected thermometrically.[88, 94, 96, 157]

In the course of preparation of this Section our aim was first of all to present a sound assessment of the potential of different methods rather than to analyse the advantages and drawbacks of all experimental techniques used in structural studies of polymer networks.

V. Curing of polymer – oligomer systems

According to experimental phase diagrams generalised in a monograph,[156] a vast majority of polymer – oligomer systems represent systems with limited compatibility of components.

A conditional phase diagram of a polymer – oligomer system is shown in Fig. 23. Depending on the component ratio and temperature, an equilibrium binary blend † can be in a single-phase or two-phase state. There are two types of single-phase polymer – oligomer systems, namely, polymer-enriched solutions (on the left of the binodal) called in the text below 'solutions *I*' (or 'phase *I*') and oligomer-enriched solutions (on the right of the binodal), or 'solutions *II*' (or phase *II*'). Owing to significant difference in the concentrations of the reactive components the curing processes in these phases are different.[160]

Depending on the state parameters, which determine the phase inversion point, two-phase polymer – oligomer systems (under the binodal) represent emulsions of (i) solution *I* in solution *II* or (ii) solution *II* in solution *I*. It should be emphasised that changes in the component concentrations in the two-phase systems do not change the concentration of the solution of each phase, but cause their volume ratio to change.

† As mentioned above, in strict sense the equilibrium in polymeric systems is usually unattainable.

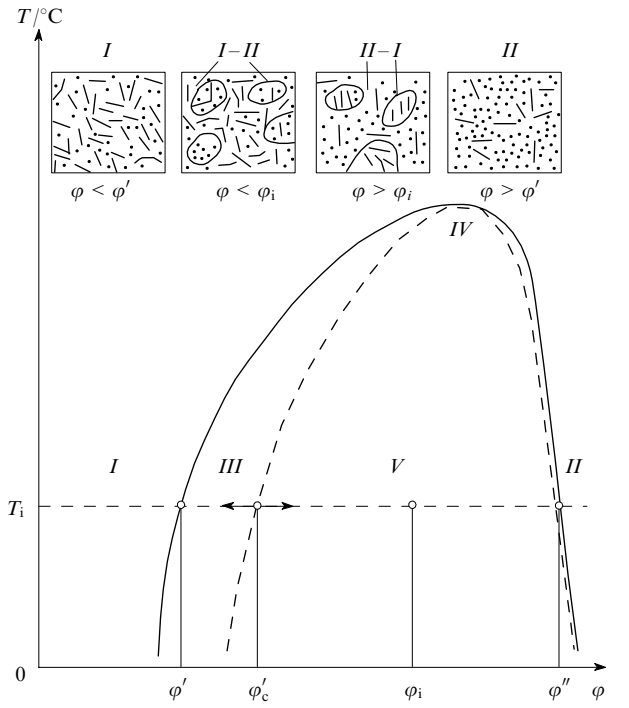


Figure 23. Schematic view of the phase diagram of a polymer – oligomer system.[160]
The solid line denotes the binodal, the dashed line denotes the spinodal, φ is the content of oligomer, φ_i is the content of oligomer at the phase inversion point, *I* and *II* denote the regions of oligomer-deficient and oligomer-enriched single-phase solutions, respectively, *III* denote the metastable region, *IV* denote the region near the upper critical separation temperature and *V* denote the two-phase region.

1. Curing of polymer-enriched solutions

To a first approximation, the curing of solution *I* can be represented as follows taking an equilibrium solution of oligoether acrylate in a linear polymer as an example.[12] Similarly to homopolymerisation of oligomers, curing in polymer – oligomer systems begins with fast initiated polymerisation in the inhomogeneities existing in the polymer – oligomer solution (associates, in which the concentration of the reactive groups is higher than its volume-average value, and sybotaxes, in which a 'kinetically favourable ordering' occurs additionally). Depending on the nature of the components, the presence of linear polymer can favour both segregation of the oligomer in solution and its molecular dispersion, *i.e.*, an increase or a decrease in the degree of aggregation of the system, respectively, and, correspondingly, an increase or a decrease in the initial polymerisation rate.[25] It is these inhomogeneities in the initial solution that are nucleation centres of the future structural heterogeneity of the cured composite. The formation of such inhomogeneities is accompanied by not only the interaction between oligomer molecules and subsequent intramolecular cyclisation (involving 'pendant' bonds), but also chain branching and intramolecular interaction between fragments of the loose network. This is the mechanism of formation of primary microgels, *viz.*, network fragments swollen in other components. Then other oligomer molecules dissolved in the polymer are involved in the process.

If, all things considered, the initial polymerisation rate is only determined by the degree of self-organisation of the supramolecular structure of the solution, in the subsequent

stages the rate constant for polymer chain propagation is to a much greater extent (compared to the homopolymerisation of oligomers) limited by the rate of diffusion of the reactive molecules towards active centres. It decreases not only due to polymerisation, but also due to the presence of the highly viscous matrix polymer. However, the rate constant for chain termination decreases simultaneously owing to an increase in the viscosity of the medium. Therefore, the resultant rate of network formation is detemined by competing factors, which act oppositely in the elementary stages of the reaction. The overall reaction rate determines the character of phase separation.

In microgels, an increase in the degree of polymerisation causes the mutual solubility of components to decrease, which leads to the onset of phase separation on the microscopic level. This stage of curing of polymer – oligomer systems also differs from homopolymerisation of oligomers. If in the latter case the system being cured is a variable-composition blend comprising network fragments of different degree of 'cross-linking', β-polymer and free (unreacted) oligomer (*i.e.*, all components are of the same chemical nature but have different topological structures), in the case of curing of polymer – oligomer system the reaction blend, in addition to the products mentioned above, contains a linear polymer, which usually differs from other components in the chemical structure. In turn, this difference predetermines specific features of phase separation in these systems on the microscopic level. First, in the presence of linear macromolecules the limiting solubility decreases and thus the phase separation requires a shorter time to begin. Second, if the mobility in microgels is limited by the local isothermal glass transition, in the course of microsyneresis a proportion of macromolecules of the matrix polymer (it is much larger than the proportion of β-polymer and moreover the free oligomer) has no time to 'displace' beyond the phase boundary due to much smaller coefficients of translational diffusion. Linear macromolecules remain 'embedded' into the forming network aggregate. Third, these 'frozen' linear macromolecules in the network structure can act as a kind of plasticiser, thus enhancing the mobility and, therefore, accessibility of the 'pendant' bonds in the intramolecular cyclisation reactions and, therefore, increasing the limiting degrees of polymerisation within microgel.

Thus, microheterogeneous inclusions formed in curing of polymer – oligomer solutions can be considered as blends of polymer networks and linear macromolecules (generally, the volume fraction of unreacted oligomer molecules can be ignored because it is much lower) of different chemical structure with incomplete separation of components. They isolate in the bulk of the cured system as spatially localised, highly dispersed particles ('grains'), which in the electron microscopy experiments are observed as globules of regular and irregular shape. Such highly dispersed particles were conditionally called 'Ångström-size particles'.[88] It should be emphasised that this term characterises only the size scale of these particles, it is similar to the more recent term 'nanoparticle',[161] which will be used in the text below following a modern trend. Thermodynamically, 'nanoparticles' are non-equilibrium particles, but they are stable in time because translational diffusion in them is completely suppressed.

From this curing scheme it follows that the highest degree of cross-linking (closest packing) in the network is attained at the centre of a nanoparticle. The density of cross-linking gradually decreases with the distance from the centre. Peripheral regions of the particle contain only a partially cyclised loose network and 'frozen' macromolecules of the linear polymer. The inter-particle space (the loosest part of the system) is filled with polymer macromolecules mixed with fragments of the loose network and unpolymerised oligomer. Thus, here one deals with the formation of a gradient structure with respect to both the density of cross-linking and molecular composition, because the 'polymer network : linear polymer' ratio changes.

The possibility of chemical interaction between different components in the course of curing of polymer – oligomer systems has been poorly studied so far. In most studies on the subject, conclusions about cross-linking of the matrix polymer with the oligomer or products of its reaction are based on indirect data. Direct proofs of the chemical interaction between different components are almost unavailable; however, tentative mechanisms of grafting of oligomers to polymer molecules have been a subject of discussion in the 1960 – 1980s.‡

Without rejecting, in principle, the possibility of chemical interaction between a linear polymer and oligomer or products of its transformations, one must admit that this is only a particular case. The formation of covalent bonds between the polymer and oligomer molecules or grafting of network fragments (oligomer curing products) to a linear macromolecule are only possible under particular conditions. First of all, this is the presence of appropriate functional groups or unsaturated bonds in the macromolecule and oligomer molecules, corresponding initiation, catalysis and temperature, *etc.* Random chain transfer to polymer or chain termination can also occur, as was convincingly proved in a study of the model system 'methyl methacrylate – 2-methylpent-2-ene'.[162] However, thorough analysis of the published experimental results suggests that the earlier assumption of universal chemical interaction between different components in the course of curing of polymer-oligomer blends is invalid.

At present, one can only say that chemical grafting of an oligomer and products of its reactions to a polymer occurs only in some cases. The best studied examples are provided by radiation-induced curing of PVC – oligoether acrylate blends,[163, 164] radiation-induced vulcanisation of rubber-oligomer blends,[165] peroxide-induced vulcanisation of blends of nitrile rubbers with polyfunctional oligomers[90] and some other processes,[94, 154] in which the formation of covalent bonds between the linear polymer and the polymer network is probable.

Yet another level of structural organisation is the morphological level. Spontaneous character of concentration fluctuations in polymer – oligomer solutions; random character of the nucleation of branching centres; dependence of the number of branching centres on the initiator, catalyst and inhibitor concentrations; diffusion limitations in the chain propagation stage, *etc.* — taken altogether, these factors predetrmine the formation of different-size dispersed particles in curing of polymer – oligomer solutions. In most cases the particle size distribution is described by a unimodal function (although, as mentioned above, sometimes polymodal distribution is also possible).[96, 102]

Experimental studies showed that the mean size of the dispersed particles formed in the course of curing of single-phase polymer – oligomer systems varies from a few tens to

‡ This problem was considered in detail in a monograph.[12]

a few hundreds of Ångströms,[88, 96, 102] however, larger phase formations up to a few thousands of Ångströms in size and even up to a few micrometres were observed in some experiments.[2, 12, 94, 96] The mean interparticle distance depends on the concentration of the reactive component and lies in the range a few tens to a few hundreds of Ångströms.[6, 67, 71]

As mentioned above, 'nanoparticles' in electron micrographs generally have a globular shape, namely, the dispersion medium contains various globular inclusions of different size. The distribution of globules depends on the nature of components, on the component ratio and on the temperature profile of curing. The continuous phase of cured polymer–oligomer solutions is either monolithic (*e.g.*, for rubber matrices) or represents a regular aggregate of domains (*e.g.*, for the composites based on PVC–oligoether acrylate solutions). In the latter case, the domain size is larger than in the initial PVC (40–80 *vs.* 20–30 nm, respectively).[96]

The particle size of the dispersion phase first of all depends on the concentration of the reactive component, while the structure of the continuous phase is governed by the component ratio in the initial blend.[96] If the content of the reactive component is low (<5%), this component is consumed prior to completion of structural reorganisation of the dispersion medium in the course of curing. Therefore, its nature is governed by the blend component that is present in excess.§

As the oligomer concentration in the initial blend (single-phase state) increases, the proportion of the matrix component 'bound' by the network formed as a result of curing also increases. For instance, the content of rubber in the gel fraction of cured SKN-26 + tetramethylene dimethacrylate blend decreases in proportion to the oligomer percentage in the initial system.[88] It was also shown[96] that at a PVC content of 70% in the initial blend with trioxyethylene dimethacrylate the amount of 'free' linear polymer molecules in the gel fraction after curing becomes almost halved. Some electron microscopy experiments reported monolithic structures of the dispersion media in such composites;[88] however, these monoliths are nonuniform in the chemical composition and can to a first approximation be considered as a 'solid solution' enriched with a certain blend component.

Curing of initially single-phase polymer–oligomer or oligomer–oligomer blends with symmetrical compositions can lead to a structure with 'dual phase continuity' (according to Sperling[4]) or to so-called inversion structures (according to Lipatov[17]). In this case each phase in the bulk can be considered as continuous. But on the microscopic level both of them remain heterogeneous.

At a low oligomer content (⩽10%), the calculated equivalent diameter of spherical particles changes in the range 100–700 nm and the distribution curve has a maximum in the region 100–200 nm.[96] As the oligomer concentration in the initial solution increases, the particle size distribution of the dispersion phase is broadened and large aggregates (to 1600 nm in size) comprised of nanoparticle clusters appear.

§ Nevertheless, examples of strong effect of small additives (oligomers) on the structure and properties of the matrix component are available.[20, 73, 88, 95, 96, 165] However, this interesting problem goes beyond the scope of this review.

Analysis of electron microscopy data led to two important consequences. First, the results of calculations suggest that the volume fraction of the dispersion phase in the cured system is 1.5 to 2 times higher than the volume fraction of oligoether acrylate in the initial system.[94] This is a strong argument substantiating the assumption that the dispersion phase contains linear macromolecules (in this case, PVC) bound by the network. Second, analysis of the micrographs obtained for various systems under different curing conditions and using different sample preparation procedures and different magnifications[88, 90, 96] showed that large, seemingly monolithic (at small magnifications) particles (including spherolite-like ones) reported by some authors (see, *e.g.*, Refs 88 and 90) are actually dense aggregates of smaller particles. Presumably, this is a result of the plasticising action of the linear polymer, which facilitates coalescence of nanoparticles resulting in the secondary supramolecular structures with additional ordering in the final stage of phase separation. The formation of such structures has never been observed during polymerisation and polycondensation of short-chain reactive oligomers.

Emphasise that the secondary supramolecular structures are only formed under particular conditions of curing of polymer–oligomer systems. For instance, if a blend of butadiene–nitrile rubber with trioxyethylene dimethacrylate is heated at 120 °C rather than 150 °C (it is this curing temperature at which the so-called spherolite was observed), a conventional globular structure is formed. And only additional heating at a temperature of 150 °C, at which the mobility of structural fragments of the system is enhanced, leads to formation of more complex secondary fragments against the background of small-globule structure. Note also that X-ray powder diffraction studies[53, 97] showed that the spherolites mentioned above are complex amorphous structures and do not characterise the onset of long-range order (crystallinity).

2. Curing of oligomer-enriched solutions

Curing of the reactive component in solution *II* (see Fig. 23) occurs, in principle, as in the case of solution *I* (see above). However, there are also significant differences due to the low concentration of the linear polymer in solution *II*. The viscosities of such solutions are a few orders of magnitude lower than those of polymer-enriched solutions[88] and the initial polymerisation rate in them is 5–10 times higher.[166] Because of this the onset of phase separation in the course of curing of solution *II* is shifted toward the region of lower integrated degrees of polymerisation. In addition, although particles formed in curing of the solutions *I* and *II* are comparable in size, nanoparticles formed in curing of solution *II* are on the average 1.5–2 times larger than the nanoparticles of cured solution *I* at the same degree of initiation. In the text below, solid inclusions formed in curing of phase *II* will be called microparticles. Here, the bodies¶ of dispersed inclusions, which are formed in the course of curing of solution *II* (*i.e.*, microparticles) are depleted of the linear polymer compared to the nanoparticles of the cured solution *I*. The number of the linear polymer molecules in the interglobule (intergrain) space of the cured solution *II*, which is similar in composition to the intergrain matter¶ of a polymer network prepared by homopolymerisation, is also much smaller. Nevertheless,

¶ Terms used in Ref. 151.

both the dispersion and continuous phases of cured solution *II* always contain linear molecules of the second component of the system, which qualitatively distinguishes them from the curing products of individual oligomers.

The structural parameters of linear poly(butyl methacrylate) (PBMA), a styrene-*co*-divinylbenzene (SDVB) polymer network and products of their co-curing † obtained by SAXS are listed in Table 10.[166]

Table 10. Parameters ρ (kg mol^{-3}), ρ_e (e mol^{-1} cm^{-3}), $\Delta\rho_c^2$ and $\langle\Delta\eta^2\rangle$ (e^2 mol^{-2} cm^{-6}) of PBMA, SDVB and products of their co-curing.[166]

Substance	φ (vol. fraction)	$10^{-3}\rho$	ρ_e	$\Delta\rho_c^2$	$\langle\Delta\eta^2\rangle$
PBMA	1.0	1.053	0.581	—	0.036
SDVB	1.0	1.048	0.564	—	0.092
PBMA	0.05	0.726	—	0.137	0.586
SDVB	0.95				
PBMA	0.2	0.979	—	0.463	0.463
SDVB	0.8				
PBMA	0.4	1.050	—	0.693	0.128
SDVB	0.6				

Experimental values of the mean square of electron density fluctuations $\langle\Delta\eta^2\rangle$ for the cured blends are much larger than the corresponding values determined for individual components. For blends, this parameter decreases as the content of the linear component increases. Additionally, from the data of Table 10 it follows that the $\langle\Delta\eta^2\rangle$ values differ from the corresponding theoretical values of the mean square of electron density fluctuations $\langle\Delta\rho_e^2\rangle$ calculated assuming a complete phase separation using the relation [53]

$$\Delta\rho_e^2 = \varphi_1\varphi_2\,(\rho_e' - \rho_e'')^2,$$

where φ_1 and φ_2 are the volume fractions and ρ_e' and ρ_e'' are the electron densities of PBMA and SDVB, respectively.

These data substantiate the assumption that curing of solution *II* does not result in complete separation of the components in the newly formed phases. The presence of linear PBMA molecules (continuous phase) in the SDVB network and the presence of fragments of the SDVB network (dispersion phase) in linear PBMA leads to loosening of each phase and to a decrease in the experimentally determined density, whose concentration dependence does not obey the additivity rule (see Table 10).

Thus, in spite of common mechanisms of curing of solutions *I* and *II*, significant differences in the component concentrations lead to different macroscopic morphologies of the cured products. They differ not only in the nature of the continuous and dispersion phases,‡ but also because some structural parameters of 'nanoparticles' and 'microparticles' (mean size, component composition, density gradient of networks, *etc*.), which are formed in the course of phase separation in each solution, differ to such a great extent that they can be considered as different-type structures.

3. Curing of two-phase blends

In the initial state, two-phase systems represent emulsions of solution *I* in solution *II* or *vice versa*. Depending on the component ratio, curing occurs simultaneously in the coexisting phases and obeys the regularities, which in essence do not differ from those considered above for each single-phase system. As a result, heterogeneous composites with structural fragments typical of each phase being cured are formed. Therefore, macroscopic structures of cured two-phase systems can be considered as blends of two types of microstructures formed upon curing of the polymer solution in the oligomer (initial phase *II*) and the solution of oligomer in the polymer (initial phase *I*).

However, a basic feature of the composites formed by curing of two-phase systems is that the distribution of these different structures in the bulk of the material is specified by the morphology of the initial blends at the beginning of curing. The sizes and distribution of polymer – oligomer or oligomer – polymer emulsion drops in the initial state (before curing) are governed by the nature of components, oligomer dosage and the prehistory of the system.[12] When polymerisation (polycondensation, polyaddition) begins, the curing processes occur in the dispersion medium and in each drop of the dispersion phase. If the dispersion phase is a oligomer-enriched solution, in the case of fast polymerisation in this phase (here, as was mentioned above, the initial polymerisation rate is five-to-tenfold higher than in the polymer-enriched phase), the droplet size is fixed. In the final structure of the cured composite they appear as large dispersed inclusions whose size is consistent with the situation in the initial liquid system.[160]

These large dispersed particles formed upon curing of two-phase polymer – oligomer systems were conditionally called [88] macroparticles.§ These are complex aggregates, which differ from clusters of particles of the dispersion phase found in cured single-phase systems in size and character of distribution. These agglomerates are comprised of close-packed nano- or microparticles. Macroparticles are detected by optical microscopy and electron microscopy at small magnifications as monoliths with well-defined boundary surfaces, but at large magnifications one can observe a more finely dispersed level, *viz*., nanoparticles in macroparticle bodies.

Heterogeneity of macroparticles is also substantiated by the results of X-ray studies.[88,96] In terms of Ref. 3, macroparticles can be classified as 'phase in phase'.

Thus, differences in organisation on the colloid-dispersion level of single-phase and two-phase polymer – oligomer systems in the initial state lead to significant differences in the morphology of composites prepared by curing. This first of all manifests itself in the formation of a single type of dispersed particles (nanoparticles or microparticles, depending on the initial component ratio) when curing single-phase polymer – oligomer systems and in the appearance of an additional level of heterogeneity, *viz*., macroparticles when curing two-phase systems.

† A homogeneous solution of PBMA in a styrene/divinylbenzene blend in the presence of benzoyl peroxide (1%) at 60 °C was cured.

‡ For cured solutions *I*, the disperse phase mainly consists of the linear polymer with loose network inclusions and the dispersion phase is comprised of nanoparticles in the form of a network 'diluted' with linear polymer; the reverse holds for the cured solutions *II*.

§ It should be emphasised again that the terms 'macroparticle', 'nanoparticle' and 'microparticle' characterise only the size scale of the dispersion-phase particles.

Typical of cured composites based on initially two-phase blends are three types of dispersed inclusions, namely, nanoparticles, which are formed as a result of chemical reactions in the dispersion medium of the initial system; macroparticles as a result of curing of the dispersion phase of the initial system; and microparticles constituting macroparticle bodies. Naturally, if the continuous phase in the initial blend is solution *II* and the dispersion phase is solution *I*, macroparticles are composed of nanoparticles and curing leads to formation of microparticles in the dispersion medium.

These propositions are taken into account in the Scheme (see Fig. 24), which was plotted to illustrate the structure formation upon curing of linear polymer–oligoether acrylate (OEA) systems,[88] but is also used to analyse the structures of other polymer–oligomer and oligomer–polymer systems.[6] The scheme is quite illustrative and no lengthy comments are needed. We only point to the following consequences:

— in the case of initially single-phase blends, the onset of heterogeneity is a result of chemical reactions of curing and formation of poly(ether acrylate) network; all things considered, the number of nanoparticles or microparticles increases with an increase in the oligomer concentration;

— in the case of two-phase blends, the macroscopic level of dispersion is specified by the morphology of the initial blends; here an increase in the oligomer concentration leads to an increase in the number and size of macroparticles and to a constant number of nanoparticles in the dispersion medium (concentration in the co-existing phases remains unchanged), followed by phase inversion with an increase in the oligomer content, while the morphology of the cured composite behaves oppositely as the composition changes.

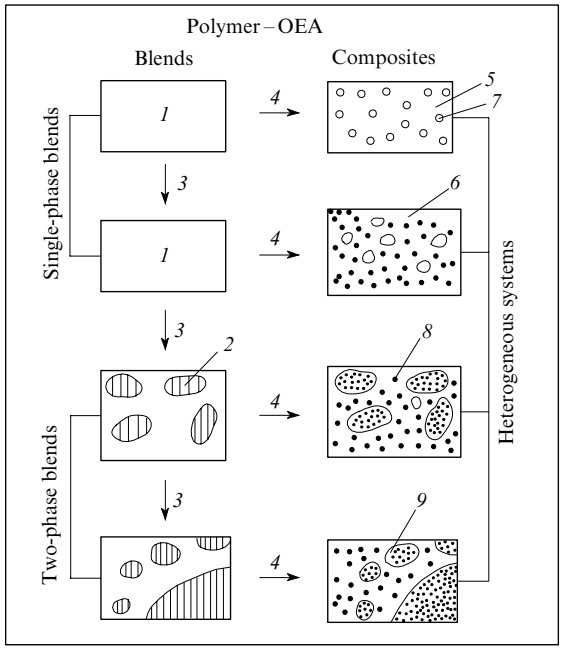


Figure 24. Comparison of scheme of formation of morphology composite upon curing of single-phase and two-phase blends.[160]
OEA solution in polymer (*1*), polymer solution in OEA (*2*), increasing OEA content (*3*), curing (*4*), 'solid solution' of OEA in polymer (*5*), 'solid solution' of polymer in OEA (*6*), nanoparticles (*7*), microparticles (*8*) and macroscopic particles (*9*).

This scheme serves a basis for the concept of control of the structure of polymer–oligomer composites suitable for optimisation of their macroscopic properties.[160, 167–169]

VI. Conclusion

In polymer materials science, the design of macromolecular structures responsible for the preset properties of a material is an evergreen complex problem whose solution requires different approaches. But it is our earnest conviction that only establishment of the physicochemical essence of the phenomena observed in the course of formation of polymer structures (including network structures) can draw nearer to the development of technologies that allow by the nature (to one extent or another) to practically implement a great potential of the properties laid one in the macromolecular structure of matter.

Unfortunately, the state-of-the-art in chemical physics of curing of oligomer systems precludes reliable calculations of all correlations between the molecular structure of oligomers and the kinetic and thermodynamic characteristics of the processes occurring in the course of oligomer curing, as well as the parameters of the supramolecular, topological and phase structures of polymer networks. The approach considered in this review is concerned with analysis of physicochemical regularities of the liquid (oligomer) → solid (polymer network) transition, which proceeds by fundamentally different mechanisms (polymerisation or polycondensation) on different levels of structural hierarchy. In some cases we succeeded in finding correct explanations for experimentally observed 'anomalies' of the macroscopic properties of oligomeric systems, which bewildered quite recently.

Of course, the problems discussed here were chosen in somewhat biased manner. That is why considerable attention was paid to polymer–oligomer blends and to topological analysis using the concept of 'bond blocks'. However, we believe that this review of modern concepts of the structure of polymer networks prepared by oligomer curing is presented without fear of favour.

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