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Formation of Network Polymers

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Methods of analysing the formation of network polymers from polyfunctional compounds and determining their structural parameters are surveyed, and experimental data obtained by these methods on the formation of network polymers from monomers and oligomers are examined. The data permit assessment of the possibilities and the establishment of general laws for the formation of polymer networks in the initial and the final stages of the reactions. The problems of the controlled synthesis of network polymers from polyfunctional compounds are discussed on the basis of the experimental results which have accumulated. The list of references comprises 114 items.

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I. INTRODUCTION

Advances in the synthesis of linear polymers and investigations of their structure stimulate the development of methods for the detailed study of network polymers. Establishment of the laws governing the formation and the structure of network polymers and also the discovery of methods for their controlled synthesis would promote a rational approach to the control of technical processes in the manufacture and processing of materials based on them, since network polymers, unlike linear polymers, are usually formed in the course of these processes.

According to the definition given long ago by Staudinger [1] network (spatial or three-dimensional) polymers are those in which the component chains are joined by chemical bonds in three directions. Among all the types of chemical and physical bonds only covalent bonds are able to form a spatially fixed structure, which is irreversible after breakdown. Other bonds, including ionic and coordinate bonds, are labile and delocalised in space, and may form three-dimensional structures, such as e.g. in ionomers, polycoordinate polymers, etc. Therefore the term "network polymers" should be applied only to polymers whose chains form a network of covalent bonds distributed in space, the so called polymer network. All other types of interaction—ionic, coordinate, hydrogen, or intermolecular bonds, physical contact and entanglement—may also appear in the polymer network, and make their contribution, often very considerable and even predominant, to its formation, structure, and properties.

Polymers which contain a large number of strong but labile bonds (ionic, coordinate, hydrogen, etc.) between the linear chains formed by covalent bonds, and which under certain conditions possess properties characteristic of network polymers, must be regarded as quasi-network polymers.

Network polymers can be obtained by cross-linking existing linear macromolecules with covalent bonds and also by introducing polyfunctional monomers, oligomers, or mixtures thereof into the reaction. Macromolecules can be combined by covalent bonds only when the polymer chains are flexible. In practice this method is applied only in the vulcanisation of elastomers. The second method is generally applicable, and enables network polymers to be obtained with almost any properties—from elastomers with an open network to the so-called "hardened" polymers with a dense network. Recently, therefore, work has been developed especially intensively in this direction. Broad investigations are being conducted into the laws of the formation of polymer networks by reactions of polyfunctional compounds, methods are being developed for the direct investigation of the structural characteristics not only of open-network but also of dense-network polymers, and ways are being studied for the directed synthesis of network polymers having a specified structure and properties. The present paper attempts to summarise the principal results obtained in these investigations.

II. METHODS FOR ANALYSING THE FORMATION OF NETWORK POLYMERS AND ESTIMATING THEIR STRUCTURAL PARAMETERS

Flory [2,3] applied a statistical method for analysing the formation of network polymers by the polycondensation of monomers containing more than two functional groups in the molecule. He correlated the degree of conversion P of the functional groups with the probability of branching of the polymer chains during their growth (branching α coefficient). The following relations exist between P and α in the reaction systems which are encountered most frequently.

1. For a polyfunctional monomer RA_f, whose functional groups react with one another,

$$P = \alpha \qquad (1)$$

2. For a mixture of a polyfunctional monomer RA_f with a difunctional monomer $R'B_2$, where the groups A react only with the groups B, we have

$$P_A = \sqrt{\frac{\alpha}{r}} \qquad (2) \quad ; \qquad P_B = \sqrt{\alpha \cdot r} \qquad (3)$$

where P_A and P_B are the degrees of conversion of groups A and B respectively, and

$$r = \frac{n_A f_A}{n_B f_B},$$

is the ratio of the initial components, n_A, n_B, and f_A, f_B being respectively the numbers of moles and the functionalities of the monomers A and B.

An infinite three-dimensional network of the monomer units interconnected by covalent bonds is formed (gel point) at a critical value of the branching coefficient

$$\alpha_{crit} = \frac{1}{f-1} \quad (4)$$

where f is the functionality of the polyfunctional compound. Until the gel point is reached, values of α lie in the range $0 < \alpha < \alpha_{crit}$.

In the polycondensation of the above reaction systems gel formation occurs ideally when conversion of the functional groups corresponds in Eqns. (1)–(3) to the critical value of α. Thus in the polycondensation of a trifunctional monomer gel formation starts when the degree of conversion of the functional groups is one-half, the corresponding conversion for a tetrafunctional monomer being one-third.

In the polycondensation of a polyfunctional monomer with a difunctional monomer a polymer network is formed only if $\frac{1}{2} < r < 2$. When $r = 1$,

$$P_{A,g} = P_{B,g} = \sqrt{\alpha_{crit}}. \quad (5)$$

where $P_{A,g}$ and $P_{B,g}$ are the degrees of conversion of groups A and B respectively at the gel point.

Statistical analysis of polycondensation beyond the gel point enables the proportion by weight of the sol W_S (the quantity of reaction products unattached to the polymer network) to be related to the coefficient of branching α, and hence to the degree of conversion of the functional groups—Eqns. (1)–(3) and (5):

$$W_s = \frac{(1-\alpha)^2\alpha'}{(1-\alpha')^2\alpha} \quad (6)$$

where $\alpha' < \alpha$ for any physically meaningful value of β in the equation $\beta = \alpha(1-\alpha)^{f-2}$, in which β is an arbitrary quantity in the range $0 < \beta < \alpha_{crit}(1-\alpha_{crit})^{f-2}$. The value of α beyond the gel point lies in the range $\alpha_{crit} < \alpha < 1$. Thus in the polycondensation of a trifunctional monomer $\alpha_{crit} = \frac{1}{2}$ and $\beta = \alpha(1-\alpha)$. For any β in the range $0 < \beta < \frac{1}{4}$, we have $\alpha' = 1-\alpha$, and then

$$W_s = \frac{(1-\alpha)^3}{\alpha^3} \quad (7)$$

Reactions of polyfunctional monomers involving step-by-step (migration) polymerisation conform to similar statistical laws [4,5].

Statistical analysis of the polymerisation of polyvinyl monomers with isolated double bonds, which is propagated by a chain mechanism, presents considerably greater difficulties [6–10]. This is due to the complexity of allowing statistically for different mechanisms of termination of growing macroradicals or macroions. In the simplest case of the copolymerisation of monovinyl and divinyl derivatives the degree of conversion of double bonds at the gel point can be calculated from the equation [6,7]

$$\beta_{crit.} = \frac{1}{\lambda(P_W - 1)} \quad (8)$$

where β_{crit} is the proportion of double bonds which have reacted at the gel point, P_W is the weight-average degree of polymerisation at the gel point, and

$$\lambda = \frac{2M_2}{M_1 + 2M_2}$$

is the proportion of the double bonds in the reaction system which is due to the divinyl monomer, M_1 and M_2 being the numbers of moles of mono- and di-vinyl monomers respectively. No statistical analysis has been made of the reactions of polyvinyl monomers outside the limits of gel formation.

The structure of the polymer network following the gel point is characterised by the frequency (density) of branch points in it, which is expressed by the concentration of effective chains, i.e. those joining two branch points, or by the average length of the chain segment between them. The concentration of chains is expressed as the number of chains N_C or the number of moles of chains n_C in unit of volume of the polymer. The length of the effective chains is estimated as the conventional mean molecular weight M_C of the segment of polymer chain between adjacent branch points. These parameters are interrelated as follows:

$$n_c = \frac{N_c}{N_A} = \frac{\rho}{M_c} \quad (9)$$

where N_A is Avogadro's number and ρ the density of the polymer.

Calculation of the structural parameters of the polymer network expected theoretically from the composition of the initial reactants and the extent of reaction after gel formation will depend on how the structure of the network is represented. A polymer network can be regarded as a combination of chain segments attached at both ends (effective chains), and segments attached at only one end (ineffective chains), to branch points in the network. In the polycondensation of a trifunctional monomer RA_3 with a difunctional monomer $R'B_2$, provided that the groups A react only with the groups B, the number of moles of effective chains after gel formation can be related statistically to the degree of conversion by the formula [11].

$$n_c = \frac{3}{2}\left[P^3\left(1 - \frac{q^6}{P^6}\right) - 3q^2P\left(1 - \frac{q^2}{P^2}\right)\right] \text{ moles of A} \quad (10)$$

where P is the degree of conversion of groups A and $q = 1 - P$ the proportion of groups A which have not reacted.

In the reaction of a difunctional compound with a small amount of a polyfunctional compound the polymer network can be regarded as comprising long chains formed by the difunctional monomer units and joined together by units of the polyfunctional monomer, which in this case can be regarded as points of a tetrahedral network. The number of moles of effective chains in unit volume of the polymer to be expected theoretically from the composition of the reaction system when the reaction has gone to completion can then be estimated by means of the equation [12,13]

$$n_c = Z \cdot \varepsilon \cdot C \quad (11)$$

where $Z = \frac{1}{2}f$ is the mean number of chains per molecule of an f-functional monomer, ϵ the fraction of the f-functional monomer which has reacted with all the functional groups, and C the number of moles of the f-functional monomer per unit volume of the reaction mass.

In the particular case of the copolymerisation of a monovinyl monomer with a small quantity (up to 3 mole %) of a divinyl monomer, with complete conversion of the double bonds, the number of effective chains per unit volume of the polymer is [14]

$$N_c = \frac{2\rho[M_2] \cdot N_A}{(1-[M_2])M_1 + [M_2] \cdot M_2} \quad (12)$$

The mean molecular weight of the effective chains is calculated as [15]

$$M_c = \frac{2M_1}{f_2}\left(\frac{1}{[M_2]} - 1\right), \quad (13)$$

and the number of moles of effective chains per unit volume is [12]

$$n_c = C(2[M_1] + 3[M_2]) \quad (14)$$

where $[M_1]$, $[M_2]$, M_1 and M_2 are respectively the mole fractions and the molecular weights of the mono- and di-vinyl monomers, $f_2 = 4$ is the functionality of the divinyl monomer, and C is the number of moles of the divinyl monomer in unit volume of the reaction system.

With increase in the content of the divinyl monomer in the reaction system above 3 mole % the length of the effective chains becomes comparable with that of the chain of the divinyl monomer. In this case three chains—two formed by monovinyl monomer units and one divinyl monomer chain—must be regarded as meeting at a branch point. The number of effective chains in unit volume of the polymer can then be calculated from the relation [14]

$$N_c = \frac{3\rho[M_2] \cdot N_A}{(1-[M_2])M_1 + [M_2] \cdot M_2} \quad (15)$$

When the initial components have complicated compositions, the mean value M_C can be most easily calculated by choosing the most probable structure for a branch point in the polymer network, i.e. the most probable number of chains converging at one such point, and their molecular weight [16].

Approximate determination of the density of branch points in polymer networks is possible either from an analysis of the products of the controlled degradation of the polymer or from certain properties of the polymer which are related theoretically to the density of branch points. The former method involves chemical breakdown of the polymer network into linear macromolecules, which are analysed by the usual physicochemical methods [17-20]. In connection with the latter method it must be noted that theories relating the structural parameters of polymer networks to the physical properties of the polymers have been worked out only for ideal, tetrahedral networks having a low concentration of branch points.

According to the theory of rubberlike elasticity the concentration of effective chains in unit volume of an ideal network is related to the equilibrium deformation characteristics [21-23]:

$$n_c = \frac{G}{RT} = \frac{E}{3RT} = \frac{\sigma}{RT(\alpha - \alpha^{-2})} \quad (16)$$

where G is the equilibrium shear modulus, E the equilibrium modulus of elasticity under tension (compression), σ the equilibrium tensile (compressive) stress calculated on the initial cross-section of the specimen, R the universal gas constant, T the absolute temperature, and

$$\alpha = \frac{\pm \Delta l}{l_0} + 1 = \frac{l}{l_0},$$

the stretch (shrinkage) factor, in which l is the length of the deformed specimen, $\pm\Delta l$ the elongation (contraction) of the specimen, and l_0 the initial length of the specimen. According to the theory of the swelling of ideal networks in solvents or their vapours n_C is related to the equilibrium swelling by the equation [3]

$$n_c = \frac{\ln a - [\ln(1-v_2) + v_2 + \chi v_2^2]}{V^0\left(v_2^{1/3} - \frac{2}{f}v_2\right)} \quad (17)$$

where a is the activity of the solvent vapour (for the liquid $a = 1$), v the fraction by volume of polymer in the swollen specimen, χ a thermodynamic parameter of polymer–solvent interaction, V^0 the molar volume of the solvent, and f the functionality of the polymer network (the number of effective chains converging at one branch point). For polymer networks with equilibrium swelling the concentration of effective chains and the deformation properties are related by the formula [3]

$$n_c = \frac{\sigma v_2^{1/3}}{RT(\alpha - \alpha^{-2})} \quad (18)$$

A relation has been established also between the osmotic pressure P_{osm} of the equilibrium (swollen) polymer network and the concentration of effective chains therein [24]:

$$n_c = \frac{P_{osm}}{RT} \quad (19)$$

III. LAWS OF THE FORMATION OF NETWORK POLYMERS FROM POLYFUNCTIONAL MONOMERS AND OLIGOMERS

In the vast majority of cases network polymers are synthesised from complicated mixtures of polyfunctional compounds of indeterminate composition, which have been termed resins. They contain not only unchanged initial monomers but also various proportions of oligomers with different numbers of monomer units and different amounts and arrangements of functional groups or other reactive centres responsible for formation of the polymer. Since the exact composition of the resin is unknown, and is easily altered by the slightest change in the conditions of synthesis, it is impossible to predict the structural parameters of the future polymer network. Therefore the numerous studies of the formation of network polymers with resins as examples have shed little light on the laws of the formation and structure of polymer networks. Only the synthesis of polymers from individual polyfunctional compounds (monomers and oligomers) or from specified mixtures will enable sufficient experimental data to be accumulated to elucidate these rules.

1. Reactions of Polyfunctional Monomers and Oligomers in the Initial Stage

The laws governing the reactions of polyfunctional compounds in the initial stage can be assessed from the agreement between experimental results on the degree of conversion of the functional groups at the instant of gel formation and values calculated theoretically (Eqns. 1–5). The degree of conversion is easily determined by the usual methods of quantitative analysis, since the system remains soluble up to the gel point, and the reactivity of the functional groups is easily developed. The accuracy of these investigations is determined largely by the accuracy with which the instant of gel formation can be fixed in the reaction system.

According to theoretical views the point of gel formation involves an instantaneous qualitative change in the properties of the reaction mass, including an infinite increase in viscosity and the appearance of a fraction which is insoluble even in boiling solvents. Most methods of establishing the gel point have been based on fixing these changes. It has also been proposed to determine the start of gel formation from the abrupt change in the electrical [25] and dynamic mechanical [26] properties of the reaction mass. These methods are both inaccurate and

complicated experimentally. They usually require rearrangement of the apparatus to continue monitoring the formation of polymer networks after the gel point has been reached.

One of the most convenient methods for fixing the gel point is to monitor continuously the variation in the modulus of elasticity of the reaction mass by means of a torsion pendulum, in which the inertial mass is suspended by a thread comprising monofils impregnated with the test material [27-31]. This method is simple and quite accurate, and it enables formation of the polymer network to be monitored until the final stage of the reaction.

Investigations of reactions of polyfunctional compounds occurring by a step mechanism (polycondensation and step-by-step polymerisation) show that in many cases the laws of the reactions preceding gel formation are very nearly statistical [2,4,5] (see Table 1). Nevertheless, Andrianov and his coworkers have shown that, for the polycondensation of several oligomeric organic ether-acids, organic alcohols, and organometallic alcohols, variation in the number of monomer units in the oligomers causes the experimental values for the extent of reaction at the gel point to vary from that calculated statistically [32-34] (see Table 1). The start of gel formation has been found to depend on the length of the chain in the polyfunctional compounds also in the reaction of diglycidic esters with amines [35] and of several oligomeric di-isocyanates with polyfunctional alcohols [36].

Table 1. Experimental and theoretical (Eqns. 1-3) degrees of conversion of several reaction systems at the gel point.

Reaction system	r	P_{gel} expt.	P_{gel} theor.	Method of fixing gel point	Ref.
Tricarballylic acid, adipic acid, diethylene glycol	1.00	0.879	0.879	measurement of viscosity by falling sphere method	2,3
	0.80	0.991	0.955		
Propanediphenylene diglycidate, hydrophthalic anhydride	1.00	0.55	0.577	formation of insoluble fraction	4,5
	0.80	0.50	0.516		
	1.43	0.68	0.690		
Dimeric diglycidic ester, hydrophthalic anhydride	1.35	0.597	0.581	ditto	
Pentaerythritol tetra-adipate +					
$HO(CH_2)_2OH$	1.0	0.20	0.575	appearance of fraction insoluble in boiling solvent	32,33
$HO(CH_2)_4OH$	1.0	0.25	0.575		
$HOCH_2CH_2OCH_2CH_2OH$	1.0	0.27	0.575		
$HO(CH_2CH_2O)_2CH_2CH_2OH$	1.0	0.33	0.575		
$HO(CH_2CH_2O)_3CH_2CH_2OH$	1.0	0.35	0.575		
$O[Si(CH_3)_2CH_2OCH_2CH_2OH]_2$	1.0	0.40	0.575		
$C_6H_5Si[OSi(CH_3)_2CH_2OCH_2CH_2OH]_3$	1.0	0.36	0.41		
$Si[OSi(CH_3)_2CH_2OCH_2CH_2OH]_4$	1.0	0.23	0.33		

Discrepancies between experimental and calculated degrees of conversion of double bonds at the gel point are observed especially frequently in the polymerisation of polyvinyl derivatives or their copolymerisation with monovinyl monomers [6,37,38].

The deviations in the formation of a polymer network in the initial stages of the reaction of polyfunctional compounds probably arise from the implausibility of several postulates underlying the statistical analysis. It is difficult to suppose that under actual conditions cyclisation is completely absent, or that reactive groups maintain constant activity. Furthermore, the increase in molecular weight during the reaction is accompanied by a sharp intensification of the role of intermolecular interaction.

These deviations may become predominant with certain reaction systems or conditions, and then the reactions of polyfunctional compounds will not obey statistical laws at all. In some cases, for example, ring closure in a polyfunctional compound is energetically more advantageous than chain growth. This results in the preferential formation of cyclopolymers, with the maintenance of solubility until the limiting stages of the reactions. Such phenomena are observed in the polymerisation of divinyl derivatives in which the double bonds are separated by the number of atoms necessary for the formation of stable rings [39-41]. Similarly the polycondensation of silanetriols may lead to the formation of polycyclic or ladderlike polymers [42-45]. The reaction of anhydrides of tetracarboxylic acids with diamines, and of tetramines with dicarboxylic acids, usually yields polycyclic or ladderlike structures [46], though under certain conditions network polymers can be formed from the same components [47].

The marked departure in the laws of the reactions of polyfunctional compounds from those to be expected statistically in the initial stages may also be a consequence of differences in the activity of the reactive groups of the polyfunctional compound or of a marked change in reactivity of still unreacted groups after addition of a monomer unit to the polymer molecule [48-50]. In the limit three-dimensional structures of restricted size may be formed, dispersed in the reaction mass, the so called microgels or popcorns [48,51,52]. In this case the gel point is the instant of aggregation of the microgels by chemical combination to form a macrogel of statistically non-uniform density.

2. Polymer Networks in the Final Stage of Formation

Analysis of the degree of conversion of functional groups in the reactions of polyfunctional compounds before the start of gel formation and comparison with the theoretical values show that the development of reactions in fairly close conformity with statistical laws (formation of a uniform polymer network at the gel point) can be accompanied by marked deviations towards the preferential formation of cyclic polymers or microgel structures. The polymer structure produced in the initial stage will obviously have a decisive effect on the further course of the reaction. Thus if polymers of polycyclic or ladderlike structure are the main products in the initial stages, the reaction will develop in this direction also in its later stages, although intermolecular reactions may become increasingly probable. If, however, gel formation occurred by aggregation of microgels, further increase in density of the network of microgels with a small number of chemical bonds between them may continue beyond the gel point. In the extreme case the polymer in the final stage of the reaction will comprise densely cross-linked particles (micrograins, popcorns) distributed in an open-network matrix [51-53]. These suggestions, together with qualitative data on the non-uniform swelling of films [52,54] and the non-uniform structure observed with the electron microscope [55-67] in investigations of several network polymers, may lead to the conclusion that formation of a statistically uniform polymer network at a late stage in the conversion of polyfunctional compounds is improbable, being an exception rather than the rule [48]. However, the globular structure of network polymers mostly observed in electron-microscopic investigations is not necessarily a criterion of the microgel structure of

the polymer network. It may, for example, result from the preservation of globular structures characteristic of the chains of the initial polyfunctional oligomers or of their restoration after formation of the polymer network, similarly to what is observed with several network polymers [68,69]. These formations characterise the morphological structure of network polymers and depend, as with polymers having linear macromolecules, on the nature of the chains and the physical state of the polymer.

When investigating the laws of the formation of network polymers from polyfunctional compounds, we must first take into account the topological structure of the polymer network, which is characterised quantitatively by the concentration of effective chains. Comparison of experimental structural parameters of the network with those calculated theoretically from the composition of the reaction system and the conversion of functional groups will make it possible to elucidate details of the formation of a polymer network in the terminal stages of the reaction.

(*a*) Experimental estimation of structural parameters of polymer networks

Quantitative analysis of the conversion of functional groups is considerably more complicated in the later stages of the reaction than before the gel point. Use can be made of infrared spectroscopy [70], analysis of functional groups by conducting reactions in polymers of equilibrium swelling [5,32,70], analysis of secondary products liberated during polycondensation [71], thermal effects of the reaction [72], dilatometric analysis [73], etc. The choice of method depends mainly on the type of reactive groups involved in formation of the network polymer.

It is almost impossible to elucidate the laws of the formation of polymer networks beyond the gel point by comparing the experimental degree of conversion of the functional groups with the value calculated theoretically from the sol fraction (Eqn. 7), since the latter tends to zero long before the degree of conversion reaches 100%. At 75% conversion of the functional groups of a trifunctional monomer the theoretical sol content is already down to at most 3.5% of the weight of the reaction mass. Such a small sol fraction lies within the limits of experimental error for an extraction with boiling solvent.

Theoretical values of the structural parameters of polymer networks are calculated from the degree of conversion of the functional groups by means of Eqns. (10) and (11), or from Eqns. (12)–(15) when conversion is complete.

Experimental methods of determining density parameters of polymer networks involving their chemical degradation can be used effectively only if two types of covalent bonds differing markedly in chemical stability—weak bonds, which can be easily broken, and more stable bonds—are present in the polymer network. Examples are provided by network copolymers of unsaturated polyesters with styrene [17,18] and certain other di- and monovinyl derivatives [19], and also network polyester-urethanes [20]. Degradation methods are suitable for polymers having any concentration of chemical branch points, but they cannot take into account the effectiveness of the network chains, and they cannot be applied to the large number of network polymers having identical and stable bonds.

Methods based on theoretical relations between the structural parameters of the networks and the physical properties of the polymers (Eqns. 16–19) are the most promising and widely developed at the present time. These rules, deduced from statistical theories of rubberlike elastic deformations and the swelling of ideal tetrahedral networks with point connections and perfectly flexible chains, agree well with experimental data when the polymer contains only chemical branch points and M_C for the network considerably exceeds a segment of the polymer, i.e. in the case of open-network elastomers [3,21–23]. In the analysis of network polymers with poor chain flexibility and in the vitreous state, only the individual correlation of the experimental network parameters found under specified conditions with those calculated from the composition of the initial components and the degree of conversion of the reactive groups will enable the applicability of the method to be established and the reliability of the results to be assessed.

The applicability of the statistical theory of rubberlike elasticity to polymer networks for the experimental determination of their parameters over a wide range of concentrations of chemical branch points resulting from the reactions of polyfunctional compounds has been investigated in detail by Tobolsky and his coworkers on copolymers of vinyl monomers with oligomeric ester–maleates having a specified structure between the double bonds [12], copolymers of vinyl monomers with oligomeric ethylene dimethacrylates [12,74–78], and products of the hardening of the propanediphenylene diglycidate with various ethyleneamines [13]. The relative deviation of the structural parameters of networks from the ideal values calculated from the composition of the reaction mixture, allowing for the degree of conversion of the reactive groups and the effective participation of polyfunctional compounds in the reaction, is measured by the coefficient

$$\Phi = \frac{G}{n_0 RT} \qquad (20)$$

where n_C (in moles cm^{-3}) is the calculated density of chemical links in the network, and G the experimental equilibrium shear modulus of the network polymer in the rubberlike elastic state.

These investigations showed satisfactory agreement between theoretical and experimental network parameters for polymers whose $G-T$ curve included a horizontal section (rubberlike elasticity plateau—Fig. 1). When G is determined for temperatures 50–100 deg above the glass point of the polymer, the value of Φ varies over the range 1–3 depending on the type of network polymer (Table 2). The quantity G reaches 10^8 dyn cm^{-2} and varies little with the nature of the polymer chains. This is characteristic of polymer networks containing ten or more σ-bonds between adjacent network points (an aromatic ring is regarded as equivalent to one σ-bond). Equation (16) cannot be applied at the higher density characteristic of most dense-network polymers. The empirical equation [79]

$$\lg G = 7.0 + \frac{293\rho}{M_0} \qquad (21)$$

(where ρ is the density of the polymer at the experimental temperature), relating the density parameters of the network to the equilibrium modulus G, can be used up to the value $G = 2 \times 10^9$ dyn cm^{-2}. Fig. 2 compares the relations between G and M_C given by the theory of the rubberlike elasticity of ideal networks and by the empirical equation [21].

Kuvshinskii and his coworkers have also shown that the theory of rubber elasticity can be used to determine the network parameters of polymers obtained by the copolymerisation of several monovinyl and divinyl monomers [14].

Gul' et al. have established[80] that the theoretical relation between the equilibrium stress and moderate and small deformations (16) can be used to estimate the concentration of effective chains in the network formed by the copolymerisation of styrene with oligomeric ester–maleates. A linear relation with a correlation coefficient of 0.8–0.85 is found between the concentration of branch points determined by degradation of the copolymer with subsequent analysis of the hydrolysis products n_{chem} and the concentration calculated from the equilibrium deformation n_{phys} (with $n_{phys} < n_{chem}$ always).

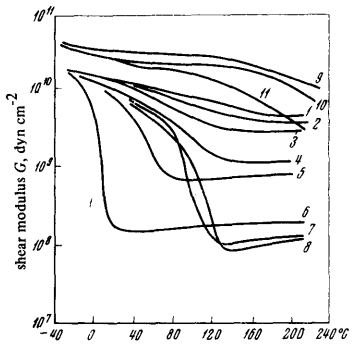


Figure 1. Temperature dependence of equilibrium shear modulus for network polymers from dimethacrylates of: 1) ethylene glycol; 2) triethylene glycol; 3) tetraethylene glycol; for network copolymers of tetraethylene glycol dimethacrylate with ethyl acrylate containing different proportions (mole %) of dimethacrylate: 4) 68; 5) 42; 6) 15.1; for network polymers from propanediphenylene diglycidate and: 7) diethylenetriamine; 8) triethylenetetramine; and for hardened resins of formaldehyde with: 9) melamine; 10) phenol; 11) urea.

Table 2. Divergence between structural parameters of polymer networks found experimentally from the equilibrium modulus of rubberlike elasticity and those calculated theoretically.

Network polymer	Equilibrium modulus G, dyn cm^{-2}	Coefficient Φ	Ref.
Сополимер стирола и тетраэтиленгликольди-			
Copolymer of styrene + 5–15 mole % of tetraethylene glycol dimethacrylate (TEGDMA)	$2.93—8.51 \cdot 10^7$	1.74—1.79	12.76
Copolymer of methyl methacrylate + 10–20 mole % (TEGDMA)	$6.67—17.2 \cdot 10^7$	1.50—1.62	
Copolymer of ethyl acrylate + 5–8 mole % (TEGDMA)	$1.37—8.93 \cdot 10^7$	0.77—1.18	
Copolymer of styrene + oligoether–maleates with mol. wt. of chain between double bonds:			
159 (70 wt.%)	$4.35 \cdot 10^8$	3.13	12
259 (20–70 wt.%)	$3.18—13.5 \cdot 10^7$	1.22—2.06	
362 (60–70 wt.%)	$2.5—2.94 \cdot 10^8$	1.99—2.79	
Polymer from propanediphenylene diglycidate + equimolecular quantity of:			
ethylenediamine	$1.43 \cdot 10^8$	1.36	
diethylenetriamine	$1.91 \cdot 10^8$	1.87	13
triethylenetetramine	$1.78 \cdot 10^8$	1.78	
tetraethylenepentamine	$1.87 \cdot 10^8$	1.88	

A fairly close correspondence between calculated (from the composition of the initial reactants) and experimental values of the modulus of rubberlike elasticity is observed also with network polymers obtained from propanediphenylene diglycidate and anhydrides of dibasic acids containing radicals of various sizes [81] (Table 3).

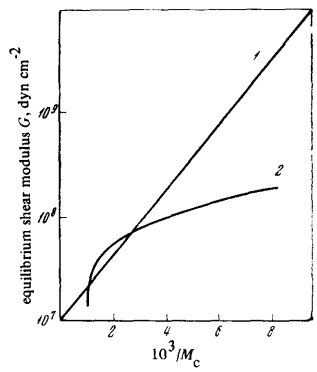


Figure 2. Dependence of equilibrium shear modulus on M_c above the glass point of network polymers from: 1) empirical equation $\lg G = 7.0 + 293\rho/M_c$; 2) kinetic theory of rubberlike elasticity $G = \rho RT/M_c$.

Quite good agreement with experimental parameters, found from the equilibrium modulus of rubberlike elasticity, is obtained for networks formed by the polymerisation of oligomeric ester–dimethacrylates with complete conversion of double bonds [82] (Table 4) if the theoretical value of M_c is taken to be not the molecular weight of the initial oligomer but its molecular weight divided by the functionality (4 in the present case).

Table 3. Calculated and experimental modulus in rubberlike elastic state of copolymers of propanediphenylene diglycidate with various anhydrides (temperature in all cases 100 deg above the glass point of the polymer) [81].

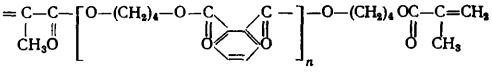
Acid anhydride	Modulus of rubberlike elasticity, dyn cm^{-2}		$\Phi = \frac{E_{exp}}{E_{calc}}$
	E_{exp}	E_{calc}	
Succinic	2.6	2.5	1.04
Methylsuccinic	1.9	2.2	0.87
Dodecylsuccinic ($C_{12}H_{23}$)	0.53	1.2	0.44
Phenylsuccinic	1.4	1.9	0.74
Maleic	3.1	2.7	1.15
Phthalic	1.9	2.2	0.87
Hexahydrophthalic	1.25	2.1	0.60

Hence the network parameters can be estimated quite accurately by determining the elastic characteristics of network polymers above their glass point. Unfortunately, there are many rigid dense-network polymers, of very great practical importance, whose glass points are above or very close to the temperature of degradation. This method cannot be applied to such polymers [12] (Fig. 1, curves *9–11*).

The relation established by Flory between the degree of swelling of polymers and the density of points in ideal

networks[3] (Eqn. 17) is of especial interest for estimating network parameters. Here the greatest experimental difficulty is encountered in determining the thermodynamic polymer–solvent interaction parameter (the Huggins constant χ). This parameter is usually determined by investigating the solubility and the properties of solutions of polymers identical in chemical composition with the network polymers[83–85]. However, especially in network polymers obtained from polyfunctional compounds, the structure of the monomer units is too diverse and is difficult to reproduce in soluble products. Furthermore, variation in the density of points in a polymer network is necessarily accompanied by a change in the chemical composition of its chains[70]. This substantial difficulty was eliminated by using solvent vapours for swelling and by linearising Eqn. (17).[86] By determining the sorption isotherm for the solvent vapour on polymers we can simultaneously determine graphically both the density of network points and the polymer–solvent interaction parameter[16,71,87]. Furthermore, determination of the degree of swelling of a polymer in the solvent vapours simplifies the experiment and improves its accuracy. Without danger of error due to extraction of the sol fraction it is possible to determine the swelling of a network polymer in the vapours of solvents over a wide range of temperatures, since at normal temperature the solvent often does not ensure destruction of physical junction points in the polymer network, and equilibrium swelling is restricted not only by chemical but also by physical junction points.

Table 4. Deviation between experimental and theoretical values of M_C for network polymers obtained from oligoester–dimethacrylates (MBP-n)[82].



Initial oligomer	Mol. wt. of oligomer	$M_{c,\,theor}$	$M_{c,\,exp}$	$\Phi = \frac{M_{c,\,theor}}{M_{c,\,exp}}$
MBP-1	446	111	85	1.30
MBP-2	666	166	160	1.02
MBP-3	886	221	280	0.78

The experimental parameter for the density of network points is, of course, higher than the theoretical value. Thus the density of branch points in a network copolymer of methyl methacrylate and methylene dimethacrylate, determined from the swelling in benzene at room temperature, is roughly ten times the value calculated from the composition of the initial mixture and supported by analysis of the degradation products of the network[88] (Table 5). Similar results have been obtained by Nielsen in an investigation of the swelling of epoxide network polymers[65].

Complete destruction of physical links in a network can be achieved by swelling the polymer in the vapour of a specially selected solvent at a certain temperature. Thus the presence of stable hydrogen bonds in networks obtained from a diglycidic ester and an oligomeric amide demands the application at an elevated temperature (70°C) of a solvent (dioxan) capable of rupturing these bonds (Table 6). Under these conditions experimental results agree with theoretical values. In the absence of stable physical links in the polymer from a diglycidic ester and an aliphatic diamine there is close agreement with theory when experiments are conducted with a non-polar solvent (dichloroethane) at low temperatures.

Table 5. Comparison of experimental estimates of concentration of chains in copolymers of methyl methacrylate with methylene dimethacrylate from degradation n_{deg} and from swelling in benzene n_{sw}.[88]

Dimethacrylate in copolymer, mole %	$10^5 n_{deg}$, moles g^{-1}	$10^5 n_{sw}$, moles g^{-1}	$\Phi = \frac{n_{sw}}{n_{deg}}$
0.201	1.61	16.0	10.0
0.509	3.56	35.7	10.0
1.04	5.61	50.6	9.2

Only acetone vapour at 50°C cleaves the hydrogen bonds in polymethylenephenols from trishydroxymethylphenol and hydroxymethyloligomethylenephenols, and the experimental values of M_C approach those calculated theoretically from the structure of the initial compounds and the degree of conversion of the hydroxymethyl groups[71,87] (Table 7). It has been found also that, on swelling in cyclohexanone vapour, only at elevated temperatures does the experimental concentration of chains approach the statistical value in the network formed by the polycondensation of phenol with formaldehyde[11].

Table 6. Structural parameters, determined under various conditions of swelling in the vapour, for network polymers from propanediphenylene diglycidate and a diamine or oligoamide[16].

Second component						
Compound	% on stoichiometric quantity	$M_{C,\,theor}$	Sorbed solvent	Sorption temp., °C	$M_{c,\,exp}$	$\Phi = \frac{M_{c,\,theor}}{M_{c,\,exp}}$
Hexamethylenediamine	100	265	chloroform	30—60	240	1.10
			dioxan	50	240	1.10
	50	492	chloroform	40—50	455	1.08
Oligoamide (Versamid)			chloroform	40	100	2.43
				50	100	2.43
				59,5	100	2.43
				35—50	110	2.20
				60	172	1.41
	75	243	dioxan	70	205	1.18
				75	205	1.18

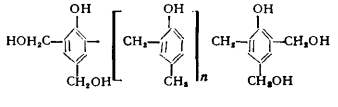
The structure of the physical links in network polymers facilitates the development of rubberlike elastic deformations and permits the use of Eqn. (18) to determine the density of chemical links alone. Table 8 shows good agreement between the parameters of network polyesterurethanes determined by this method and those calculated from the composition of the reaction mixture[89].

Thus investigation of the equilibrium swelling of polymers in solvents and especially in their vapours, and study of the deformation properties of the swollen polymers, are the most promising methods for estimating the structural parameters of polymer networks. Successive destruction of physical links by choice of solvent and the temperature of its vapour will significantly enrich our views on the role and stability of the physical links in polymer networks.

(*b*) Formation of polymer networks in the later stages of reaction

Experimental analyses of the structural parameters of polymer networks indicate that in most cases the concept of the topological structure of a network polymer as a statistical distribution in space of chains linked at points is sufficiently close to reality. In the microgel (heterophase) structure of networks it is difficult to expect such good agreement between the experimental chain concentrations found by means of physical theories of polymer networks and those calculated theoretically from the structure of the initial reactants and the degree of conversion of reactive groups. The often observed low experimental density parameters of the networks compared with the theoretical values can be explained by the presence of defects in the structure of the network at chemical links, and high values by the presence of stable physical links, which produce an apparent increase in the concentration of effective chains in the network.

Table 7. Structural parameters of network polymethylenephenols determined under various conditions of swelling in vapours [71,87].

Polymethylenephenol from:		$M_{c,calc}$	Sorbed solvent	Sorption temp., °C	$M_{c,exp}$	$\Phi = \frac{M_{c,calc}}{M_{c,exp}}$
Trishydroxymethylphenol		41	benzene	25	40	1.01
			acetone	50	55	0.75
Hydroxymethyl-oligomer	$n=1$	100	benzene	25	50	2.00
			acetone	50	95	1.05
	$n=3$	200	benzene	25	60	3.35
			acetone	50	220	0.92
	$n=5$	320	benzene	25	60	5.40
			acetone	50	380	0.84

Experimental methods of estimating structural parameters of polymer networks which involve destruction of all physical links reveal the causes of imperfection of networks which occur at chemical branch points during their formation. If the formation of network polymers in the initial stages preceding the gel point is very nearly random, the imperfection of the polymer network with respect to chemical links at a later stage in the reaction may be caused by the appearance of ineffective chains, i.e. chains attached at only one end to network points or forming closed rings (loops).

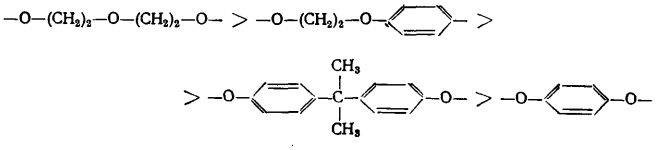
If the reactive groups are present in the central portion of the initial polyfunctional compound (of molecular weight M), even on complete conversion the proportion of the total number of chains which are ineffective is $2M_c/M$. [3,90] Hence there is no point in using polyfunctional oligomers having reactive groups near the centre if the expected value of M_c for the network is less than one-tenth of the molecular weight of the oligomer. An example of such structures is provided by polyester-maleates hardened by copolymerisation with styrene. The concentration of effective chains in them, found by physical methods, is considerably lower than the theoretical value or that found by analysis of the degradation products, if the proportion of ineffective chains in the network is disregarded [12,80].

The imperfection of a network produced by a polyfunctional compound with terminal reactive groups is determined solely by their degree of conversion and by the consumption of functional groups in the formation of rings (loops).

Table 8. Comparison of structural parameters determined from the equilibrium deformation of swollen and unswollen specimens of network polyester–urethanes formed from polyester (PE) from diethylene glycol and adipic acid ($M = 1600$) + tolylene di-isocyanate (TDI) + 1 : 1.5 mixture (A) of bis- and tris-hydroxyethylamines [89].

PE:TDI:A	$M_{c,calc}$	$M_{c,exp}$ when swollen	$M_{c,exp}$ when unswollen	$\frac{M_{c,calc}}{M_{c,sw}}$	$\frac{M_{c,sw}}{M_{c,unsw}}$
1:1.10:0.035	33800	33000	3700	1.02	8.90
1:1.15:0.070	24000	25000	3300	0.96	7.60
1:1.20:0.100	20000	24000	2600	0.92	9.20

In consequence of the tendency of polyfunctional compounds to cyclisation, a polymer network may not be formed at all, as already noted. If, however, a network is formed, its imperfection beyond the gel point, as a result of the consumption of functional groups in the formation of rings, should be especially marked in open networks. In some cases it has been possible to estimate the part played by ineffective groups in network polymers obtained by the copolymerisation of monovinyl derivatives with small quantities of divinyl derivatives, provided that conversion of double bonds is complete. In the copolymerisation of styrene with various divinyl derivatives, for example, the tendency to cyclisation varies with the structure of the chain in the divinyl component as follows [15]:



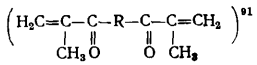
The extent to which the divinyl derivative was involved in cyclisation was estimated from the difference between the theoretical network density (from Eqn. 12) and the value found experimentally from the swelling of the copolymer in solvents (Eqn. 17). The tendency to cyclisation increases with increase in the functionality of the polyvinyl derivative [15].

Table 9 also illustrates the effect of the length and rigidity of the chain between the double bonds in the divinyl component on its ability to form ineffective loops [91]. The density of network points was calculated theoretically from the composition of the mixture and the degree of conversion of the double bonds, and was determined experimentally from measurements of the rubberlike elastic deformation of specimens in the swollen state (Eqn. 18).

The increase in network imperfection in polyether–urethanes with increase in length of the flexible chains of the oligomers, consisting of ether links [92,93], is probably also determined mainly by the formation of ineffective

loops (Tables 10 and 11). The high experimental parameters in the case of the denser networks [92] are evidently caused by a greater concentration of physical links in the form of hydrogen bonds. With increase in the density of chemical links in the polymer network it obviously becomes increasingly difficult to separate effective chains and ineffective loops, and in the case of dense-network polymers this becomes altogether impossible. The imperfection of a network formed from oligomers having terminal functional groups is then determined solely by the degree of conversion of the functional groups.

Table 9. Degree of cyclisation of dimethacrylates



on copolymerisation with styrene as a function of the structure of R. [91]

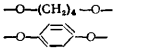
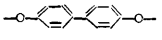
R	Cyclisation, %
—O—	52
—O—$(CH_2)_4$—O—	28
	11
	0

Table 10. Effect of molecular weight of macrodi-isocyanate (from different glycols and 3-methylpentane-1,1′,5-triol) on deviation of concentration of effective chains in the network polyurethanes from calculated values [92] (network parameters determined experimentally from equilibrium modulus of rubberlike elasticity).

Polyoxypropylene glycol		Polyoxytetraethylene glycol	
mol. wt. of di-isocyanate	$\Phi = \frac{n_{exp}}{n_{theor}}$	mol. wt. of di-isocyanate	$\Phi = \frac{n_{exp}}{n_{theor}}$
650	1.54	500	2.05
960	1.14	1000	1.06
1450	0.94	1500	0.80
1930	0.71	2000	0.57
3000	0.58	3000	0.58

Table 11. Deviation in network parameters from theoretical values for network polyurethanes (from a tri-isocyanate and a polyethylene glycol) having effective chains of different lengths [93].

Poly-ethylene glycol	$M_{c,\,theor}$	$\Phi = \frac{M_{c,\,theor}}{M_{c,\,exp}}$
Di-	351	1.29
Tri-	395	0.90
Tetra-	439	0.72
Hexa-	527	0.66
Octa-	615	0.66
Deca-	763	0.57

In complete conversion of functional groups in the terminal stage of the formation of network polymers may be due to diffusion and steric hindrances [94,95], which depend on the length and flexibility of the chains in the polyfunctional compounds and on the number and arrangement of the functional groups. Steric hindrance increases with increase in the density of network points and with intensification of the physical interaction between the network chains, i.e. with diminished probability of collision between functional groups. If at some stage the temperature of the reaction system falls below the glass point of the resulting polymer, reaction almost ceases [43,96]. In the copolymerisation of monovinyl monomers with divinyl monomers, for example, increase in the concentration of the latter makes the attainment of complete conversion of the double bonds more difficult owing to the rise in the glass point of the network copolymer, which becomes higher than the reaction temperature [43] (Fig. 3). Increase in the length and flexibility of the chain in the divinyl derivative raises the limiting degree of conversion of the double bonds. Similarly, in the formation of a network polymer from propanediphenylene diglycidate and a tetramine raising the reaction temperature above the glass point of the polymer diminishes the imperfection of the polymer network [65] (Table 12). A diminution in the functionality of the components also facilitates conversion of functional groups at the terminal stage of the synthesis of a polymer [97]. In the hardening of a diglycidic ester with acid anhydrides, increase in the bulk of the anhydride molecule, and hence increase in the steric and diffusion hindrance, increase the difference between calculated and experimental network parameters [81] (Table 3).

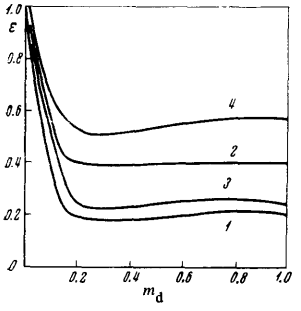


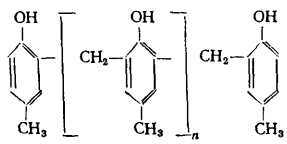
Figure 3. Dependence on their mole fraction m_d of the efficiency ϵ with which various divinyl monomers (dimethacrylates of different diols) are involved in the formation of a network polymer when copolymerised with methyl methacrylate [43]: 1) ethylene glycol; 2) decamethylene glycol; 3) 2,2-dimethylpropanediol; 4) 2-butyl-2-ethylpropanediol.

In the homopolymerisation of oligomeric ester-diacrylates it has also been established [72] that formation of the polymer network following the gel point is retarded by diffusion and steric hindrance, and the degree of conversion of the double bonds hardly ever reaches 100%. Increase in the length and flexibility of the oligomer chains facilitates attainment of the limiting degree of conversion of the double bonds.

The role of diffusion restrictions has been variously assessed in the synthesis of certain open-network polymers, especially polyether-urethanes [20,98-101].

There is a conviction that, when rigid polyfunctional molecules are used in the synthesis of network polymers, it is altogether impossible to achieve complete conversion

of functional groups owing to insuperable steric and diffusion hindrance[102]. In certain cases, however, a suitable choice of the structure of the initial reactants and of the reaction conditions may permit almost complete conversion. For example, the polycondensation of trishydroxymethylphenol proceeds until the hydroxymethyl groups have been completely converted[103] (Fig. 4). Trimeric methylenephenol containing hydroxymethyl in the terminal groups undergoes polycondensation with similar almost complete conversion of hydroxymethyl groups[71,87] to form a polymer network approximating to that calculated statistically (Table 7). With increase in the number of monomeric units in the oligomer to five and seven the proportion of hydroxymethyl groups which do not react is 33% and 38% respectively, obviously owing to steric and diffusion restrictions. The reactivity of the active hydrogen atoms in the phenolic rings of the oligomethylenecresols



drops similarly as soon as the number of units in them exceeds four[104,105]. The explanation offered[105] for this phenomenon is that the oligomers coil up owing to the presence of hydrogen bonds between the hydroxy-groups, which hinders access to the reactive groups.

Table 12. Effect of reaction temperature on structural parameters of polymer networks from propanediphenylene diglycidate and triethylenetetramine (proportions 7 : 1)[65].

Max. temp. of reaction, °C	Glass point of polymer, °C	$\Phi = \frac{M_{c,\,theor}}{M_{c,\,exp}}$
40	92	0.82
60	93	0.83
120	97	0.87

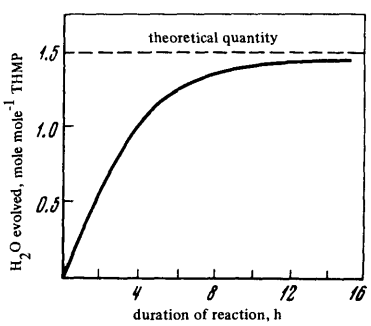


Figure 4. Kinetics of the polycondensation of trishydroxymethylphenol at 130°C.[103]

The presence, during formation of a polymer network, of a solvent or a plasticiser to promote the coiling of molecules into dense tangles increases the probability of intramolecular cyclisation and the formation of a microgel structure[20,48,77]. On the other hand, the presence of a plasticiser diminishes steric and diffusional hindrance, which allows greater conversion of functional groups and diminishes the imperfection of dense networks[78]. Long side radicals in the initial components may act as an intramolecular plasticiser[78].

Table 13. Effect of plasticiser on formation of polymer network from propanediphenylene diglycidate and triethylenetetramine in the proportions 7 : 1.[65]

Diglycidate / Plasticiser	Glass point, °C	Dynamic modulus at T_{gl} + 30 deg $10^{-7}G$, dyn cm^{-2}	M_c calc	M_c expt, from G	$\Phi = \frac{M_{c,\,theor}}{M_{c,\,exp}}$
100/0	92	8.6	305	367	0.83
90/10	84	6.8	425	411	1.04
80/20	65	4.9	544	496	1.10
70/30	60	3.9	664	580	1.14
60/40	50	3.6	783	615	1.28
50/50	26	1.5	903	1950	0.42
30/70	10	0.84	1142	3640	0.31

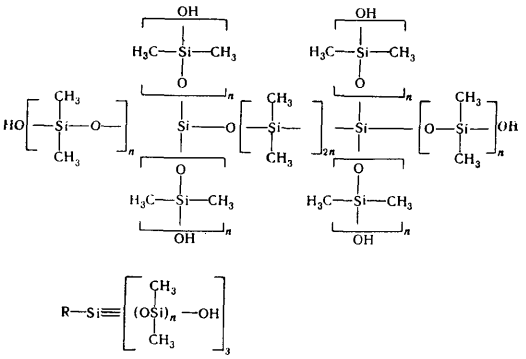
The presence in the propanediphenylene diglycidate–triethylenetetramine system of a small quantity of an active plasticiser, e.g. an oligomeric ester with a terminal carboxy-group, promotes more complete conversion of functional groups, and thus diminishes the imperfection of the network. With a high plasticiser content the tendency to cyclisation is predominant. This leads to formation of a polymer having structural parameters which differ markedly from the theoretical (Table 13).[65] Under such conditions the polymer network may have a microgranular (heterophase) structure, as is confirmed by a study of the dynamic mechanical properties of these polymers[79].

IV. CONTROLLED SYNTHESIS OF NETWORK POLYMERS

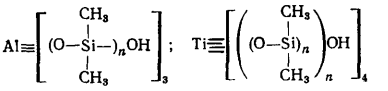
The experimental results which have accumulated on the formation of network polymers from polyfunctional compounds permit us to assess the prospects of developing syntheses of such polymers having a controlled structure. The choice of the initial compounds should obviously ensure the maximum probability of formation of a polymer network having a uniform distribution and a specified concentration of branch points, and also ensure that all monomer units are involved in effective chains. The most promising for the controlled synthesis of network polymers are oligomers containing reactive groups in the terminal units (telofunctional oligomers), since the use of oligomers having functional groups in intermediate units will result in the formation of a polymer network having a large number of ineffective terminal chains even with complete conversion of the functional groups.

The use of individual telofunctional oligomers containing two or more functional groups capable of reacting among themselves, in which the chains between the terminal units differ in nature and length, enables the structural parameters and the properties of the network polymers to be controlled within quite wide limits.

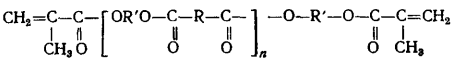
Andrianov and his coworkers have developed methods for synthesising network polymers of controlled structure



by the polycondensation of oligomeric polyfunctional organosiloxanes [106]. By regulating the value of n we can obtain network polymers which are in the vitreous or in the elastic state at room temperature. Similarly, we can obtain various network polyalumino- and polytitano-organosiloxanes



A procedure has been developed for the controlled synthesis of network polymers from oligoester–telo-acrylates



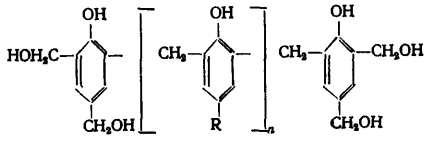
by chain polymerisation at the terminal acrylate groups [72].

Table 14. Some properties of network polyester–acrylates as functions of nature and length of oligomeric block in initial oligomers [72].

Initial oligoester-dimethylacrylate				Shrinkage on polymerisation, vol. %	Mechanical constants			
symbol	R′	R	n		hardness H_B, kgf cm^{-2}	effective modulus, kgf cm^{-2}	specific impact strength, kgf cm cm^{-2}	bending strength σ_b, kgf cm^{-2}
MDP-n	—CH$_2$—CH$_2$—O—CH$_2$—CH$_2$—		1	7.5	12.0	—	5.0	1150
			2	4.8	8.6	—	10.0	1600
			3	4.3	6.9	—	11.4	1550
			4	3.7	1.1	—	16.0	930
			5	—	0.9	—	19.0	740
MBP-n	—(CH$_2$)$_4$—		1	—	12.8	8700	3.5	845
			2	—	8.9	8650	5.7	1120
			3	—	6.4	7170	10.5	900
MBS-n	—(CH$_2$)$_4$—	—(CH$_2$)$_8$—	1	—	0.9	—	9.7	195
			2	—	0.4	—	10.2	65

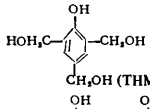
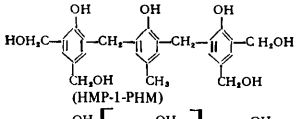
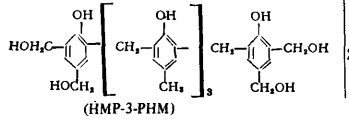
The network density is regulated by the number of ester units between the acrylate groups, and the rigidity by the structure of the radicals R and R′. The properties of network polymers from oligoester–acrylates differing in nature and size are listed in Table 14.

Network polymethylenephenols (phenol–formaldehyde polymers) of controlled structure can be obtained by the polycondensation of trishydroxymethylphenol and hydroxymethyl derivatives of oligomethylenephenols (hydroxymethyl-oligomers) having the structure [71,87]



The structural characteristics of the resulting polymer networks and several properties of the network polymers are given in Table 15.

Table 15. Properties of network products of the polycondensation of hydroxymethyl-oligomers as a function of the structural characteristics of the network [71,87].

Initial hydroxymethyl oligomer	M_c(expt.) based on		Density at 20°C, g cm^{-3}	Mechanical constants				
	chem. links	chem. and H bonds		bending modulus, kgf cm^{-2}	Rockwell hardness	specific impact strength, kgf cm cm^{-2}	compressive strength, kg cm^{-2}	δ_{bend}, kgf cm^{-2}
 (THMP)	55	40	1.300	43500	35 32— —37	3.5 2.8— —4.0	1100	600
 (HMP-1-PHM)	95	50	1.280	41500	32 30— —33	7.5 6.7— —9.2	1250	1200
 (HMP-3-PHM)	220	65	1.230	40000	30 30	9.5 8.4— —10.6	1120	1650

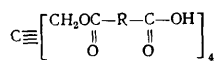
Nevertheless, the use of individual telofunctional oligomers does not always make it possible to control the density of the polymer network by varying the length of the oligomeric block without changing its nature. Variation in the length of an oligomer leads to a sharp change in the conditions for formation of the polymer network. Increase in length usually results in an increased tendency to intramolecular cyclisation of the oligomer and a decreased maximum degree of conversion of functional groups. As a consequence the imperfection of the network with respect to chemical links increases, and is difficult to control. This effect can be diminished by using binary systems for the synthesis of network polymers. They should comprise a telofunctional oligomer of a particular nature, with a definite number of units between the terminal functional groups (depending on the proposed density of network points), together with a polyfunctional compound of considerably lower molecular

weight (a hardener). The low molecular weight of the second component facilitates the achievement of limiting conversion of functional groups for almost any length of oligomer. In order to prevent the competing process of intramolecular cyclisation, it is necessary that functional groups on the same component should not interact. This method is being used increasingly to control the synthesis of open-network polymers (vulcanised rubbers). Thus the polymerisation or copolymerisation of dienes in the presence of telogens of definite structure yields rubbers of low molecular weight (polynomers) with functional groups in the terminal units, which are involved in formation of a polymer network on reaction with a vulcanising agent [90,107].

Esters containing hydroxy-groups in the terminal units, obtained by the polycondensation of dibasic acids with excess of dihydric alcohols, are used as telofunctional oligomers for the controlled synthesis of elastic open-network polyurethanes. Oligomeric ethers obtained by the polymerisation of hydroxylated rings contain similar terminal groups. The vulcanising agent can be a tri- or a tetra-isocyanate [93,108].

Oligomeric ethers and esters containing terminal alcoholic hydroxyls yield with excess of di-isocyanates oligomers, containing terminal isocyanato-groups, termed macrodi-isocyanates (precondensates). The hardeners are polyfunctional alcohols or amines of low molecular weight [89,108].

The use of such hardeners promotes more complete formation of polymer networks from oligomeric acid esters [32-34,109]



In the case of oligomeric diglycidic esters the best conditions for the production of polymer networks are provided by the use of hardeners of low molecular weight—amines or acid anhydrides [35,97].

The use of telofunctional oligomers of a specified structure to synthesise network polymers having a controlled structure permits the establishment of a relation between the network parameters and the properties of the polymers, and hence the production of polymers having specified properties. Besides the data in Tables 14 and 15 and in a review [79] there is some information on the effect of the structural parameters of networks on the properties of epoxide polymers [81,96,110,111], polyurethanes [108], copolymers of divinyl oligomers with monovinyl monomers [112,113], and several other network polymers [114]. However, it is difficult to establish an unambiguous relation between the structure of the initial oligomers and the properties of the network polymers, since the properties especially of dense-network polymers are often determined in decisive measure by other factors besides the network density. Among these are the conditions of formation of the polymers, which determine their morphological structure, shrinkages in volume resulting in the appearance of internal stresses, the test conditions, the presence of fillers, etc. Many properties of network polymers depend more on their physical state than on the density of chemical links in the polymer network. In this connection more experimental data must be accumulated on the formation of network polymers and their properties with careful control of the structure of the initial oligomers and the parameters of the resulting networks.

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