Translated from *Uspekhi Khimii*, **45**, 1817 - 1841 (1976) U.D.C. 541.61

Some Aspects of the Theory of Gel Formation in Reactions of Polyfunctional Compounds

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Various theories of gel formation by three-dimensional polymers derived from polyfunctional monomeric and oligomeric compounds, ranging from the theory of Carothers and Flory to the modern theories of Gordon, Kilb, Frisch, Bruneau, and Stepto, are discussed. The role of kinetic, thermodynamic, and structural factors in processes leading to the development of the gel fraction are analysed. The reactions involving polyfunctional compounds are classified, and the fundamental scheme of the three-dimensional reaction leading to gel polymers is described taking into account the altered ideas and the new criteria which have been established. The conclusions reached at a symposium on gel formation processes in polymers held in England in 1974 are examined.
The bibliography includes 149 references.

CONTENTS

I. Classical concepts and laws of functionality 931
II. The role of applied mathematical methods in the further development of the theory 934
III. The gel fraction and development of the structural and thermodynamic aspects of the gel formation theory 937
IV. Conclusion 942

...The theory and its scope are at the half-way point between chemists, physical chemists, and biologists on the one hand, and mathematicians on the other.
C.Bruneau, Am. Chim., 1, 271 (1966)

I. CLASSICAL CONCEPTS AND LAWS OF FUNCTIONALITY

The ability of a polymeric system to be converted irreversibly into an infusible and insoluble state, i.e. to promote gel formation†, has been used for a long time in various branches of industry. It is not therefore surprising that, ever since the first steps were taken in polymer chemistry, numerous applied and theoretical studies have been devoted to the phenomenon of gel formation in three-dimensional polycondensation and polymerisation and to its interpretation and characteristics.

The role of the functionality of compounds (i.e. the number of functional groups per monomer molecule) was noted and analysed before all other factors exerting the most marked influence on the development of the gel formation process in polymers during three-dimensional polycondensation. In 1932 Bozza [1] characterised for the first time the dependence of the degree of reaction of Glyptal polymers, including the degree of condensation at the instant of gel formation (the gel formation point), as a function of the functionality of the system.

This study stimulated the development of ideas about gel formation in polymers. It had a definite influence on Carothers, who presented evidence in his 1935 paper "Polymers and Functionality" [2] that the dependence of the degree of reaction on functionality in gel formation by polymers is of a general type. Carothers' initial postulates (1) that the onset of gel formation is due to the formation of infinite three-dimensional (spatial) networks and (2) that the importance of the intramolecular cyclisation of the initial compounds is negligible determined for a long time, together with subsequent studies by Flory, a unilateral development of the theory of gel formation. Perhaps the most complete and at the same time briefest assessment of Carothers' "classical" ideas is given in the monograph of Cotter and Matzner [3]: "It is interesting to speculate whether Carothers' work, being so basic and all-encompassing, served to inhibit subsequent creativity in synthetic polymer chemistry. Frequently, when rapid, broad studies are made in a field of scientific endeavour, they can serve as unintentional barriers to further advances... The wide scope that is only now emerging for ring-forming polymerisations of polyfunctional monomers to linear polymers is indeed remarkable. Its appearance may well have been delayed by the functionality laws of polymer science".

The derivation of the system of Carothers' fundamental equations, subsequently called the "law of functionality", is based on a simplified analysis of the formation of a polymer molecule from N_0 monomer molecules with an arithmetical mean functionality f'. In the absence of intramolecular reactions, the combination of each two monomer molecules by a single covalent bond (i.e. as a result of the disappearance of two functional groups) corresponds to an overall decrease in the number of molecules equal to $2(N_0-N)$, where N is the number of molecules in the system after the attainment of a particular degree of reaction. Having referred the number of groups which have reacted to their initial number, Carothers arrives at the degree of conversion at any polycondensation stage before the attainment of the gel formation point:

$$P=2(N_0-N)/N_0f. \quad (1)$$

† In the present review the terms "gel formation", "micro- and macro-gels", "the point of gel formation", "the theory of gel formation", "the gel formation period", "the sol fraction", etc. refer to the description of the formation of polymers with a three-dimensional macromolecular structure produced only as a result of covalent bonds on condensation or polymerisation of polyfunctional compounds.

Putting $N_0/N = X$ (the number-average degree of polymerisation), we obtain

$$P = 2/f - 2/Xf, \quad (2)$$

whence

$$X = \frac{1}{1 - Pf/2}. \quad (3)$$

Assuming that $X = \infty$ at the gel formation point, Carothers defines the conversion at this point in the following way:

$$P_{cr} = 2/f. \quad (4)$$

Analysis of the above equations shows that their application is rigorously limited by the following condition: none of the functional groups of the monomer or the polymer molecule is involved in the formation of any cyclic groups or fragments. The unreality of this condition was noted already in the course of the first discussion after Carothers' report on this subject. Using the model of a three-dimensional process illustrated in Fig. 1, Houwink[4] showed that Eqns. (1) and (2) are invalid. According to Houwink, when a polymer molecule A with functional groups X has reacted with another molecule B as a result of the interaction between groups *1* and *4*, then, following the further development of their process, for example on interaction between groups *2* and *5* or between groups *3* and *6*, there is no increase in the degree of polymerisation $X = N_0/N$, since the number of molecules N does not decrease. Consequently the degree of conversion actually increases, while according to Eqns. (1) and (2) it should have remained constant. Furthermore, Eqn. (3) loses its physical significance for conversions in excess of $2/f$, when the number-average degree of polymerisation becomes negative.

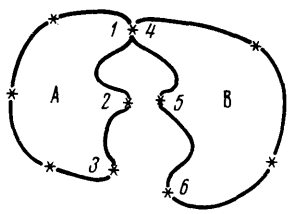


Figure 1. Houwink's model of the intramolecular cyclisation process[4].

Later it was shown[5] that the number-average degree of polymerisation at the gel formation point is extremely low, as a result of which Eqn. (4) is also contradictory.

The specific nature of the initial postulates of Carothers' theory has now also become evident. Various causes and mechanisms of gel formation in polymers, according to which the formation of an infinite three-dimensional macromolecular network is by no means a necessary criterion of this phenomenon, will be examined below. As regards the second postulate, neglect of intramolecular cyclisation processes in the macromolecular system was not only unjustified, as stated above, but actually became a definite obstacle to the development of theoretical ideas.

A more fundamental mathematical approach to the analysis of gel formation in polymers was achieved a few years later in Flory's studies[6-9], where the statistical theory of probability was first applied to three-dimensional polycondensation. It is striking that, like Carothers, Flory believes that the onset of gel formation is caused by the generation of "infinite" spatial polymeric structures. For the statistical analysis and derivation of fundamental relations, Flory employed the diagram describing the formation of a three-dimensional macromolecule illustrated in Fig. 2*a*. The same model has been frequently used by other investigators in the form of modifications 2*b* and 2*c*. Considering the probability that any chain selected at random from the polymer mixture, for example the chain in sphere *1* in Fig. 2*a*, is part of an infinite three-dimensional molecule, Flory bases his treatment on two hypotheses which he adopted *a priori*. The first is that all processes leading to the formation of cyclic groups or fragments are unlikely and are therefore disregarded. The second hypothesis is that all the reactive groups have the same reactivity throughout the process regardless of their position. Thus having placed at the head of his theory the same postulates as in Carothers' treatment, Flory actually examined one of the specific instances of three-dimensional polycondensation, namely the instance where only statistical relations and not chemical relations are dominant.

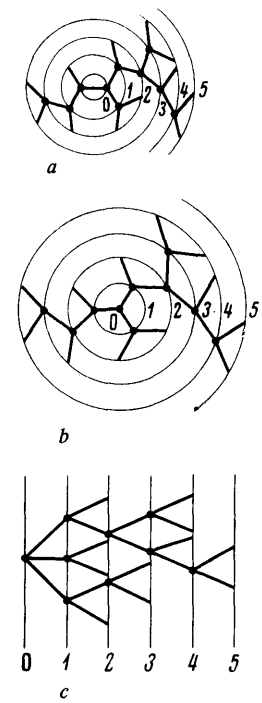


Figure 2. A topological scheme of the development of a three-dimensional polymerisation reaction: *a*) Flory's model[6]; *b*) the "growing tree" model[36]; *c*) the cascade process model[36]. The numerals represent the generations.

One of the most important parameters of Flory's theory is the branching coefficient α, which he defined as the probability that one branching component (the monomer with $f > 2$) becomes bound as a result of the reaction with

another branching component. The author identified the onset of gel formation in polymers or the gel formation point with the critical conditions for explosion in certain gas-phase reactions, having shown that the overall critical value of α can be represented thus:

$$\alpha_{cr} = \frac{1}{f-1}, \quad (5)$$

where f is the arithmetical mean functionality of the branching components only [for example f for a mixture of two moles of glycerol, one mole of pentaerythritol, and give moles of dicarboxylic acid is $(2 \times 3 + 1 \times 4)/3 = 3.33$]. On the other hand, the statistical method leads to a dependence of α on the degree of condensation P:

$$\alpha = rP_A\rho/[1 - rP_A^2(1-\rho)] = P_B^2\rho/[r - P_B^2(1-\rho)], \quad (6)$$

where r is the ratio of the total number of groups A to the total number of groups B in the system, ρ is the ratio of the number of groups A belonging to polyfunctional monomers to the number of groups A in the system, and P_A and P_B are the degrees of conversion with respect to either groups A or B [Eqns. (5) and (6) were derived by Billmeyer[5]]. Evidently in the calculation of α_{cr} it is necessary to know only the functionality of the reactants. Using Eqn. (6), it is easy to calculate the degree of conversion in the reaction at the gel formation point of the polymers when α_{cr} is known.

It was found that Flory's theoretical ideas made it possible to describe the onset and development of gel formation in any polycondensation system without resorting to experiment. This appeared to be very promising, particularly from the standpoint of the practical application of the theory.

Table 1. The degree of conversion P, the branching coefficient α, and the functionality f in systems of polyfunctional monomers (according to Flory[6-9] and Carothers[2]).

Monomer system*	According to Flory			According to Carothers	
	f	α_{cr} from Eqn.(5)	P_{cr} from Eqn.(6)	f	P_{cr} from Eqn.(4)
$2A_3 + 3B_2$	3.00	0.50	70.71	2.40	83.33
$A_3 + B_3$	3.00	0.50	50.00	3.00	66.66
$A_4 + 2B_2$	4.00	0.33	57.73	2.66	75.00
$3A_4 + 4B_3$	3.42	0.41	41.17	3.42	58.33
$A_4 + B_4$	4.00	0.33	33.33	4.00	50.00

*The subscripts correspond to the number of groups per molecule.

Emphasising the generality of the relations obtained, Flory also noted that the conversion in the reaction at the gel formation point P_{cr} is independent of process conditions such as temperature, catalyst, reactant concentrations, etc.[6] Table 1 presents the characteristics, in terms of the Flory and Carothers theories, of a number of heterofunctional condensations in which the ratio of the interacting functional groups A, and B is 1:1, i.e. $r = 1$ in Eqn. (6). It follows from the data in Table 1 that the degree of conversion at the gel formation point, calculated from the Carothers theory, is greater than the value calculated from the Flory theory, which is due to the incorrect estimate of X in Eqn. (2), as a result of which the second term assumes a value close to zero and Eqn. (2) assumes the form of Eqn. (4).

Flory compared his theoretical treatment with the comparatively few available experimental data. The scant experimental material at that time and possibly also pure chance led to the adoption of polyesters as a practical model. Comparison shows (Table 2) that the discrepancies between theory and experiment are comparatively small, but exceed the permissible deviations in theoretical studies[6-9]. Although the author attributes the observed discrepancies to neglect of intramolecular cyclisation reactions in the calculations, he excludes them from the first phase of polycondensation (before the instant of the gel formation), evidently because they are inconvenient for mathematical treatment, and transfers them wholly to the second stage—beyond the gel formation point. This is illustrated by the course of the analysis itself and by the working scheme (Fig. 2). According to the initial postulate of the Flory theory, gel formation is a process involving the growth in the reaction mixture of giant macromolecules with a three-dimensional structure. The latter are none other than a statistical set of cyclic fragments linked in space. As can be seen from Fig. 2, Flory analyses the probability of the formation of an infinitely large branched (but not cross-linked) polymer, which suddenly begins to undergo three-dimensional cyclisation only at the gel formation point, and not the probability of the formation of such polycyclic *macroensemble*.

Table 2. The experimental and calculated degrees of condensation and the branching coefficients at the gel formation point (according to Flory) for systems comprising tricarballylic acid, diethylene glycol, and dicarboxylic acids.

No. of expt.	P_{cr}		α_{cr}		No. of expt.	P_{cr}		α_{cr}	
	expt.	calc.	expt.	calc.		expt.	calc.	expt.	calc.
1	0.911	0.879	0.59	0.50	3	0.894	0.843	0.62	0.50
2	0.939	0.916	0.59	0.50	4	0.990	0.995	0.58	0.50

Stockmayer and Weil[10] subsequently attempted to test experimentally this artificial subdivision—into a polymer branching process alone in the first stage and mainly the formation of a three-dimensional macromolecular network structure in the second. In their attempts to refine the fundamental equations of the Flory theory, Stockmayer and Weil[10] and subsequently Weil[11] diluted the reaction mixtures with inert solvents. This method made it possible to take into account quantitatively the specific contribution of the intramolecular cyclisation reactions. Having determined the gel formation point in highly dilute mixed solutions of adipic acid and pentaerythritol, where intramolecular cyclisation should have played a significant role, Stockmayer subsequently proceeded to more concentrated solutions. Having observed that the graphical relation between P_{cr} and the volume of the reaction mixture is a straight line, he extrapolated it to zero volume and obtained values of P_{cr} in good agreement with those calculated by Eqn. (6).

Numerous cyclisation reactions of various monomers not only in dilute solutions but also in reaction media without solvents are now known[12]. In the light of the

accumulated experience, the relation which Stockmayer obtained by extrapolation is characteristic of the given specific instance only.

Summarising the initial period of the establishment of a theory of gel formation in polymers, we may note that, as a result of the development of the first theoretical ideas based on the few experimental data available at the time, a number of characteristic relations, illustrated graphically in Figs. 3–5, became generally adopted in 1940 to 1945.

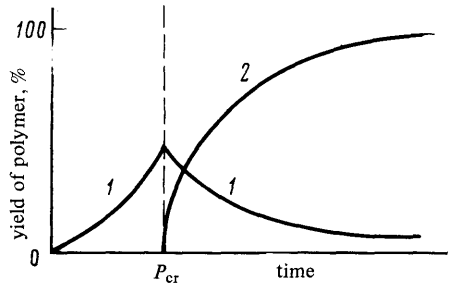


Figure 3. The yield of soluble polymeric products (curve *1*) and of the gel fraction (curve *2*) in the three-dimensional condensation of polyfunctional compounds.

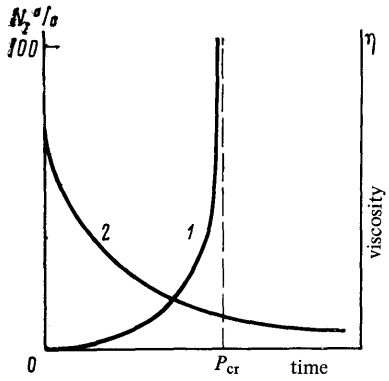


Figure 4. Variation of the viscosity of the products η (curve *1*) and of the content of functional groups in the system N (curve *2*) during condensation.

It follows from the graphs that the gel formation point of a polymer was adopted as the turning point in the reaction, dividing the process into two stages. The formation of oligomeric products is characteristic of the first stage. Their interaction with one another and with the initial monomers is responsible for the appearance of branched macromolecules, whose yield increases during the condensation, reaching a maximum at the gel formation point (Fig. 3, curve *1*). A gradual decrease of the sol fraction because of the involvement of the polymer molecules in the formation of the spatial network, i.e. the increase of the content of the gel fraction in the reaction system, is characteristic of the second stage of the condensation (Fig. 3, curve *2*).

It follows from the data in Fig. 4 that only a slight increase of the viscosity of the products is typical for the first reaction stage, but, as the reaction approaches the gel formation point, the tendency towards a sharp rise in the kinetic viscosity curve is observed (curve *1*). Diffusional factors play an increasing role at this stage and the curve describing the consumption of functional groups becomes less steep and approaches an asymptote (curve *2*).

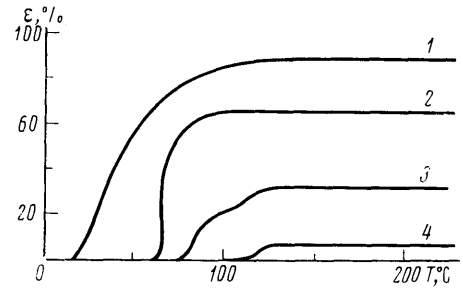


Figure 5. Variation of the thermomechanical properties of polymers beyond the gel formation point with increase of the density of cross links (a higher number of the curve corresponds to a higher density of cross links); ϵ —modulus of elasticity.

Beyond the gel formation point, it is more difficult to follow the conversion in the reaction on the basis of the content of functional groups. However, the change of the physicomechanical characteristics of the gel fraction makes it possible to infer a further development of the process. Thus an increase of the modulus of elasticity and an increase of the glass point (Fig. 5) as well as changes in other characteristics correspond to an increase of the density of cross links in the growing network owing to the continuing polycondensation within the gel particles. However, even for high degrees of conversion of the polymeric system into a gel, it is possible to extract from the latter a soluble fraction (the sol fraction), the molecular weight of which is low.

The above mechanism of the three-dimensional polymer formation process, whose arose as a result of the period of "classical" studies and ideas, was used subsequently by many investigators as the fundamental model. The main component of this model, the gel formation theory, was elaborated and adjusted. However, as long as the ideas and postulates underlying it remained unchanged, further progress was bound to be limited.

II. THE ROLE OF APPLIED MATHEMATICAL METHODS IN THE FURTHER DEVELOPMENT OF THE THEORY

A characteristic feature of the subsequent development of the theory was a comprehensive analysis of the known relations governing the process in conjunction with various mathematical methods. The mathematical procedures and approaches would merit only a simple enumeration if they did not reveal at the same time "latent" relations and characteristics in the formation of macromolecules with a three-dimensional structure, demonstrating thereby the

primitive nature of the "classical" gel formation mechanism as well as the importance of a wide variety of factors which had been neglected previously.

In the course of the study of the mathematical models of three-dimensional polycondensation, the complexity and many-sided nature of this process, the role of the activity of functional groups and their distribution in the molecule, the importance of various characteristic macrochains, the structural forms of oligomers and polymers, etc., became increasingly clear. At the same time there was a growth of the complexity of the mathematical expressions describing particular characteristics.

However, instead of carrying out specific chemical tests of the relations obtained, investigators moved further into the region of purely mathematical manipulations. Thus Flory[6] described gel formation in terms of the model of a branching process (based on Semenov's theory[13] developed in the 1930s and describing the critical conditions in the explosion in certain gas-phase reactions) in combination with a statistical method of calculation. Stockmayer employed another analytical method[15-17] adopted from the theory of non-ideal gases[14]. Applying this method, he used the analogy between the phase transition from gases to liquids and the transition from the liquid soluble polymer at the gel formation point to the insoluble and infusible macrogel. The method yielded more general expressions for the fundamental characteristics of three-dimensional processes and made it possible to consider cases which Flory was unable to solve[15-17]. In particular, Stockmayer analysed the copolymerisation of vinyl and divinyl monomers, requiring a special approach, and found a general expression for the description of the "critical state" of the system. He also attempted to take into account the erroneous assumptions of the "classical" theory, namely to determine the contribution of the processes involving the formation of cyclic fragments in the molecular chains before the gel formation point[10].

Gordon[18] and Good[19,20], who applied the methods used for the description of cascade processes[21,22], found a greater scope for the mathematical analysis of polymerisation processes. The cascade theory or the theory of stochastic processes was a more advanced and convenient instrument compared with previous theories. The relation which Good found between the number-average degree of polymerisation DQ_w and the branching coefficient α has the following simple form:

$$DQ_w = \frac{4 - \alpha - \sqrt{4\alpha - 3\alpha^2}}{3\alpha - 4 + 3\sqrt{4\alpha - 3\alpha^2}}.$$

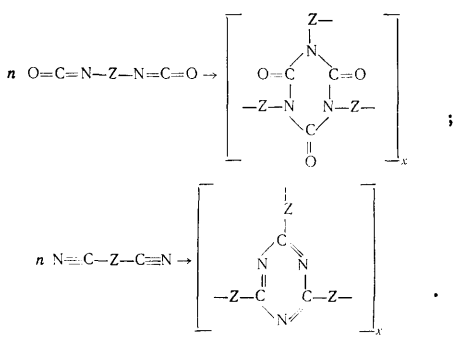
Furthermore, Good tabulated the calculated values of DQ and α for monomer systems with a tetrafunctional branching unit.

Thus the studies of Gordon and Good permitted an advance in the methods of mathematical analysis in this field. The cascade method was developed further a few years later in Whittle's studies[23,24]. Having examined the problems of the formation of bonds between reacting species with functional groups having different reactivities as well as the probability of their aggregation, Whittle extended the analytical method to more realistic but also more complex cases of the aggregation of macromolecular species with groups having different reactivities. His mathematical expressions were not, unfortunately, sufficiently simple and complete for practical applications.

Studies by Case[25-28] and Giacomo[29] played a major role in the progress in the physicochemical description of the gel formation process. Bearing in mind the primitive nature of Flory's mechanical model of the monomer, as an indefinite particle with functional groups, these workers took the first step on the way to the analysis of a monomer model with a definite structure, attempting to take into account the influence of the symmetry of the disposition of the functional groups in the molecule. This was the first attempt at a mathematical approach to the true behaviour of real compounds in three-dimensional processes. Despite the fact that Giacomo and Case took into account only one of the numerous characteristics of monomeric compounds influencing the gel formation process, namely the asymmetry of the distribution of the functional groups in the molecule manifesting different reactivities, they noted significant differences in the behaviour of these more realistic models compared with Flory's model.

Improvement of the mathematical procedures in the analysis of three-dimensional polycondensation led in its turn to the consideration of more complex and realistic models. Erlander and Fench[30], Tang Au-Chin[31], and Allen[32] achieved a mathematical description of the three-dimensional polycondensation of monomers whose molecules contain various functional groups or identical groups with different reactivities.

The studies of Fukui and Yamabe[33-35], devoted to the mathematical analysis and description of at first sight seemingly highly specific instances of three-dimensional processes, were published in 1960–1964. In the development of the synthesis of thermoreactive resins, the authors considered and analysed the formation of a three-dimensional polymer from polyisocyanates, polynitriles, and certain other monomers:



Apart from the isocyanuric and triazine cyclic *macroensembles* illustrated above, the polycyclic hexadihydrotriazine, boron oxide, and other polymers have similar structures.

It follows from the reaction equations that a branched cyclic structure is formed from the very beginning in such processes, and is converted in the course of further development into a three-dimensional structure. The formation of rings is the main process in this case and must be described by the main equation and not with the aid of average corrections, as has been done previously by Stockmayer, Case, and others. Using the old statistical methods, Fukui and Yamabe arrived at an expression describing the critical state in such systems:

$$\alpha_{cr} = \frac{1}{2(f-1)}.$$

Unfortunately due attention was not subsequently devoted to the mathematical analysis of polycondensation occurring with simultaneous and regular cyclisation and branching in the macromolecular chains.

The specific features of the formation of various chemical bonds, intermolecular and intramolecular, as well as the characteristics of the macromolecular structure

generated were analysed some years later by Bruneau [36-40]. His studies were, as it were, a logical continuation, but at a higher mathematical level, of the research of Fukui and Yamabe. Bruneau examined the changes in a polyfunctional system during the reaction from two standpoints—structural and stochastic. The structural or topological aspect revealed an *ensemble* of the possible conformations of the intermediate products in the form of a Konig graph [41], while the stochastic approach made it possible to describe the chemical reaction at each instant in the form of a statistical distribution of the chemical bonds formed between the reactive molecule. The stochastic analysis led to the isolation of two types of systems of polyfunctional compounds, the real existence of which is evident: (1) the homogamous system in which a bond is formed between any pair of species (molecules) and (2) the heterogamous system where chemical bonds are formed in a specific manner. Bruneau did not insist categorically on the universality of the relations obtained, bearing in mind apparently the wide variety of factors which are difficult to take into account and which have different effects (depending on the type of reactants) on the critical parameters of gel formation. In concluding one of his communications [40], he emphasises that one can determine with the aid of his equations the critical parameters of gel formation only subject to the condition "that the mechanism of the reaction of polyfunctional monomers is known, that the formation of the three-dimensional structure satisfies the conditions of the theoretical method, and that the technique of the determination of the sol–gel transition is sufficiently sensitive and accurate".

Claiming that the gel formation theory is at the half-wave point between physics, chemistry, and biology, on the one hand, and mathematics, on the other, the author [36] endeavoured to demonstrate to workers in the former field the importance of the graph theory in the determination of the statistical structure of macromolecular compounds and to stimulate workers in the latter field to turn their attention to a particular branch of chemistry, with its topological possibilities in the study of the structure of polymers, which is exceptionally important in practice.

Apart from the above aspects of the study of the phenomena of gel formation by means of various mathematical approaches, it is also necessary to consider specifically the kinetic method of treating the problem. A number of workers supporting the kinetic approach in this field believe that the foundations of the statistical methods have been by no means adequately investigated and that this precludes *a priori* inferences about the possibility of applying it to calculations on processes of any specific type [42,43]. In contrast to the statistical method, based on the determination of the probability of the formation of macromolecules of a particular size and structure, the kinetic analytical method makes it possible to discover relatively general procedures for the calculation of the fundamental statistical characteristics of the distribution and to establish relations which determine the conditions governing the onset of gel formation in polymers.

Gordon and Scantlebury [44], who, among others, pioneered the kinetic approach to the study of gel formation in polyfunctional systems, used the statistical kinetic method to describe the condensation of adipic acid with pentaerythritol and tri(hydroxymethyl)ethane. In their assessment of the non-kinetic Whittle [23,24] and Bruneau [36] methods, these authors describe them as highly unrealistic statistical procedures, because they are not based on configuration statistics. Gordon and Scantlebury justified the proposed model for the gel formation process by solving equations involving functions of the ratio of carboxy- and hydroxy-groups. They found that at the beginning of gel formation about 10% of all the ester linkages formed are intramolecular. Such a high percentage contribution of the intramolecular cyclisation reactions threw doubt on the validity of models of the Carothers–Flory type (see Fig. 2), although the authors themselves did not discuss problems of this kind.

A very detailed mathematical description of the kinetics of the condensation of polyfunctional monomers was achieved recently by Pis'men and Kuchanov [42,45,46]. Using the reaction of glycerol with dicarboxylic acids as an example, they carried out calculations on the kinetics of the polycondensation of monomers containing reaction centres of different activities and obtained an analytical solution to the kinetic equation relating the molecular weight distribution of the products in the general case. These investigators also proposed for aromatic monomers a kinetic polycondensation mechanism in which the activity of the functional groups changes in the course of the reaction and showed that such instances cannot be described by a statistical method. The solution of the differential equations proposed [42] for the generating functions is, however, fairly difficult in most cases [47]. The application of this type of method to the description of condensation is further limited by the instant of gel formation.

In order to simplify the kinetic analytical method and the final equation, Irzhak [47] proposed a combinatorial method combining the familiar procedures and the criteria of the statistical method. In those cases where the detailed mechanism of the condensation process is known, he introduces the time characteristics of the reaction taking place. However, together with the statistical approach, the author introduced into his treatment the earlier assumptions of the statistical theory.

Summarising in 1968 the progress achieved in the mathematical description of polymerisation processes accompanied by gel formation, Gordon and Scantlebury noted [48] in the first place the importance of employing kinetic factors in the analysis (including the so called substitution effect [49], which determines the change in the rate of formation or dissociation of bonds during the reaction) and, in the second place, the greater attention paid by mathematicians to the problem of intramolecular cyclisation [50-52]. The analytical description of this simultaneous process still constitutes an unsolved problem [43,56], despite the continuing elaboration of the method [53-55].

In connection with the improvement of the mathematical procedures for the analysis, one can also expect much interest in other secondary reactions, which are no less important than intramolecular cyclisation. The influence of secondary reactions on the fundamental gel formation parameters and the properties of polymers has been frequently noted for many known classes of polymers [57]. The role of such processes is particularly important in the synthesis of elastomers [58], where the contribution of secondary reactions depends to a large extent on the conditions and increases with the degree of conversion of the monomer. One of the simplest cases of the analysis of secondary reactions—chain termination in the development of three-dimensional structure—has been examined in a study [59] where use was made of the theory of branching processes [18-21]. The mathematical description of three-dimensional polycondensation with simultaneous allowance for at least two similar factors, for example of chain transfer and cyclisation reactions, has not so far been achieved.

The characteristics of the development of the sol fraction in structured systems still require a mathematical treatment; certain variants of the analysis of its formation in conjunction with the series of assumptions and simplifications used previously have been examined [60-63]. The models of the development of the sol fraction in the studies quoted above differed little or not at all from the models proposed previously by Carothers [2] and Flory [6-9] (Fig. 2). For this reason, the studies concerned with the statistical mechanics of polymers with the star structure [64-66] adjoin this field in the mathematical analysis of three-dimensional processes.

The updating of the mathematical procedures for the investigation of three-dimensional polycondensation together with the development of synthetic methods had a further positive aspect, namely it helped to discover the error of certain assumptions and the final equations of the statistical method forming part of the procedures inherited from the 1930s. Andrianov and Emel'yanov [67,68], Pis'men and Kuchanov [42], and Raspopova et al. [43] showed that the logical and mathematical errors have been caused by the invalid application of certain procedures of the statistical method, which are in essence inapplicable to the description of chemical processes of this kind.

The latter may be illustrated by the studies of Bruneau [38,39] and certain other investigators [69-73] who demonstrated the formal contradictions arising from the "classical" theory of gel formation in a system of polyfunctional compounds. Whiteway et al. [69-71] noted with astonishment that the errors made by Flory in his first studies dealing with three-dimensional polycondensation have been frequently repeated by other investigators in the course of several decades.

III. THE GEL FRACTION AND DEVELOPMENT OF THE STRUCTURAL AND THERMODYNAMIC ASPECTS OF THE GEL FORMATION THEORY

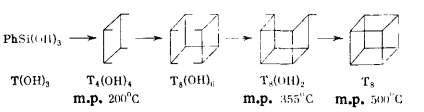
The concept of the "gel formation point" in a system of reacting polyfunctional compounds as the instant of the appearance in the reaction mixture of infinite polymeric three-dimensional structural networks (more correctly networks bounded by the walls of the reaction apparatus) was first introduced by Carothers [74] in 1931. Several years later, Staudinger [75-77] and then Flory [6] completed the formulation by defining a necessary condition for gel formation—the infinite growth of macromolecules in three directions. Thus, at the start of the development of polymer chemistry, three of the greatest authorities closely related the concept of the "gel" or the gel fraction to two factors: (1) the three-dimensional or spatial structure of macromolecules and (2) the "infinite" molecular weight.

Whereas the structural factor, which determines the most characteristic properties of the gel formation—its infusibility and insolubility in all solvents (not causing the dissociation of covalent linkages)—has not so far aroused any doubts, it was subsequently discovered that the necessity for the second factor does not by any means apply to all types of three-dimensional polymers.

The obligatory requirement of the formation of infinitely large gel macromolecules, in fact of a single macromolecule, was justified initially by the idea that a three-dimensional gel can be formed either by the cross-linking of macromolecules with a linear structure formed beforehand or via the family tree [multifunctional branching] mechanism proposed by Flory [6] (Fig. 2). Polymeric gels synthesised in accordance with the first variant did indeed correspond to all the factors mentioned above. This pathway is characteristic of the synthesis of elastomers and rubbers—polymeric materials subjected to some type of treatment in the last stage of their synthesis, for example by irradiation. A mathematical analysis of polymer-analogue reactions of this kind has been carried out by a number of investigators [78-81].

The ideas concerning the development of the process via the family tree mechanism with conversion of the branched macromolecules at the gel formation point into a three-dimensionally cross-linked polymer changed appreciably following the accumulation of experimental data. These changes were a consequence of advances in the synthetic methods of polymer chemistry and were determined primarily by the development of ideas concerning the three-dimensional processes proceeding via the microgel formation stage.

Despite the fact that studies devoted to the "embryonic" development of microgel molecules in processes of the above type are at present in the initial stage of their development, fairly thoroughly investigated pathways to the synthesis of a number of polycyclic homologues, which to a certain extent can serve as a model of developing three-dimensional structures, have already been described in the chemistry of polyorganosiloxanes for example. Thus the homocondensation of trihydroxyphenylsilane yields, apart from other polycyclophenylsiloxanes [82], a series of molecules with increasingly complex structures [83,84] (T denotes the trifunctional phenylsiloxane unit):

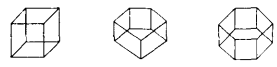


In the series of homologues illustrated, the solubility decreases and the melting point increases as the three-dimensional structure is formed and becomes more complex.

The influence of factors such as the flexibility of the molecular chain between the units of the polymer network on the capacity of the system for gel formation has been investigated in a number of studies by Andrianov and Emel'yanov [85-88] in relation to the three-dimensional polycondensation of tetrafunctional acid esters with tri- and tetra-hydric alcohols, various glycols, and diamines. The gel formation parameters determined in the reaction of oligomeric compounds (the critical degree of reaction and the critical branching coefficient) showed that, with increase of the length of the chain between the units of the polymer network, the instant of the appearance of the gel fraction is displaced towards increasing degrees of reaction, i.e. in the direction of the formation of more complex molecular structures. A similar relation was observed with increase of the flexibility of the chains between the units of the polymer network owing to another factor—the chemical nature of the macromolecules [67,68].

Among other structural factors directly responsible for the onset of the development of gel formation, the appearance of an additional number of units in the polymer network owing to the intertwining of the chains (entanglement) is important [89]. Despite the complexity of the analysis of this type of problem, the formation of hooking units can be followed, for example, by analogy with the method of Gartsman and Gorelik [90] or other workers [91].

A characteristic feature of molecules with a three-dimensional structure, namely the dependence of the melting point on the flexibity (elasticity) of the three-dimensional skeleton, has been traced also in another homologous series (polyphenylsilsesquioxanes) [84]:



T_8, mol. wt.1052 m.p. 500°C — T_{10}, mol. wt.1290 m.p. 418°C — T_{12}, mol. wt.1548 m.p. 385°C

Here the melting point decreases from T_8 to T_{12}, i.e. with increase of the elasticity of the lattice owing to the increase of the dimensions of the component rings.

Despite the logical incompleteness of the homologous series illustrated (the lack of the simplest model species which is built up to give a more complex three-dimensional lattice and which loses in this process both its fusibility and solubility in all solvents), certain purely structural characteristics can be traced in these instances: (1) the increase in the complexity of the molecular structure of the product during the reaction from dimeric to trimeric with its subsequent development is responsible for the gradual loss of solubility by the reaction products and for the increase of the melting point. (2) The loosening of the three-dimensional structure, i.e. the decrease of the number of bonds per unit volume and the consequent increase of the flexibility of the lattice, leads to the reverse effect—the increase of the solubility of such macromolecules and the decrease of their melting point.

In their study on the development of a theory of gel formation in the chemistry of alkyd resins, Bobalek et al. [92] proposed in 1964 a model for the process different from that of Flory (Fig. 6). This model differed in the first place by the fact that it actually altered the earlier concept of the gel formation point as the "critical instant resembling explosion in certain gas-phase reactions". It follows from Fig. 6 that the author distinguished two gel formation points. The first corresponds theoretically to the instant of the appearance in the reaction mixture of the first particles with a three-dimensional structure characterised by infusibility and insolubility. At this moment, the system is virtually homogeneous (there are only a few macromolecules with a three-dimensional structure) and, according to classical ideas, is not in a critical state. The second gel formation point corresponds to a much later reaction stage—the conversion of the fluid reaction mixture into an elastic polymer. In the author's terminology, this "physical" instant of gel formation is identical in terms of some of its characteristics to the established concept of the "classical" gel formation point (the loss of fluidity, fusibility, and solubility), but at the same time it exhibits fundamental differences—the gel particles appear and develop in the reaction mixture much earlier. Thus the hitherto clear-cut term "gel formation point" was transformed into the indefinite "gel formation period".

Studies by the Soviet polymer school later demonstrated, in relation to polyurethanes, the desirability of replacing the concept of the "gel formation point" by the more realistic "gel formation region" [93]. Electron microscope, molecular weight, and molecular probe studies by Lipatova, Lipatov, Zubko, and others in the course of the formation of polyurethanes with a three-dimensional structure [94-99] made it possible to demonstrate the appearance, already in the early stages, of globular formations with a greater or lesser degree of order in the supermolecular structures as a function of the number and positions of hydrogen bonds, the length and chemical nature of the chain in the initial compound, the reaction coditions, etc. The development of gel formation has then the properties of interglobular cross-linking and cross-linking within the globular structures. The two processes are interrelated and each may be dominant under certain conditions. The formation of the first sections of the microgel in the early stages does not in fact have any appreciable influence on the properties of the system (the latter remains fusible and fluid) but, as the microgel particles accumulate, there is a gradual transition from homogeneous to microheterogeneous conditions and then to macroheterogeneous conditions [100].

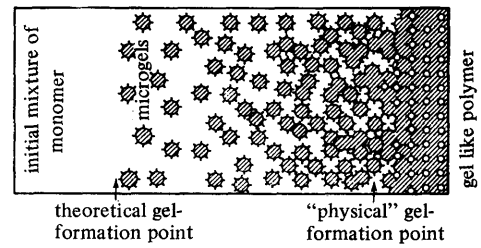


Figure 6. Schematic illustration of the formation of Glyptal polymers according to Bobalek et al. [92]

As in the study of Bobalek et al. [92] quoted above, two gel formation periods may be distinguished in the formation of polyurethanes. In the first stage network microgel particles are generated and their number increases. In the next stage, the main process involves the linking of the microgel particles as a result of which the system loses its fluidity and fusibility [98]. The indeterminate and diffuse nature of the boundaries of individual stages (homogeneity–microheterogeneity and microheterogeneity–macroheterogeneity) did indeed expand the "classical" definition of the gel formation point to the gel formation region or period.

The tendency to study the problems of gel formation in a number of investigations during 1960–1970 [101,102] promoted a more detailed description of polymerisation processes, including transitional stages in microheterogeneous states. There was an increase in the publication of experimental data in the periodical literature, showing that macromolecules, oligomers, or monomers do not exist in an isolated state even in dilute solutions. According to the investigations of Lipatova and Proshlyakova [103], Kargin, Fakirov, and Bakeev [104,105], as well as other workers [106], the primary associated species, in the form of packets or aggregates combined in definite supermolecular structures, constitute the initial forms of the future microgel particles [107]. The involvement of the microgel particle formation stage in the three-dimensional processes was demstrated during these years for various types of polymers: polyacrylates [107-109], polyesters [92,109], polyurethanes [93-100], polyepoxides [110,111], etc. Ultimately it became evident that the specific contribution of the three-dimensional processes leading to spatial polymers via the microgel formation stage is no less significant than the contribution of the three-dimensional processes involving the formation of linear and branched macromolecular structures. In this sense, the model of a three-dimensional process proposed by Bobalek et al. becomes general.

The new mechanism has not been examined theoeretically in conjunction with a mathematical description.

The application of various physical methods to the study of three-dimensional reactions at the stages corresponding to the transition from homogeneous to microheterogeneous conditions made it possible to determine in many instances the size of the microgel particles [93,109,110].

The radius of the average globular formations in structured polyurethanes varies between 85 and 500 Å according to Lipatova's data [93]. With decrease of the molecular weight of the initial oligomer or with increase of the reaction temperature, the size of the nuclear gel particles then decreases, other conditions being equal.

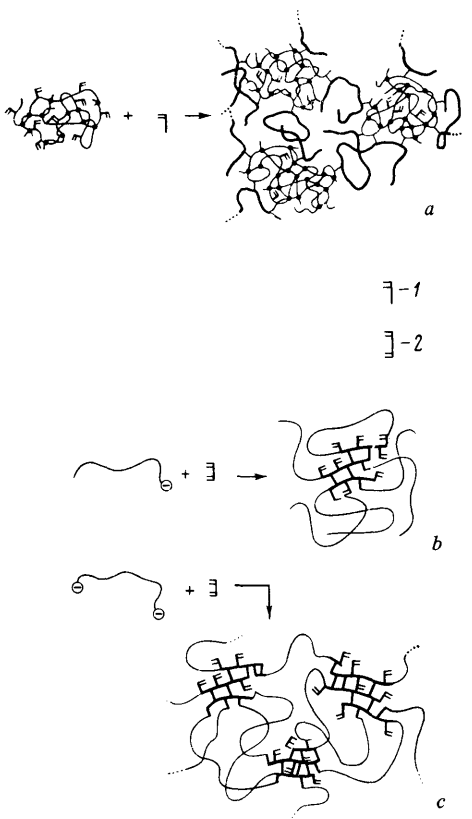
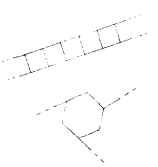


Figure 7. Schematic illustration of the directed "microgel" synthesis of three-dimensional polymers according to Funke [112] and Rempp [113]: *a*) reaction with participation of the microgel as the cross-linking agent in a three-dimensional process; *b*) synthesis of a polymer with a "star" structure containing a microgel nucleus; *c*) synthesis of a three-dimensional polymer with a porous structure; 1) vinyl monomer; 2) divinyl monomer.

Then, depending on the nature and properties of the microgel particles formed (the density of cross-linking within the microgel, the size and shape of the particle, the number of functional groups on the surface, etc.), the final product of the three-dimensional reaction is characterised to some extent by the inhomogeneity of its supermolecular structure. According to Funke [112], the homogeneity of the supermolecular structure of cross-linked polymers is an exception rather than the rule; on the other hand, the inhomogeneity of the structure of polymers can be regulated during the synthesis and it can assume organised forms. In his study of the general cases of the synthesis of three-dimensional polymers with inhomogeneous supermolecular structure, Funke put forward fundamental schemes for the synthesis of products with a predetermined structural heterogeneity (Fig. 7). It follows from Fig. 7*a* that the particles of the microgel formed beforehand can play the role of polyfunctional centres (cross-linking via the functional groups on the surface of the microgel), while the formation of linear chains between the centres can be achieved by the polymerisation of monovinyl compounds. Using the divinyl monomer and "live" poly(methyl methacrylate) chains, it is possible to synthesise either a polymer with a dense microgel nucleus and long side branches (Fig. 7*b*) or a cross-linked polymer with a supermolecular structure of a different type (Fig. 7*c*). [113]

Table 3. The development and products of polymerisation processes involving polyfunctional monomers.

Type of reaction	Development of reaction	Reaction products	References
I. Linear polycylisation	Two-dimensional development	Macromolecules with ladder or cycloladder structures	3,12,114, 117,119
II. Cyclotrimerisation with branching	Three-dimensional development of a polycyclic structure		
III. Branching with three-dimensional cyclisation		Macrogel	33-35
		Soluble and fusible branched polymer containing two-dimensional and three-dimensional cyclic products	82-84,53 118,125
	(a) Simultaneous competing branching and cyclisation reactions with the latter predominating;	See scheme in Section III	
		Microgel 	112,115, 116
	(b) analogous process under associative conditions;		
	(c) statistical mean development of the same processes	Macrogel (with or without preliminary microgel formation) (see Fig.6)	92-100

The new trends in the synthesis of polymers, which developed as a result of the study and utilisation of polycyclisation reactions [3,12], altered radically the concept of the functionality of the monomer as the sole factor determining the possibility or impossibility of gel formation in polymers. To illustrate this fact, it is sufficient to compare Carothers' "law of functionality" [2,74] (the monomer system is incapable of forming a three-dimensional structure for $f \leq 2$ and a three-dimensional macrogel is necessarily formed for $f > 2$) with the development of only three types of polymerisation reactions, where the average functionality of the initial monomer mixture is $f > 2$ (Table 3).

The data in Table 3 show that the range of polymerisation processes in which polyfunctional compounds are used is limited, on the one hand, by reaction of type I and IIIa leading to soluble and fusible linear and polycyclic compounds and, on the other hand, by reactions responsible for the formation of three-dimensional macrogel products (type IIIc). Within the limits of this range, one can evidently expect a wide variety of combinations of the above types.

The role and importance of various factors in the development of gel formation in systems with a high functionality have been investigated in two-, three-, and six-component mixtures of organosilicon monomers. The results showed that, under certain conditions, the reaction can be directed towards the formation of soluble polycyclic systems. Such directing factors may be the nature of the solvent[118], the nature of the organic group[120], the pH of the medium[121], and others[122].

The high functionality of the initial compound thus frequently cannot serve as a criterion of the capacity of the system for the formation of three-dimensional polymers. Furthermore, when a polyfunctional monomer exhibits an enhanced tendency towards cyclisation, an increase in the tendency of the reaction products towards the formation of polymers with a three-dimensional macromolecular structure can be achieved by reducing the overall functionality of the system. In the manufacture of organosilicon polymers, an analogous operation is achieved in the synthesis of varnish and enamel binders of type KO (the introduction of a bifunctional compound into the reaction with a trifunctional compound). Characteristics of a similar type have been investigated in relation to the condensation of a tetrafunctional monomer whose capacity for the formation of three-dimensional structures appeared only following a decrease of the overall functionality of the system as a result of the introduction of a bifunctional compound, which interferes with the intramolecular cyclisation process[123]. Similar phenomena were observed also in multicomponent systems with a high average functionality[124].

Secondary processes such as rearrangement or chain-transfer reactions can also play a decisive role in controlling the development of the three-dimensional process. Thus, in a study of the polymerisation of bicyclic siloxanes ($f = 4$), Andrianov and Zachernyuk[125] established that, under certain conditions, the yield of the three-dimensional polymer passes through a maximum and then begins to decrease owing to the increasing importance of the rearrangement process, leading ultimately to completely soluble polycyclic systems.

The probability, degree, and causes of cyclisation in three-dimensional polymerisation processes constituted an urgent problem for both mathematicians and physical chemists from the very beginning of the theory of gel formation. As the problem became more complex and many-sided, the approaches to its solution also altered. The updating of the analysis of cyclisation proceeded along these lines gradually from the study of the influence of the dilution effect[11,51,52] to the study of the conformational statistics[36,116] of polymeric and oligomeric molecules and the discovery of more general relations.

Various methods have been proposed in recent years for the quantitative estimation of the degree of polycyclisation. A number of studies by Karyakin and coworkers[126-128] were characterised by attempts at a thermodynamic approach to the analysis of polyheterocyclic polymers with a linear structure, while kinetic solutions of problems of this kind were considered by Jacobson and coworkers[129,130]. However, the above analytical procedures were far from being universal[56].

The study and description of the laws governing the formation and development of three-dimensional cyclic structures, resembling, for example, the cubic polyphenylsilsesquioxanes, microgel structures of different types, and the conversion of the latter into macrogel forms undoubtedly constitute an even more difficult problem.

Thermodynamic and kinetic factors have evidently played a decisive role in the general characteristics of the properties of structured systems. In the kinetic and thermodynamic interpretation of gel formation in a system of polyfunctional monomers, two tendencies have been noted. The characteristic feature of one tendency is analysis of the early stages of the process[43,93,115,116]: (1) of the generation of a swarm of complexes and globular aggregates via physical interaction forces; (2) of intraglobular processes before the appearance of the first microgel particles; (3) of the conditions and causes of macro- and micro-gel formation. In terms of the mechanism of Bobalek and coworkers (see Fig. 6), these studies include the stage of the three-dimensional process up to and including the theoretical gel formation point.

The principal aim in the second trend is to study the relations governing the syneresis phenomenon in the polymer–solvent system, i.e. the phenomenon of the separation of the gel and sol fractions. The region beyond the theoretical gel formation point in Fig. 6, including the instant of "physical gel formation" (syneresis), corresponds to studies of this kind[109,131-135].

In the study of the development of the three-dimensional process in polyurethane systems, one of the principal causes of the involvement of the microgel formation stage in the reaction—the large energy of the intermolecular interactions in the initial system of components—was discovered[93]. In the assessment of the vigorous intramolecular cyclisation reaction in the synthesis of three-dimensional polymers, a number of investigators suggested that the cause of the anomalous process be sought by abandoning the model of intertwined macromolecular coils in solution[43,115].

In the course of the conformational analysis of polymer chains in concentrated systems, it was shown that the free energy of the system is determined not only by the free energy of the given chain but depends also on the nature and energetic state of other macrochains in the system. According to the results obtained, the fixation of the conformation of the molecules via physical forces in the first stage of the interaction is then completed by the cyclisation reaction occurring within a much more tightly coiled polymer compared with the θ-conformation and leading to a large number of cross links within the microgel particle.

A series of studies by Dusek[131-135] were devoted in recent years to the thermodynamic investigation of syneresis in three-dimensional processes. The author's approach to the analysis of the phenomenon is characterised by a distinction being drawn as a function of the type of conversion into a three-dimensional structure, which proceeds either via microgel or macrogel formation[131]. Assuming the employment of a solvent (or the initial monomer as the reaction solvent) to be the cause of the thermodynamic instability of the system during the reaction and also the cause of the inhomogeneity of the final polymer, Dusek calculated two critical parameters of syneresis. He considered a system of polymers where syneresis is determined by the increasing density of cross-linking in the macromolecule and the gel and sol

fractions are separated after the attainment of the critical number of cross links ν per unit volume of the gel. In this case, when the separation of the system is due to polymer–solvent interaction forces, syneresis occurs following the breakdown of equilibrium and the attainment of the critical value by the interaction parameter χ. A combination of critical conditions with respect to ν and χ is evidently characteristic of the majority of three-dimensional processes. For the simplest version of a binary system, a formula has been found, whose solution leads to the determination of the parameters, i.e.

$$(\Delta\mu_i)_{\text{mix}} + (\Delta\mu_i)_{\text{network}} = \ln(1-\Phi_p^0) + \Phi_p^0 + \chi(\Phi_p^0)^2 + \nu\overline{V}\Phi_p^0/2 = 0,$$

where μi is the chemical potential of a given component in the mixture or in the three-dimensional network, Φ_p^0 the degree of swelling of the three-dimensional product in the given solvent, and $\overline{V}$ the partial molar volume of the solvent.

Evidently, among the multiplicity of objective factors responsible for the syneresis of the system, account was actually taken of only three and the observed relation governing the syneresis conditions in a polymer system constitutes therefore a convenient mathematical model rather than a universal equation. In an experimental test of the equation, a satisfactory agreement of the observed and calculated values was noted in the case of macro-syneresis. The calculations on microgel formation processes agreed with experiment less satisfactorily.

The state of the theory of gel formation in polymers and its present problems were considered at the April 1974 symposium in England devoted to gel formation processes and gels of all four types as defined by Flory [136]. The greatest attention in studies concerned with the formation of covalently linked three-dimensional polymer networks was devoted to the problems of inter- and intramolecular reactions, the aim being to create a single general theory.

In our view, Flory's introductory report [136] constituted a disturbing factor in this respect. Together with the likely usefulness of the statistical method in the theory of gel formation, he emphasised the legitimacy of arbitrary assumptions concerning the insignificant contribution of cyclisation reactions and the constancy of the reactivity of the functional groups in the course of condensation, i.e. the assumptions introduced into the analysis of gel formation as early as the 1930s.

The possibility of the development of the three-dimensional polycondensation process virtually without cyclisation up to the gel formation point, i.e. the possibility that the reaction proceeds via the family tree mechanism, was examined by Peniche-Covas et al. [137] in relation to the system of decamethylene glycol and benzenetriacetic acid. However, the only fundamental argument quoted by the authors in support of the cascade mechanism of the development of the reaction is the possibility of highly efficient extraction of strongly branched macromolecules with molecular weights up to 10^8 from the polymer system beyond the gel formation point (the system contained between 1 and 5% of the gel fraction). They did not confirm experimentally their conclusion that the "newly generated" gel should be virtually free of cyclic structures; furthermore, they did not take into account the kinetic features of the development of the process, in particular the change in the probability of the involvement in the reaction of each of the three carboxy-groups, after the first, second, etc. group have reacted.

The opposite view concerning the importance of cyclisation reactions in three-dimensional polycondensation was reflected in a number of studies by other participants in the symposium. Referring to the considerable percentage contribution of the intramolecular cyclisation reaction even in the absence of a solvent [138], Stepto [139] examined the validity of the employment of the Kilb and Frisch theories on the basis of the available literature data (for polyesters and polyurethanes). In contrast to Flory, who excluded from consideration intramolecular cyclisation processes, both Kilb [140] and Frisch [141] described the gel formation point by the equation

$$\alpha_{cr} = \frac{1}{(f-1)(1-\lambda)},$$

where λ is a parameter absent from Flory's theory and characterising the degree of intramolecular reactions. The two authors treat λ to a certain extent differently, as a function of the concentration of the functional groups in the system at different reaction stages.

Having noted that the analogous equations proposed recently by Gordon and Scantlebury [44], Gordon and Temple [142,143], and Stamford [144] suffer from the same defect—the failure to take into account the details of the three-dimensional process (as a result of which their agreement with experiment was observed only for low degrees of conversion in the condensation reaction), Stepto proposed, on the basis of the analysis carried out, a combinatorial equation describing the critical conditions:

$$\lambda = \frac{\alpha_{cr}(f-1)-1}{(1-\alpha_{cr})\alpha_{cr}(f-1)} = \left(\frac{3}{2}\pi\nu b^3\right)^{\frac{3}{2}} K/N_A c_{\text{int}},$$

where c_{int} is the concentration of functional groups which have been involved in the intramolecular cyclisation reaction, ν the number of bonds in the smallest ring, b the effective bond length in the smallest ring, N_A the Avogadro number, and K a constant. The agreement between the equation and the experimental data for polyesters and polyurethanes is satisfactory in the case of polyesters according to the author.

Apart from Stepto's study dealing with the analysis of the Frisch and Kilb theories and describing the dependence of the gel formation point on the molecular structure of the components (the length and nature of the chain) as well as the reaction conditions (dilution, component ratio), a number of reports at the symposium confirmed the finding that the time has come for an experimental test of theoretical ideas and the search for and analysis of real model polymer systems.

New methods for the synthesis of model three-dimensional polymers, which permit an exact control of the number of intermolecular bonds and make it possible to guarantee a specific topology of the macromolecules, have been proposed [145,146]. According to Beinert et al. [145], model systems can be synthesised by the interaction of previously obtained linear macromolecules containing amino-groups along the entire chain with a similar polymer containing isocyanato-groups along its chain.

It has been suggested that three-dimensional macromolecules with the chain length between the network nodes specified beforehand be obtained [146] from "live" polystyrene, polyisoprene, and polyvinylpyridine macromolecules with a narrow molecular weight distribution and from branching agents—divinylbenzene or tri(allyloxy)triazine. The influence of network defects on physicomechanical properties was investigated on the models obtained and it was established that the number of "entanglements" (intertwined parts of the chain) is independent of the frequency of cross-links. According to Beinert et al. [145], the concept of the

gel formation point in a three-dimensional process has lost its initial significance.

The attempts at a mathematical analysis of the dependence of the capacity of the polymer for the formation of three-dimensional structures on the chain transfer reaction in the course of the synthesis of vinyl macromolecules were described at the symposium [147]. The methods of cascade theory were used for the purpose. However, the region of applicability of the analytical expressions obtained is restricted to the reaction stages with low conversions with respect to the monomer.

The mathematical approach to the description of the dynamic behaviour of a growing three-dimensional macromolecule was used by Edwards [148]. Assuming the macroscopic behaviour of the polymer to be a consequence of the set of properties of the microscopic components, the author examined the influence of the increasing number of branching nodes in the macromolecule (intra- and intermolecular bonds, intertwined parts of the chains) on the changes in the properties of the polymer when the latter passes from the viscofluid state to the elastic state. He states that the creation of a complete dynamic theory of such systems is a more difficult problem. The problems of the study of gel formation with the aid of the new technique have been described by Wun et al. [149]

IV. CONCLUSION

In assessing the advances achieved in recent years in the development of a theory of gel formation in covalently linked three-dimensional polymers, one must note in the first place the considerable progress in the study of intramolecular interactions and cyclisation reactions of polyfunctional compounds. The solution of a number of fundamental problems of cyclisation in three-dimensional processes made it necessary to revise not only "classical" but also more modern theories of gel formation in polymers (the Gordon, Kilb, Frisch, Bruneau, etc. theories).

New experimental data showing that the functionality of the initial monomers is not a decisive factor extended the limits of the region of three-dimensional processes. In this sense, the classification of polymeric reactions involving highly functional compounds on the basis of structural features in the properties of final products can be represented as follows.

1. Reactions leading to fusible and soluble polycyclic products with a three-dimensional structure.
2. Reactions leading to polymer systems with ladder and cycloladder macromolecular structures (without gel formation).
3. Reactions proceeding in a more complex manner with simultaneous branching and cyclisation, which result in the formation of a macrogel or microgel polymer: (a) processes with insignificant degrees of cyclisation, the nature of the development of which resembles the "family tree" mechanism and which are responsible for the "homogeneous" (in the terminology of Flory [136] and other workers) formation of macrogels (the number of such reactions is evidently small); (b) processes with a fairly high degree of cyclisation proceeding via the microgel formation stage to macrogel formation; (c) processes with a high degree of intramolecular reactions leading to microgel polymers only.

The advances in the study of the early stages of the formation of three-dimensional polymers made it possible to differentiate the phenomena of micro- and macrosyneresis in a polymer–solvent system (or a polymer–low-molecular-weight reaction products system) from the phenomena involving the generation and development of three-dimensional gel particles. Taking into account these factors and also the modified concepts concerning the critical state of the system (including the "gel formation point") and the establishment of new criteria, it became possible to devise a fundamental mechanism of the process leading to covalently linked micro- and macro-gel polymers. This mechanism can include the following stages.

1. The formation of a swarm of complexes, aggregates, or globular structures via intermolecular interaction forces in solution or in the melt of polyfunctional monomers or oligomers.
2. The development of the reaction preferentially within the primary formations, or intermolecularly, or via a mixed mechanism: competing inter- and intra-molecular interactions.
3. The formation of the first microgel or macrogel particles without the manifestation of syneresis phenomena (an intermediate equilibrium state of the system containing sol and gel fractions).
4. The manifestation of micro- or macro-syneresis in the system following the breakdown of thermodynamic equilibrium.

The wide variety of the real factors associated with the physical and chemical characteristics of the initial monomers and intermediates and with the reaction conditions may lead to appreciable changes in the development of a specific process compared with the fundamental mechanism described above, for example: (a) to the coincidence of stages 3 and 4; (b) to a change in the sequence of stages—stage 4 first and stage 3 second; (c) to the absence of stage 4; (d) to the specificity of a particular stage, etc.

The development of gel formation in systems of previously obtained macromolecules can proceed via pathways different from those described and may not fit within the framework of the above mechanism. This is why the description of three-dimensional polymerisation reactions in terms of unique mathematical relations has not so far been achieved in practice. The procedures for the creation of a general theory of the formation of polymers with network and three-dimensional macromolecular structures probably require a differential investigation and description of various types of reactions of polyfunctional compounds.

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