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Formation, Structure, and Properties of Polymer Gels

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A gel is taken to be a polymer-solvent system in which the polymer, present at very low concentration, forms a quite stable three-dimensional network in the solvent. Consideration is given to the properties of gels in which the network is formed both by chemical and by physical bonds; attention is paid mainly to the second group of gels, in which variation in temperature produces a reversible transition between gel and solution. Existing views on the thermodynamic nature and structure of gels are subjected to critical analysis, and specific gel-forming systems are examined. A detailed analysis is made of the macroscopic phenomena accompanying the reversible solution-gel transition, as well as the strength, rubber-elastic, plastic, and relaxation properties of gels. A list of 399 references is included.

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I. INTRODUCTION

Many, often controversial papers have now been published on the nature and structure of gels, the laws of the transition from solution to gel-like state and the mechanism of gelation, the peculiarities of the physical and mechanical properties of gels, and also specific features of gels of polymeric and non-polymeric substances. The reasons for the appearance of different views on the nature and the sturcture of gels are firstly the disconnectedness of independently developed colloid-chemical, thermodynamic, structure–kinetic, and rheological approaches to the process of gelation, and secondly the substantial differences among the gel-forming systems themselves, from whose study various investigators have drawn their own conclusions. The Reviewers will endeavour to define what systems must be regarded as gels and what differentiates polymer gels from disperse colloidal systems and from concentrated solutions of polymers, as well as which thermodynamic, structural, and rheological changes in a coagulating system are inherent in gelation and which are characteristic only of certain classes of gelling systems.

The concept of a gel first arose in colloid chemistry[1-20]. It implied a disperse two-phase system in which particles of the disperse phase, mostly of elongated form and present in very low concentration, from a three-dimensional framework filled with a very large quantity of the dispersion medium. The framework in such systems was formed by various relatively simple compounds, crystalline or amorphous, mostly inorganic. From the start of the investigation of gels formed by compounds of high molecular weight, however, many specific features due to the nature of the polymers themselves were observed, together with the properties common to all systems of this class. The term "studen' [jelly]" appeared in the Russian scientific literature at this time. Several investigators attempted to separate the concepts of "jelly" and "gel", using various criteria. Thus systems possessing rubberlike elasticity were termed "jellies", and brittle systems were "gels"[21,22]; sometimes systems which were incapable of swelling after removal of the solvent were regarded as gels, and strongly swelling systems as jellies[21]. In other cases gels were two-phase disperse systems, while jellies were single-phase systems constituting true solutions of polymers, in which a three-dimensional network of intermolecular bonds was present between individual macromolecules[23]. However, such separation of these concepts merely introduces confusion, since, for example, systems formed by polymerisation or polycondensation in solution, in which a molecular network is certainly present, are usually termed, not "jellies", but *gels* (they are formed at a characteristic "gel" point[24]); on the other hand, jellies, formed from true solutions of polymers, may be either single-phase or two-phase systems, as we shall show below. It therefore appears to the Reviewers that, as in Ref. 25, the concepts "gel" and "jelly" must be regarded as identical, referring to the same broad range of systems, which in turn can be subdivided according to various criteria. We shall use the single term "studen'"†.

A gel is a polymer–solvent system containing a three-dimensional network of quite stable bonds of non-fluctuating character (i.e. almost unbroken by thermal motion). If such a polymer network is surrounded by the solvent (as a result of swelling of the solid polymer or diminution of the solubility of the polymer in the solution), the system is a gel independently of whether this three-dimensional framework is formed by chemical bonds or intermolecular bonds of physical nature, whether the system has been obtained without phase separation of a true solution or as a result of such separation. A gel may be either a two-component or a multicomponent system.

When gels are formed from solutions, each system is characterised by a critical concentration of gelation, below which a gel is not formed. This concentration is determined by the amphiphilicity of the macromolecules and the degree of regularity of the chemical structure of the polymer, the form of the macromolecule, the interaction between polymer and solvent, the molecular weight, and the flexibility of the polymer chain (the more flexible

† Since the above distinctions do not appear to have been made in the English language literature, "studen'" will henceforward be translated throughout as *gel* (Ed. of Translation).

the higher the critical concentration)[26]. We shall examine in greater detail below the action of all these factors on the process of gelation.

The formation of branch points in the network is accompanied by a considerable increase in viscosity, the appearance of rubberlike elasticity, and at a high polymer concentration by normal elasticity, a yield-point stress, and the capacity for retention of shape and loss of fluidity under the influence of its own weight and small stresses (as we shall see later, considerable irreversible deformations appear in gels under higher stresses). Another characteristic feature of a gel is its inability under isothermal conditions to dissolve in the solvent from which it has been formed, whatever quantity of this solvent is added[27]. Gels can be divided into two large groups depending on the nature of the bonds forming the three-dimensional network[28-30].

Gels of type I are irreversible systems with a three-dimensional network formed by chemical bonds between macromolecules, incapable of reversible fusion and coagulation, and breaking down only on degradation of the polymer itself. They include swollen three-dimensional polymers (e.g. swollen vulcanised rubbers, tanned gelatin, etc.), systems whose network has been formed by polymerisation of a monomer in solution in the presence of very small quantities of a cross-linking agent, and spatially cross-linked systems obtained in a solvent by the polymerisation or polycondensation of monomers having three or more functional groups.

Gels of type II are heat-reversible systems whose network is formed by various kinds of intermolecular bonds, obtained either by the limited swelling of solid linear polymers or from solutions of polymers by appropriate variation of the thermodynamic conditions.

II. GELS INCAPABLE OF MELTING (IRREVERSIBLE GELS)

Gels of type I containing the equilibrium concentration of solvent are equilibrium single-phase systems[31,32]; their three-dimensional network is usually regarded as macromolecular. Studies of such gels have been concentrated mainly on the thermodynamics of the swelling of cross-linked polymers in various solvents, which enables the interaction between polymer and solvent to be assessed[30,33-36]; the dependence of the swelling and the thermoelasticity of the systems on the degree of cross-linking[24] and on the polymer concentration[37-49] has also been investigated. The properties of such gels are significantly affected by whether they have been formed directly by the cross-linking of a polymer in a solvent or by the swelling of a three-dimensional system obtained with a specified degree of cross-linking in the absence of solvent[37,40,50]. On the formation of a network in solution, when the solvent concentration considerably exceeds the equilibrium value corresponding to the given degree of cross-linking, the gel is a non-equilibrium two-phase system, in which syneresis‡ takes place until the solvent has the same chemical potential within the gel and in the fluid liquid phase[31,32,51,55]. The phase ratio and the size of the structural units in gels of this type have been studied by various optical methods[37,55-58]. One of the main factors determining the properties of gels whose network has been formed in a solvent is the concentration of polymer in the system. Another important factor is the nature of the solvent, which determines both the ability of the polymer to form a supermolecular structure in solution[59,60] (in the case of poor solvents; the three-dimensional network is then also supermolecular—not molecular—in character) and the rubberlike elasticity of the resulting networks, which governs the subsequent shrinkage of the gel[61]. Both these properties play a decisive part in the forming of a polymeric solid via a stage of gelation with subsequent removal of solvent, i.e. in the so called xerogel state[62], whose structure (porosity) is completely determined by the structure of the original gel and the mode of solvent removal. The porosity of xerogels plays a very important part in their use as ion exchangers[63], and in recent years as carriers in the vigorously developing gel chromatography[59,64]. The preparation of gels having various specified porosities[65-67] requires the study of a wide range of novel gel-forming systems, solvents, and methods of cross-linking: research in this field is growing vigorously at the present time[68-70]. Such porous structures can be obtained also be evaporating the solvent from gels whose networks are formed by bonds that are physical—not chemical—in nature; the properties of such systems have been described for agar-agar[71], poly(vinyl) acetals[72], and cellulose acetate[73].

‡Syneresis is the expulsion of solvent during the compaction of particles of the disperse phase in the case of a colloidal system or during the establishment of thermodynamic equilibrium in a polymer–solvent system[51-54].

III. HEAT-REVERSIBLE GELS

We have been concerned mainly with gels in which the reversible solution–gel transition is of the greatest interest, occurring usually with change either in temperature, pressure[74], or solvent composition (addition of a precipitant, change in pH, introduction of various additives, etc.).

The properties of heat-reversible gels can be approached in various ways. Most authors consider that a gel is always a non-equilibrium heterogeneous two-phase system, since formation of a three-dimensional gel network is possible, in their opinion, only on phase separation of a single-phase solution[29,75,76]. Several authors hold the view that gels are formed without phase separation, as a result of formation of local intermolecular bonds between individual macromolecules present in true solution: gels are thus regarded as homogeneous, one-phase systems[77-79]. A number of authors think that gels may be either single phases or two-phase systems, structurally either homogeneous or heterogeneous[80-83]. It is noteworthy in this connection that the question of the phase constitution of polymeric gels is almost completely ignored in the foreign literature, where interest is concentrated mainly on the change in properties of the system with the formation of branch points of the three-dimensional network. Soviet investigators, however, pay great attention to the phase constitution of gels, and we shall examine in greater detail existing approaches to this problem.

1. Formation of Two-phase Gels with Phase Separation of a Solution

Gels of compounds of high molecular weight are regarded in colloid chemistry, by analogy with those of low molecular weight, as disperse two-phase systems, in

which particles of the solid disperse phase form a framework. Such an approach has been widely developed by the Rebinder school[84], who have worked out a detailed theory of structure formation in colloidal systems, applying generally to such diverse compounds as clays, concretes, and supersaturated solutions of synthetic and even natural polymers. A distinction is made between structure formation by coagulation and by condensation[23,84-87]: in a coagulated structure contact between the particles is effected by weak van der Waals forces, so that the system is characterised by low strength, plasticity with slight elasticity, and thixotropy; in a condensed structure strong cohesive or adhesive contacts are established between the particles, which confer durability and elasticity on the system. According to the ideas of the Rebinder school, the formation of a three-dimensional structure by means of such strong contacts between coalescing particles of a new polymer phase separating from a true solution with spontaneous formation of a colloidal system below the consolute temperature is the cause of gelation and the strengthening of the gel. Results obtained on gelation in aqueous gels of gelatin[88,89], polyvinyl alcohol[90,91], and cellulose acetate[92,93] have been interpreted in terms of the above concepts. These ideas, which are not open to doubt for gels that are typical lyophobic colloidal systems (they may also be polymer—non-solvent systems), obviously cannot be true in other extreme cases, when phase separation of the solution involves formation of two liquid phases, or when gelation is unaccompanied by phase separation. Because of the high viscosity of polymer systems, of course, and also at low interfacial energies, gels of both types can be formed, differing as little as we please. For these transition systems the actual difference between them, of course, is devoid of meaning.

It is noteworthy also that the transition from typical polymer gels (formed with liquid phase separation or without phase separation at all) to typical colloidal gels is determined by the nature of the solvent, which has a significant influence also on the flexibility of the polymer chain: as the solvent becomes poorer and the rigidity of the polymer chain increases, its ability to swell diminishes (without which a polymeric type of gel cannot be formed), and the gel becomes increasingly colloidal in nature, i.e. it becomes a two-phase system with a three-dimensional framework formed by rigid macromolecules or their aggregates, which do not swell in the solvent. The above views on the formation of a solid polymer phase may therefore apply mainly to gels of rigid-chain polymers.

According to modern views, which originated in the work of Kargin, Papkov, and Rogovin[94-96], polymers form true solutions[28], interaction between polymer and solvent being regarded as the mixing of two liquid phases[97-99]. The concept of liquid phase separation underlies Papkov's concept of gelation[29,97]§, the theoretical principles of which will be briefly considered.

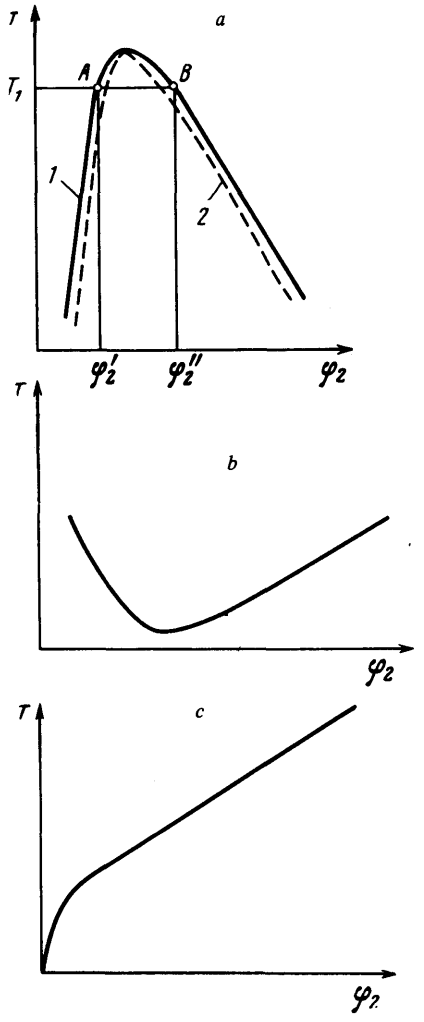


Figure 1. Equilibrium diagrams for systems with: *a*) an upper consolute temperature; *b*) a lower consolute temperature; *c*) a polymer crystallisable from solution, where T is the phase-separation temperature, φ_2 is the polymer concentration, and φ_2' and φ_2'' are the polymer concentrations in the equilibrium phases: 1) binoidal; 2) spinodal.

Gelation can occur either with a fall or a rise in the temperature depending on the type of temperature variation of solvent power[28]: gels are formed on cooling or on heating according as the systems have upper or lower consolute temperatures. Fig. 1 illustrates phase diagrams for various systems. The curve separating the regions of existence of stable single-phase and of metastable solutions is termed a binoidal (curve *1*), and that separating the regions of existence of metastable and unstable solutions is a spinodal (curve *2*). The temperatures and concentrations corresponding to the binoidal represent the conditions under which the thermodynamically stable true solution of a polymer passes into the metastable state and forms a colloidal solution containing the nascent new phase. The existence of a diagram having a consolute temperature suggests the existence of a region of phase separation of the polymer into two new, liquid phases.

§ The possibility of liquid phase separation in the formation of gels was mentioned long ago by Hardy[7,9,10], who investigated the gelatin—water—ethanol system, and showed that the single-phase solution separates into two liquid phases below a certain temperature. As these phases set further, the three-dimensional skeleton of the gel is produced by one or the other phase depending on the concentration of gelatin in the system and on its rate of cooling, which leads to a significant difference between the mechanical properties of the gels.

The diagrams are quite different in form (Fig. 1*c*) when a new solid crystalline polymeric phase separates from solution. The type of phase diagram may therefore indicate whether phase separation involves nucleation of a new polymeric solid phase or formation of two liquid phases, one of which is strongly enriched with the polymer.

According to Papkov[100] a gel is formed only in the region of phase separation if the viscosity of the concentrated polymer phase is very high, which prevents complete spatial separation of the system into two liquid phases. He therefore regards a gel as a non-equilibrium two-phase system with incomplete separation of the phases, which, in contrast to the above colloidal views on gel structure, comprise a swollen polymer forming a cellular framework with the almost pure solvent distributed in it as drops. The existence of these two phases is responsible for the presence of a gel. On Papkov's view a gel does not exist outside the region of phase separation, but a concentrated solution is present, possessing different properties—unlimited fluidity, low elasticity, etc.

Fig. 1 shows that at temperature T_1 the equilibrium state of the system corresponds to separation into two phases having concentrations φ_2' and φ_2''. Any gel of concentration below φ_2'' will therefore be a non-equilibrium system, and solvent will separate with time until the chemical potentials in the two phases become equal. Syneresis in these systems is completely analogous to that in gels which have been chemically cross-linked within the solvent (Section II). Its progress is more intense the lower the concentration of polymer in the gel, which undergoes considerable shrinkage.

Since at a given temperature the system undergoes phase separation until the concentration φ_2'' is reached, the gel obtained directly from a solution of this concentration is a thermodynamically equilibrium system[101], which means that its composition should be the same independently of the route—from the solution or by swelling of the solid polymer—by which it has been obtained. Such independence forms the basis of the plotting of phase diagrams for gelling systems: owing to the impossibility of determining the composition of a concentrated polymer phase during phase separation, points on the right-hand portion of the binoidal are determined experimentally from the equilibrium swelling of the dry polymer[89]; the left-hand portion is plotted as usual from the cloud points of the solutions[28].

Only a few experimental phase diagrams of gelling systems have been published (Fig. 2).[90,92,102,103] In most cases they are similar in shape to miscibility diagrams for partly miscible liquids. Right-hand portions of phase diagrams have been obtained experimentally from the swelling of solid films, i.e. from the view that a mixture of polymer and solvent comprises two liquid phases. However, gelation in the region of phase separation is then interpreted as emergence of the solid polymer as a new phase. As we have mentioned above, these two approaches are incompatible.

Nevertheless, the complexity of obtaining phase diagrams for gelling systems and the limited possibility of using them result from the fact that structure formation in complicated polymer systems leads to a dependence of the state of the system on the approach to it and to irreversibility of several processes. These features of polymer systems have been discussed theoretically[104,105]. It has been shown during recent years that the swelling of a polymer film also depends on the previous history, i.e. on the character of the solvent from which the film has been obtained and on its thermodynamic affinity for the polymer[60,63], on the temperature to which the solution has been preheated and on the rate of cooling, which govern the presence and character of a supermolecular structure in the film[106-109], on the concentration of the solution, which determines the proportions of intra- and inter-molecular bonds in the system and also the conformation of the polymer macromolecule[110-113], and on the temperature at which the solvent had been evaporated to obtain the film.

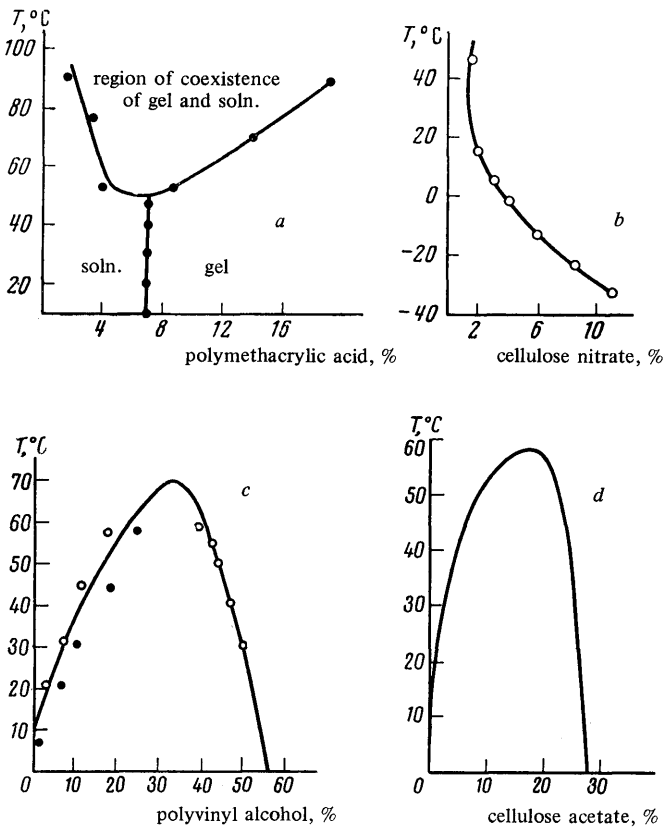


Figure 2. Experimental equilibrium diagrams for the gelling systems: *a*) aqueous polymethyacrylic acid[102]; *b*) ethanolic cellulose nitrate[103]; *c*) aqueous polyvinyl alcohol[90]; *d*) cellulose acetate—3,6-dioxaoctanol[92].

This last fact is well known for gelatin. If the solvent is evaporated at a temperature above the helix–coil transition point (considered in greater detail below), macromolecules are preserved in the loop conformation in the film; when evaporation occurs below the transition point, the macromolecules are preserved in the spiral state[114]. Furthermore, vaporisation of the solvent below the gel point of the system yields a film via a gel stage. Both these factors effect significantly the ability of the films to swell[29,115,116]. The degree of swelling of a film obtained from an aqueous gelatin gel depends very considerably on the concentration of the gel: the lower the concentration, the larger the number of cavities filled

with solvent, and the greater the swelling of the film, obtained by evaporation of this solvent, when replaced in the solvent (Fig. 3).[117]

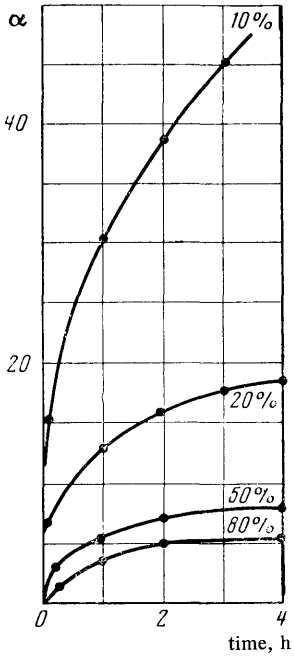


Figure 3. Dependence of swelling of film α on polymer concentration (indicated on curves) in gel from which it has been obtained[117].

For the above reasons the swelling of a film in fact depends on its previous history, and the right-hand branch of the phase diagram plotted from these values is displaced along the concentration axis (by 15—20%) depending on the various factors enumerated above[109]. As a consequence the region of phase separation in gelling systems can be determined only very roughly, and the characterisation of specific gelling systems by the temperature—concentration phase diagram is largely devoid of meaning unless the precise conditions under which it was obtained are indicated.

Two-dimensional phase diagrams are applicable only to binary systems, so that they can be used to characterise gelation only with a narrow molecular-weight distribution, when the polymer can be regarded as a single component. In this connection we must again mention the necessity of cautious use of the concept "component" in such multimolecular systems as polymers[118]. In real gel-forming systems—which are, of course, polydisperse—change in temperature is accompanied by loss of solubility initially of the higher fractions and then of the lower fractions. Gelling is therefore a multistage process[75] occurring in a multicomponent system[119], which it is illegitimate to characterise by a binary phase diagram[28,97]. The practical possibility of using such diagrams to represent gelation in polydisperse systems is due to the experimental fact that the position of the right-hand portion of the binoidal varies very little with molecular weight[120].

The investigation of gelation on narrow fractions[121-123] showed that the lower fractions play no specific part in gel formation, since it obeys the same laws in unfractionated and fractionated polymers. Fig. 4 illustrates the molecular-weight dependence of several parameters of gelation, and shows that the rigidity of the gel, as well as the melting point[124] and the "aggregation" temperature (i.e. the temperature at which viscosity begins to vary with time[125]), increases with molecular weight (in several cases only to a certain value).

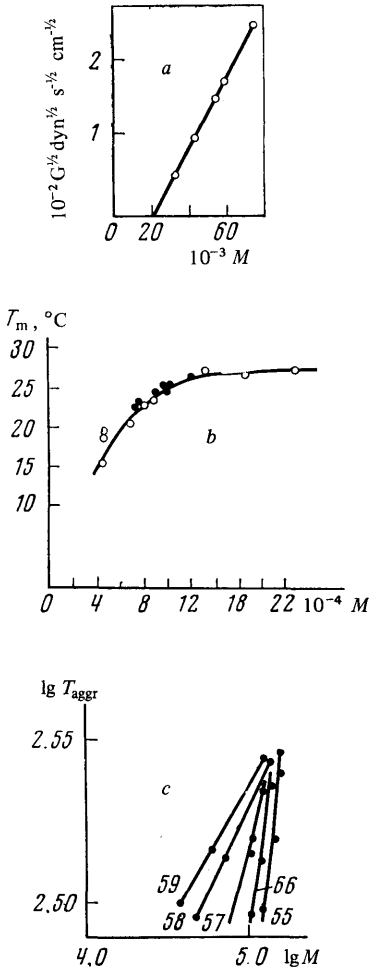


Figure 4. Influence of molecular weight of polymer on the properties of gels: *a*) modulus of elasticity G; *b*) melting point (for aqueous gelatin gels)[121]; *c*) "aggregation" temperature (for gels of cellulose acetate of varying degrees of substitution in benzyl alcohol)[125].

The above concepts on gel formation with phase separation are applicable also when the solubility of the polymer is diminished, with change not only of temperature but also of solution pH (ion-reversible gels)[112,126] and especially on introduction of a precipitant[29,127-130] (which is often encountered in the fractionation of polymers).

Under these conditions the range of existence of a gel can sometimes be determined by means of ternary diagrams[28]. In some cases not only two-phase but also multiphase systems are formed depending on the interactions of all the components[129,131,132].

2. Single-phase Gels obtained without Phase Separation

At polymer concentrations above the equilibrium value φ_2'' (Fig. 1), i.e. to the right of the binoidal, single-phase gels are formed without phase separation (Fig. 2*a*) either as the solubility of the polymer in the solution decreases or with limited swelling of linear polymers. Similarly to the swelling of network polymers, gel formation here is due to the existence of branch points in a three-dimensional network resulting from local interactions of macromolecules. Since gels are usually formed by polymers, amphiphilic in nature, in thermodynamically poor solvents, limited swelling of the polymers is evident under thermodynamic conditions such that the polymer–solvent interaction is sufficient to overcome some polymer–polymer contacts but insufficient to overcome other, stronger contacts, which form a three-dimensional network within the solvent.

Addition of excess of a lower component to an equilibrium gel cannot produce any change until the thermodynamic conditions change[27]. With rise in temperature, and also with improvement in the solvent power of the medium surrounding the gel, the number of branch points may decrease, ultimately with destruction of the gel. If the lifetime of the branch points becomes so short (owing to heating or change of medium) that the movement of macromolecules is virtually unrestricted by existing short-lived bonds, a transition will occur from the "stable" gel network to a purely fluctuational network, i.e. to a flowing liquid.

Transitions due merely to the kinetics of the formation of branch points, unaccompanied by change in the thermodynamic state of the system, are not associated with the presence of different phases, and such gels may therefore be single-phase systems. Gels comprising a single phase can be produced not only by variation of the temperature but even under isothermal conditions, with variation of the concentration during transition from the solid polymer to its dilute solution. Results obtained for such an isothermal transition in the poly(vinyl chloride)–dibutyl phthalate[133] and gelatin–glycerol[134] systems show (Fig. 5) a successive transition from vitreous to rubber-elastic state and to viscous fluid.

Rubberlike elasticity can appear only in solids possessing a three-dimensional network with sufficiently large distances between branch points, which is a necessary condition for the development of flexibility in the macromolecular segments forming the network. If the rubber-elastic state arises in solution owing to strong intermolecular bonds, i.e. because of formation of a stable three-dimensional network, the range of existence of the solution coincides with that of the gel. In solutions in which such strong bonds are not present, the rubber-elastic state is largely masked by fluidity, and the system passes from the solid polymer to a dilute solution via a concentrated-solution stage, not via a gel stage. There are then no grounds for assuming that the appearance of a rubber-elastic state as the polymer swells coincides with intersection of the binoidal, as is stated by Frenkel'[105]: i.e. rubberlike elasticity may appear equally in the one-phase and two-phase states of gels. Characterisation

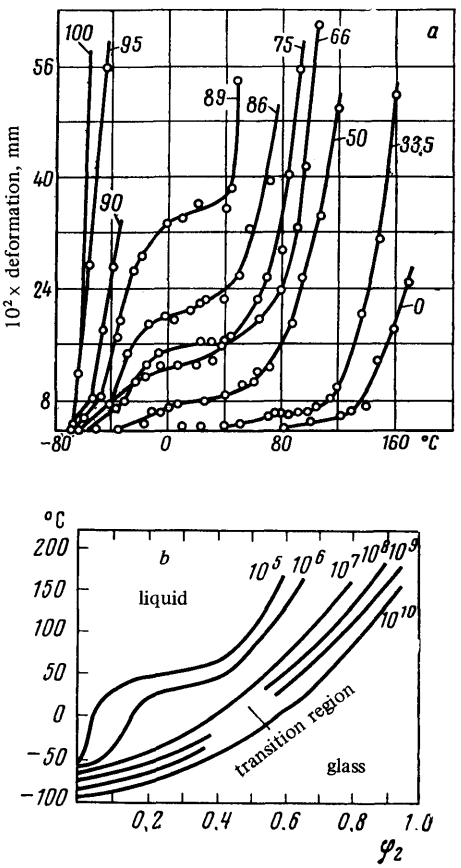


Figure 5. Isothermal transition from dilute solution to solid polymer via gelation stage: *a*) thermomechanical curves for the poly(vinyl chloride)–dibutyl phthalate system (numerals on curves denote concentrations of dibutyl phthalate)[133]; *b*) variation of modulus of elasticity of gelatin–glycerol system with temperature and concentration φ_2 (numerals on curves denote moduli of elasticity; a gel is present in the range $G = 10^5$–10^7 dyn cm^{-2}).[134]

of the gel-like state of polymers therefore requires, as stated by Papkov[29] and shown experimentally by Meerson[135], examination both of phase diagrams (which have limited applicability, as we have noted) and the concentration dependence of glass and yield points (for amorphous systems) or melting points (for crystalline systems) (Fig. 6).

The mechanism of the formation of single-phase gels of uncrystallisable polymers is analogous to vitrification of the polymers themselves[78], except that in the vitreous state bonds are formed between a considerable number of repeating units, whereas a kind of partial vitrification, i.e. formation of a small number of the strongest bonds, occurs in gels, leading to a stable network structure¶.

¶ Thus in the case of amorphous polymers gels, being systems intermediate between liquid and solid, are also intermediate between solutions and condensed systems in the vitreous state[79].

The presence of two types of intermolecular interactions—strong and weak[79]—causing the appearance of a three-dimensional network forms the basis of the gel-like state, independently of the phase state of the polymer in which it develops.

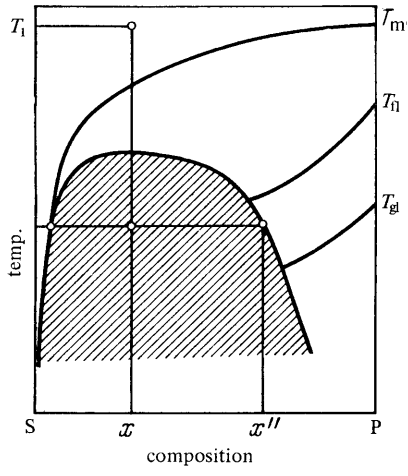


Figure 6. Concentration dependence of glass point T_{gl}, flow point T_{fl}, and melting point (S = 100% solvent; P = 100% polymer).[29]

3. Role of Crystallisation in Gelation

In contrast to the above discussion, most investigators consider that gelation is inseparably associated with crystallisation of the polymer within the solvent. This view is based firstly on the Herrmann—Gerngross micellar model[136], according to which crystalline regions (regions of parallel packing of segments of many macromolecules) form the branch points of the three-dimensional network, independently of whether the chemical structure of the polymer permits its crystallisation. It is based secondly on the fact that gelation is characteristic only of polymers whose macromolecule contains strongly interacting polar groups; such a structure leads to chain rigidity, which in the opinion of several investigators, increases the tendency to crystallisation[119,137-139]. On this hypothesis many authors assume that crystallisation accompanies gelation in polyacrylonitrile[140-142], poly(vinyl chloride)[143,144], and even random copolymers[138,145,146]. Sufficient regularity of the chain, in most cases a necessary condition for crystallisation, can hardly be achieved in ordinary statistical copolymers. In polymers and copolymers containing sufficiently extended blocks of uniform structure, however, local crystallisation is possible in solution[147], with the formation of more stable "branch points" of the gel network.

Crystallisation in solution is characterised thermodynamically by the phase diagram illustrated in Fig. 1*c*, representing the equilibrium between the pure crystalline polymer and its saturated solution. However, hardly any such diagrams have been published for specific gel-forming systems. Phase diagrams of crystallisable polymers were first obtained, for polyethylene in various solvents, by Richards[148], who showed also that, after the crystalline phase has melted completely, the system may separate into immiscible liquid phases, possibly accompanied by gelation. Thus crystalline and amorphous phase separations are independent processes, as is emphasised by Papkov[29].

The presence or absence of crystallisation is indicated also by the thermal effects and volume changes accompanying gelation[149-151] (see below) and by direct structural methods[150,152-154]. The concentration dependence of the melting points of crystallisable gels, in contrast to the corresponding relation for amorphous gels, follows Flory's equation

$$\frac{1}{T_m} - \frac{1}{T_{m_0}} = (R/\Delta H_u^1)(V_1 - \chi_1 v_1^2)(V_u/V_1) \qquad (1)$$

for mixtures of a crystalline polymer and a component of low molecular weight, in which T_{m_0} and T_m are the melting points of the polymer in the absence and in the presence of solvent, χ_1 is an interaction parameter, V_1 the molar volume of the solvent, ΔH_u the heat of fusion, v_1 the volume fraction of the solvent, and V_u the volume of the repeating unit of the polymer.

The combined application of these methods suggests that completely amorphous gels are obtained in several systems (polyacryloglycinamide in water[150,155-160], copolymers of acrylic acid, acrylamide, and acrylonitrile in water[161-163], poly(vinyl chloride) in dibutyl phthalate[143], and copolymers of methyl acrylate and methacrylic acid[164]). Nevertheless, amorphous (atactic) poly(methyl methacrylate) does not form gels in any solvent, whereas the crystalline stereoregular poly(methyl acrylate) exhibits a strong tendency to gelation because of the formation of complexes between iso-segments and syndio-segments[165-169]. The same effect is observed with polyacrylic acid[170], which forms gels only when in the isotactic form, whereas polymethacrylic acid forms gels in the amorphous (atactic) state[102,112,171-173]. The ability of several polymers to crystallise depends so strongly on the composition of the solvent that, as has been shown with polyacrylonitrile[142,174] and polyvinyl alcohol[175], they are able to give amorphous gels in some solvents, and crystalline gels in others.

When a polymer shows a strong tendency to crystallise in a solvent medium, the gels may have the character of crystalline solvates[176,177]. With intense crystallisation of the polymer the gels are devoid of the typical properties of gels, notably elastic and rubber-elastic properties: i.e. they are, rather, pastes[178] (polyvinyl alcohol in aqueous acetone[29], methanol[29], and glycerol[175], polycaproamide—formamide systems[29], and poly(alkyl acrylates) with straight-chain alcohols[176]). The other systems in which reversible gelation has been observed comprise polyvinyl alcohol in water (in the absence[179-183] and in the presence[184-186] of complexing agents) and in aqueous glycerol, diethylene glycol[124,149,187], methanol, and acetone[29], as well as in anhydrous solvents (formamide, *N*-methylpyrrolidone, and dimethyl sulphoxide[175]); poly(vinyl chloride) in dibutyl phthalate[143] and in dimethylformamide[144]; polysaccharides[188,189], alginates[190,191], pectins[192], and agaroid[193] in water; cellulose and its ethers in organic solvents[194-196]; polyacrylamide in water[197]; copolymers of vinyl chloride and methacrylic acid, acrylic acid and ethyl acrylate[198], styrene and caprolactam[199], styrene and oxiran[200], and styrene and isoprene[201] (so called "mesomorphic gels"); and gels of

cellulose and other polymers in water, obtained in a special way and containing large regions of the crystalline phase[202-205].

It is thus clear from the above account that both amorphous and crystalline gels exist: i.e. gelation often involves crystallisation, but the latter is not an inherent part of the process[163,175]. The tendency to associate gelation with crystallisation often arises from the well defined structure formation in solutions and gels of polymers, which we shall very briefly examine.

IV. STRUCTURE OF GELS

It was considered for a long time that formation of a single-phase gel involves merely the formation of a three-dimensional network of separate macromolecules[23,77,79]. However, true solutions of polymers, like solutions of liquids of low molecular weight, are inhomogeneous[28], strongly characterised by association. The presence of fluctuating association complexes is evident even in very dilute solutions and in good solvents[206-220] long before the consolute temperature. Great interest is aroused by the variation in the conformation of macromolecules during association with increase in concentration and by the dependence of this process on the flexibility of the polymer chain[221-228]. Which conformation is most favourable for gelation is also of interest[169,229].

The influence of macromolecular conformation on gelation has been studied in greatest detail on gelatin, the most widely distributed gel-forming compound. The helix—coil conformational transition, which is typical of many polypeptides and biological macromolecules, occurs in gelatin at 35°C. Gelation takes place only below this temperature, i.e. with the helical conformation of the macromolecule. When a dilute solution undergoes concentration above 35°C, with the macromolecules remaining in the coiled state, only a significant increase in viscosity occurs up to very high concentrations, with complete absence of gelation. Thus formation of the helical conformation of macromolecules and gelation are interlinked processes: i.e. the formation of intramolecular aggregates during helix formation and the formation of intermolecular bonds (branch points of the three-dimensional network) leading to gelation are due to interactions of the same nature. As we shall see below, the energy and other parameters of the gelation of gelatin are largely determined by the characteristics of the above conformational transition in the macromolecule (Section V, 1). Most other biological macromolecules do not form gels in the native state, and several of them are capable of gelation only when denatured. A favourable conformation of the macromolecule, with a considerable number of groups capable of forming intermolecular bonds facing outwards, obviously plays an important part here as well. Determination of the conformations of macromolecules in synthetic polymers involves great experimental difficulties, and therefore available data are ambiguous.

Processes preceding phase separation—aggregation and nucleation of a new phase, which appears near the consolute temperature—take place with change in temperature. However, if gelation occurs as a consequence of the formation of branch points of a three-dimensional network with change of thermodynamic conditions without phase separation, the system loses solubility and fluidity, with of course, the fixation of association complexes present at the instant of loss of fluidity. Thus, as stated by Glikman[76] for the separation of a new phase, structure formation unaccompanied by phase transition converts fluctuating association complexes present in solution into aggregates[174], i.e. into quite stable structures, the three-dimensional network within and between which is no longer fluctuating but stable in character. The viscosity of an associated true solution does not vary with time, whereas that of a solution undergoing cross-linking (a so called "gel-solution"), in which the structure of association complexes become fixed, varies considerably with time[21,75]. It appears to the Reviewers that a sharply defined transition from a solution of invariable viscosity to a solution whose viscosity varies with time does not necessarily indicate the start of separation of a new phase, as certain authors assert[33,75,88,89]. This is often evidence of the appearance of individual stable branch points of a three-dimensional network, whose formation takes a long time[21] and results ultimately either in a single-phase gel or in phase separation. Many investigators have pointed out the two-stage character of gelation (aggregation and formation of individual branch points leading to a diminution of fluidity, followed by formation of a continuous network leading to a complete loss of fluidity)[81,82,230]. The gel network would obviously be formed both inside aggregates (between separate macromolecules) and between aggregates (supermolecular structures). Theoretical aspects of the production of gels from aggregated particles have been discussed by Joly[231-233].

It may be supposed that a truly molecular network is very rarely formed in gels. It may appear either in very dilute systems or in solvents in which formation of a polymer structure is feebly developed (but these are usually thermodynamically good solvents, in which gels are seldom formed). A special case of the formation of a macromolecular network is possible in solvents possessing good affinity for the polymer but whose molecules each contain two functional groups, and can therefore act, as it were, as cross-linking agents, forming hydrogen or other intermolecular bonds between the polymer macromolecules[175].

The possibility of the formation of macromolecular and supermolecular networks in gels had already been considered by Ferry in his early papers[234,235], in which he distinguished between "coarse" and "fine" networks. He linked the different network structures with the conditions of production of the gels: the lower the temperature the less favourable the conditions for aggregation and the "finer" the networks formed. Heating the gel to near the melting point causes reorganisation with the formation of "coarser" networks. The same feature was found by Stainsby[236] from a study of the mechanical properties of gels. He stated that at low temperatures many bonds are formed of poor stability but preventing further ordering of the network, whereas near the melting point few but very stable bonds are formed, so that ordering is possible. The dependence of the structure of a gel on the temperature conditions of its formation has been confirmed also by sedimentation in an ultracentrifuge[237,238], as well as by a thermodynamic method[239], but the correctness of the latter is open to doubt.

The above considerations show that the majority of gels, including single phases, are structurally microheterogeneous systems. This is well supported by direct structural methods of investigating gels, primarily electron microscopy (with special procedures to ensure high resolution[240,241]). Results illustrated by Fig. 7 indicate that the gel networks of gelatin in water[240,242,243], as well as of cellulose diacetate in aqueous acetic acid[244] and of

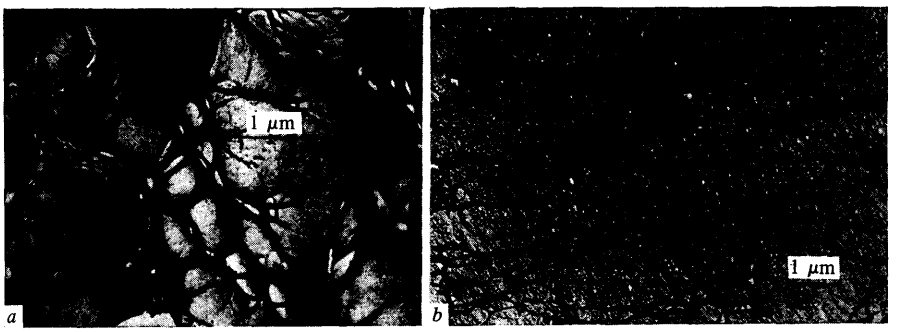


Figure 7. Electron micrographs (×8400) of gels of: *a*) gelatin in water (20% concentration);[243] *b*) cellulose diacetate in 35% aqueous acetic acid[244].

polystyrene in decalin[245], are made up of fibrillar structural units (of diameter ~1000 Å), whereas aqueous polyvinyl alcohol gels comprise globular units (diameter of globules ~1000 Å).[246-249] The electron micrographs cannot indicate, however, whether the observed structural units are at equilibrium or fluctuating in character; it must also be remembered that the presence of coarse particles in the case of polymers, *pace* Ref. 70, are quite unable to determine the phase state.

Another direct method for examining the structure of polymer solutions and gels is the scattering of light[250]. Application to concentrated solutions of polymers[251] reveals an extremal concentration dependence of scattering, which indicates that the association complexes increase in size until a fluctuating network appears in the solution, after which the scattering begins to diminish owing to the ordering of the network[252]. A similar variation is observed in coagulating systems[253,254]: the turbidity increases with aggregation, to reach a maximum on formation of the first branch points; with further increase in the latter the network becomes increasingly ordered, and the scattering of light diminishes to become independent of the number of branch points in the gel network[83,255]. The coarser scattering particles in polymer solutions and gels are therefore determined from the turbidity spectrum[56,256-259], obtained by measuring the optical density at various wavelengths of the incident light and processing the experimental results on the basis of Mie's theory[260-263]. During recent years a laser technique of measuring anisotropic small-angle scattering of polarised light has been successfully used to determine the size of the structural units of a gel[57,58,264-266]. Prins and Bueche have shown[267,268] that a random distribution of gel branch points is present over a certain concentration range and in certain solvents, but in most cases the branch points are formed by supermolecular structural units whose size varies with the temperature and with the nature of the solvent. According to this method the structural units of aqueous gels of gelatin and of polyvinyl alcohol have diameters of 3000–6000 Å, in good agreement with results obtained by electron microscopy.

The distinction between the hypothetical network and cellular structures of gels, which for a long time attracted great attention[33,269,270], disappears in considerable measure when the structural units are large. If the particles that are growing together into a network occupy a considerable volume, the space between them, filled with solvent, resembles a cell: i.e. the gel has a peculiar network–cellular structure, as is readily seen from Fig. 7. The predominance of one or other type of structure depends on the polymer–solvent system and on the concentration of the polymer. Transitions from open to closed gel structures have repeatedly been observed experimentally[93,271].

V. MACROSCOPIC PROPERTIES OF GELS DUE TO THEIR NATURE AND STRUCTURE

1. Properties characterising a Reversible Solution–Gel Transition

The temperature at which a gel passes from the rubber-elastic to a fluid state with destruction of the three-dimensional framework is termed the melting point of the gel. As this transition is somewhat diffuse, no absolute methods are available for determining the melting point; various research methods for detecting the melting of gels have been described[272-274], among which the most widely used is to measure the movement of a sphere, placed below the surface of the gel, when the temperature is slowly varied at a constant rate[275].

The gel point, i.e. the temperature at which formation of a gel first becomes possible, is usually determined as the temperature at which the viscosity of the system begins to increase rapidly (when each temperature is maintained for a given time). In all gel-forming systems the melting point is higher than the gel point. The magnitude of the difference, i.e. the hysteresis of fusion and gelation, varies within very wide limits for different gels: thus in 5% aqueous gels of gelatin the melting point is only 3 deg above the gel point[235], but in certain other gels the difference amounts to tens of and even a hundred degrees (e.g. the gel and melting points for a 5% gel of poly(vinyl chloride) in diethyl hexyl phosphate, a gel of cellulose triacetate in trischloroethyl phosphate, and a gel of polyvinyl alcohol in a 60 : 40 mixture of water and glycerol are respectively 36° and 108°C,[144] 3° and 120°C,[144] and −20° and 90°C, etc.). The hysteresis is probably due to a significant difference between the mechanisms of the formation and the fusion of a gel[114]. Formation involves a succession of many stages requiring a certain degree of supercooling and a long time, which results in a wide set of branch points in the three-dimensional network. Yet the melting of a gel has all the signs of a concerted transition, requiring the simultaneous rupture of several weak bonds followed by a rapid disordering of the chain units.

Even with infinitely slow cooling, therefore, the gel point will evidently not coincide with the melting point, as is supposed by certain authors[276], although some approach of these temperatures does occur. The difference in mechanism between formation and fusion of a gel is evident also in a difference between the energies of formation and rupture of the bonds in the network: gels of polyvinyl alcohol in various solvents show that the energy of destruction of the branch points always exceeds the energy of their formation[187,277] (since the latter corresponds experimentally to only one of the stages of gelation, whereas the former corresponds to the completely formed gel structure).

The hysteresis of melting and gel points is associated also with the often described Arisz effect[29,116,117], consisting in the dependence of the melting point of a gel on its previous history with respect to temperature. The melting point of a gel depends in several cases on the time and especially the temperature of its formation. This variation is connected firstly with different forms of cross-linking of the system at different temperatures, these determining the types and stability of the branch points formed (Section IV). The melting points of gels formed by cooling rise as the temperature of formation falls[122], but at very low temperatures of gelation (e.g. near 0°C with an aqueous gelatin gel[121]) the melting point becomes lower owing to inadequate mobility of the macromolecules involved in forming the network. Secondly, the dependence of the melting point of a gel on the conditions of its formation is determined by the completeness of the stress-relaxation processes following formation of the network[77,78].

Several quantitative approaches to the investigation of gels are based on the applicability of the theory of rubberlike elasticity and other statistical methods of polymer chemistry to the formation and properties of gels. From the analogy between the formation of a three-dimensional physical network and a network of chemical bonds within a solvent, Ferry applied to heat-reversible gels the Flory–Stockmayer theory[278], according to which a condition for formation of an infinite three-dimensional network is the relation

$$P_c = \frac{1}{\rho(\lambda_\omega - 1)} \qquad (2)$$

where λ_ω is the weight-average number of residues in the macromolecule, ρ the proportion of groups capable of forming cross-links, and P_c the proportion of these groups which actually form intermolecular bonds, i.e. the probability of cross-linking. If $\lambda_\omega \gg 1$, we have $P_c = 1/\rho\lambda_\omega$, which can be rewritten[239,279]

$$fm_{cl} = C/2M_\omega \qquad (3)$$

where m_{cl} is the molarity of cross-links (allowing for the fact that formation of a bond involves two groups) at the gel point, M_ω the weight-average molecular weight, C the concentration (g litre^{-1}) of macromolecules, and f a coefficient representing the proportion of groups capable of forming branch points that are involved, not in intermolecular, but in cyclic intramolecular bonds. Assuming that 1–2 bonds per macromolecule are required for formation of an infinite network, Ferry showed[235] that the critical concentration of gel formation by gelatin was 1%, in good agreement with experiment.

Experimental determination of the number of cross-links in the gel network and the number of groups involved in forming one cross-link is based on the equation of state

$$\tau = \alpha(d/M_0)RT\left[\left(\frac{l}{l_0}\right) - \left(\frac{l_0}{l}\right)^2\right] \qquad (4)$$

representing the relation between the stress τ and the elongation (in which $\alpha(d/M_0)RT = G$ is the modulus of rubberlike elasticity, l_0 and l are the initial and final lengths of the specimen, d is the density of the gel, M_0 is the molecular weight of the repeating unit, and α is the proportion of groups in the chain that form cross-links), deduced for three-dimensional networks from the theory of rubberlike elasticity, and the equation of swelling

$$\mu v_2 = -\ln(1 - v_2) - v_2 - \rho_2 \bar{V}_1 v_2^{1/3}/\bar{M}_c \qquad (5)$$

where μ is a polymer–solvent interaction parameter, v_2 the concentration by volume of the polymer, ρ_2 the density of the polymer, $\bar{V}_1$ the molar volume of the solvent, and $\bar{M}_c$ the molecular weight of the chain segment between branch points. It is then necessary to examine the swelling of films obtained by drying the gel (not by evaporating the solvent from a solution—Section III, 1), in which films the structure (i.e. the number and nature of the branch points) is fixed.

Most of the results calculated by using the above approach[279–284] lead to the conclusion that one cross-link is formed by many (20–30) groups, which is regarded as evidence that branch points in the gel network are formed by crystallites comprising many macromolecules. Sometimes, however, calculation shows that branch points are formed between two active groups, i.e. that association complexes are absent[155,156].

Although reasonable values are obtained in several cases for the number of branch points by transferring to cross-linked systems the theory of rubberlike elasticity developed for a macromolecular network, this theory is in large degree arbitrary and gives an idea, not of the number of real branch points in the system, but of the equivalent number in an ideal molecular network possessing the same properties as the test system†. We would like to lay special stress on this aspect, which is often overlooked.

From Eqn. (3) and the van't Hoff equation for the equilibrium formation of cross-links, Eldridge and Ferry[292] obtained the concentration dependence of the melting point T of a gel as

$$\ln C = -\frac{\Delta H}{RT} + \text{const} \qquad (6)$$

where ΔH is the energy of formation of a bond in a gel network. Pouradier established the relation

$$\frac{\Delta H}{RT^2} = \frac{1}{T} - \frac{d\lg G}{dT} \qquad (7)$$

between this energy and the temperature dependence of the modulus of elasticity of the gel[239,293]. Equations (6) and (7) enable us to determine the energy of formation (more correctly, of destruction) of branch points in a gel network. The same quantity can be determined by other methods not involving the premises of the theory of rubberlike elasticity. Firstly, it is determined as the apparent activation energy of flow (which is necessarily

† The same considerations apply also to investigation of the birefringence of gels, when the optical stress coefficient characterises the system[285–287], whereas the difference between the refractive indices, according to the theory of rubberlike elasticity, is related to the structural characteristics of the gel network[288–291].

connected with rupture of the cross-links of the gel network) from the temperature dependence of viscosity in the region of irreversible deformation of the gel (see below)[293]. Secondly, the bond energy ΔH or heat of gelation is measured by a direct thermographic or calorimetric method[294-303]. The examples of gels of gelatin, polyvinyl alcohol, and other polymers show good agreement among values of bond energies obtained by all these methods[157,175,187,299,301].

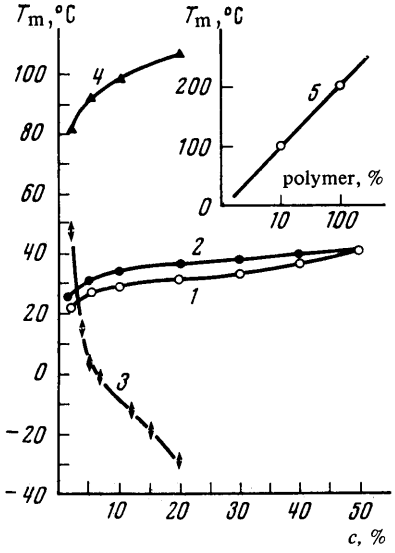


Figure 8. Concentration dependence of melting points of gels of: 1) aqueous gelatin[303]; 2) as (1) from Ref.88; 3) ethanolic cellulose nitrate[103]; 5) poly(vinyl chloride) in dibutyl phthalate[143]; 4) polyvinyl alcohol in 60% aqueous glycerol[175].

Because of the experimental simplicity ΔH is most often determined from Eqn.(6). Most of the gels investigated (gelatin, polyvinyl alcohol, poly(vinyl chloride), polyacryloglycinamide, polyacrylonitrile, etc.) exhibit proportionality between the melting point and the logarithm of the concentration. In several gels of well crystallisable polymers the melting point is proportional to the concentration (not its logarithm) in conformity with the Flory equation (Section III, 3). Equation (6) shows that the sharp concentration dependence of melting point, illustrated in Fig. 8 (curves *3–5*) for gels of poly(vinyl chloride), polyvinyl alcohol, and cellulose nitrate, and typical of the gels of most synthetic polymers, corresponds to a small energy of bonding.. Gelatin gels exhibit a quite different type of dependence (curves *1* and *2*)[303-305]: the melting point changes so little with concentration over the range 5–40% that it is often regarded as constant; the energy of formation of a bond in this region is very large, amounting to 50–200 kcal mole^{-1} depending on the conditions of preparation of the gel. The high heats of gelation and fusion of gelatin[294-303] were regarded for a long time as evidence that gelation is a phase transition of the first kind. Examination of gels of synthetic polymers of various types showed, however, that the energy of formation of a bond does not exceed 5–12 kcal mole^{-1} with amorphous polymers (which corresponds to 1–3 hydrogen bonds)[151,156,300] and 18 kcal mole^{-1} with crystallisable polymers[151,175,187]. The high heats of fusion and gelation of gelatin are due to the large helix–coil transition energy, which, as mentioned above, makes a most significant contribution to the formation and destruction of the gel. Thermogravimetric analysis with very slow stepwise heating reveals two fusion peaks, one attributed to the helix–coil transition, and the other to destruction of cross-links[302]. These peaks are preceded by an exothermic effect due to the formation of more stable bonds in the network when the gel is heated near the melting point. Calorimetric experiments show only one fusion peak[298].

The heat of the helix–coil transition has closely similar values in other proteins and polypeptides[306-309]. In cases in which these compounds form gels, e.g. with poly-(γ-benzyl L-glutamate), the heat of melting of the gels is of the same order as with gelatin[157], although slightly smaller in magnitude.

It must be remembered that heat effects in calorimetric experiments are expressed in calories per gram of the dry material, whereas energies of bonding determined by means of the Ferry–Eldridge equation are obtained in kilocalories per mole. Comparison of these quantities is difficult, since the number of bonds in a gram of the dry material is unknown.

The above considerations show that the magnitude of the heat of gelation cannot indicate that a phase transition is necessarily involved. The large heats of gelation found with gelatin and other natural polymers are explained by the large thermal effect of the intramolecular helix–coil phase transition, which cannot be separated from the heat of gelation itself. In all other gels the thermal effect is significantly lower and corresponds to the energy of formation of a few (with crystallisable polymers) or one or two (with amorphous polymers) intermolecular bonds. This can be regarded as an indication that gelation always involves structural conversion with the appearance of new branch points, the nature of which influences variation of the thermal effect within narrow limits.

The heat evolved on the formation of a small number of relatively weak bonds can be determined only in very high-sensitivity calorimeters. Hence the heat of gelation in such systems often could not be detected in the early work. In thixotropic colloidal systems formed by relatively weak van der Waals forces, in particular, the sol–gel transition occurs without a measurable thermal effect.

Analysis of the literature shows that the change in volume accompanying formation of a gel may vary. An increase occurs only when the gel is formed as a result of a chemical reaction with production of a new substance which remains in the system (e.g. the generation of hydrogen chloride in the formation of silicic acid gel)[21]. A decrease in volume on gelation has been observed with methylcellulose in water[310] and in several systems in which gelation is accompanied by crystallisation of the polymer, in particular on the gelation of polyvinyl alcohol in aqueous glycerol[149]. For a long time the volume change accompanying the gelation of gelatin was a matter of controversy[311-316]. Thus Neiman[313] assumed that the apparent change was due solely to volume relaxation (of both solution and gel) on variation of the temperature: when these factors are assessed correctly, no change in volume is detected. This view can hardly be correct, since the change in volume accompanying the helix–coil transition

and subsequent crystallisation makes a significant contribution to the gelation, and has been subjected to detailed dilatometric investigation by Flory and Garrett[317]. They discovered an appreciable, abrupt change in volume accompanying the gelation of collagen in ethylene glycol. The volume change, like other properties of a gelling system, probably depends significantly on the polymer concentration; in dilute gels and also in gels having weak intermolecular bonds, therefore, gelation takes place without a measurable change of volume. An abrupt change is evidently observed only when gelation is accompanied by rapid crystallisation of the polymer: in the absence of crystallisation, only a slight and gradual volume change takes place.

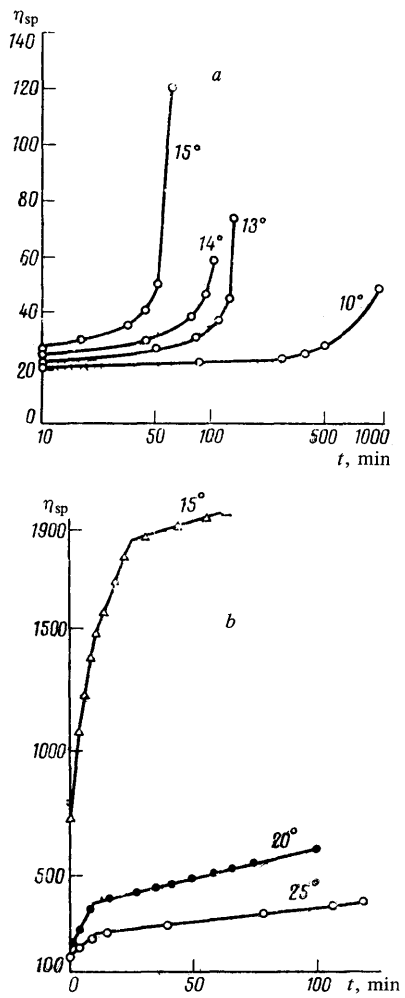


Figure 9. Variation of viscosity on gelation: *a*) cellulose nitrate in ethanol[103]; *b*) copolymer of acrylic acid and acrylonitrile in water[162].

The formation of stable branch points is most clearly evident in a change in the rheological properties of a gelling system. These properties may vary with temperature and concentration, but variation with time at constant concentration and temperature is most characteristic of gelation. Change in viscosity was for many years regarded as the most characteristic parameter of the solution–gel transition, and was studied intensively[317-324]. In several cases the viscosity isotherms have the typical shape (Fig. 9*a*) of the crystallisation isotherms of polymers[103]‡; this was used as an argument in support of the identity of gelation and crystallisation. In other cases the viscosity–time curves show several inflexions (Fig. 9*b*), which were attributed[81,180] to various cross-linking stages preceding formation of the gel.

However, the solution–gel transition is characterised not only by an increase in viscosity but also by the emergence of elastic properties in the system[11,325,326] (a reversible proportion of the deformation, a modulus of elasticity, i.e. rigidity) and a limiting shear stress[75], which increase with time§, as well as a change in the spectrum of relaxation times[327,328].

As Schwedoff emphasised, the elasticity and the viscosity of a system are not interrelated unambiguously: a system may be highly viscous and possess no shear elasticity; and conversely, the latter may be significant while the viscosity is very low. The second case is typical of dilute gels of gelatin, whose elasticity vanishes when they pass into the state of a dilute solution (melt). In contrast to dilute solutions, sufficiently concentrated solutions of polymers also exhibit elasticity, which is due to the presence of a fluctuating network (when sparse branch points are linked by flexible chain segments this is apparent as the rubberlike elasticity of solutions)[338-341]. In the gelling of a sufficiently dilute solution the increase in number and change in character of cross-links in the network lead to an increase in the rubberlike elasticity of the system; when a too dense network is present, however, the rubberlike elasticity diminishes, so that rubber-elastic deformation of a gel becomes less with increase in its concentration[342]. In concentrated solutions rubberlike elasticity is masked by flow, and adequate separation of reversible and irreversible portions of the deformation is important for a correct description of the rubberlike elasticity of solutions (as with gels and with the polymers themselves)[339,343,344]. Concentrated solutions, gels, and rubberlike polymers then exhibit closely similar moduli of rubberlike elasticity[134,339,344,345] at 10^4–10^6 dyn cm^{-2}.

Thus the rheological distinction between gels and concentrated solutions lies not in the elasticity of the former but in their yield stress[346]. Gels, like other bodies possessing a spatial framework (e.g. many disperse colloidal systems), are "quasi-Bingham" plastic solids[62]: i.e. they are characterised by a yield stress, below which they behave as solids (i.e. exhibit only elastic properties), but above as viscoelastic or viscous liquids (i.e. capable of irreversible deformation). This is evidently the decisive rheological property of gels[277,347-349], so that the long held view of gels as non-fluid systems must be regarded as incorrect. Such extremely low yield stresses were observed by Mishod in simple experiments[349] even for very

‡ A close similarity is observed also in the temperature variation of the rates of growth of cross-links and of crystal nuclei.

§ This time variation of properties, which is characteristic of a gelling system, demands that the system be brought to equilibrium—if at all possible—in order that the concentration or temperature dependence of these properties may be studied, or else that the rate of change of the properties should be taken into account.

dilute (0.2%) agar-agar gels. Later work showed that a limiting stress was absent from non-gelling concentrated solutions[345,350,351], but it also appears in filled solutions (e.g. a solution of polyisobutylene containing added particles of carbon black), in which a three-dimensional framework is formed[352].

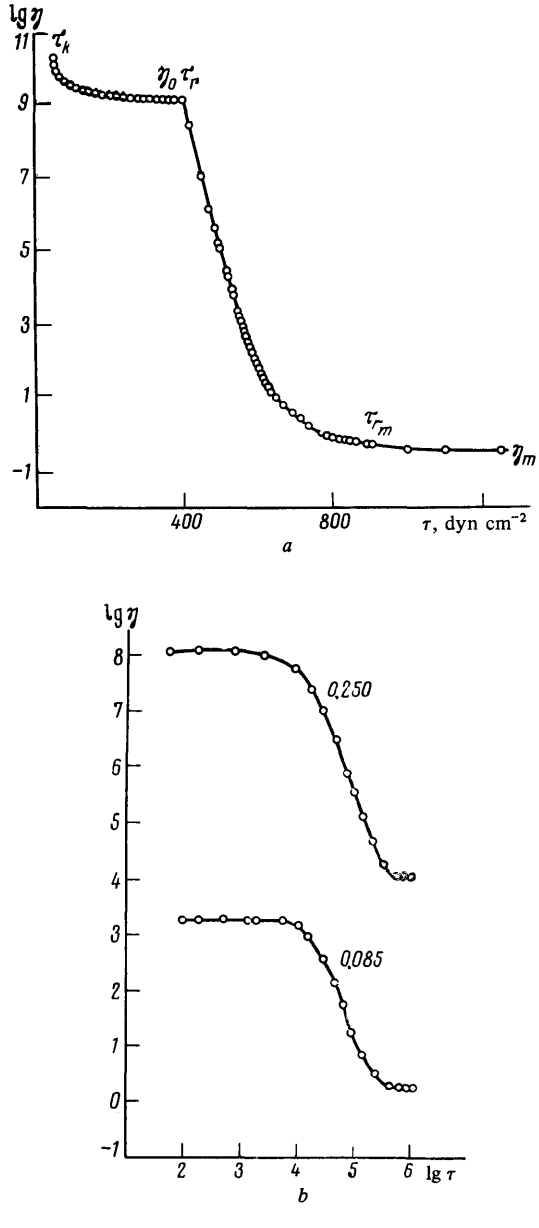


Figure 10. Variation of viscosity with shear stress in: *a*) a disperse colloidal system—an aqueous suspension of bentonite[357] (where τ_k is the limiting shear stress, τ_r the stress corresponding to the start of breakdown of the structure, τ_{r_m} the stress corresponding to complete breakdown of the structure, η_0 the maximum Newtonian viscosity, and η_m the minimum Newtonian viscosity); *b*) solutions of cellulose acetate in cyclohexane (concentrations denoted on the curves)[357].

During recent years it has become obvious that absolute limiting values do not in fact exist. According to Shurkov's theory of durability[353-355] the framework of a gel can be broken down by a sufficiently long-acting stress, even if considerably lower than the usually determined limiting shear stress. This, of course, is indissolubly connected with the development of irreversible deformations of the gel. A similar view was expressed by Trapeznikov, who considered that irreversible deformations, even in gels, could develop at any stress, and regarded the limiting shear stress as corresponding to a change in the character of the flow—Newtonian with unresolved structure below this limit, and plastic flow with resolution of the gel structure above it[356]. Shear at sufficiently high rates and stresses resolves the whole structure, and the flow again becomes Newtonian in character. Fig. 10 illustrates examples of complete rheological curves obtained both for plastic colloidal systems[357] and for concentrated solutions of macromolecular compounds[358,359]. Curves of the same type have recently been obtained also for dilute polymer gels[360] (since the limiting stress increases so much with gel concentration that it is almost impossible to realise a "quasi-Bingham" flow of gels).

Destruction of the gel structure on application of an external stress is a particular aspect of the thixotropic properties of gels[14,361,362]. In the initial stage of gel formation, when the spatial bonds have not yet become stable, thixotropy is apparent in the reversible transition of the gel into a solution under the action of external stress (and regelation after removal of the latter)[14]. Several gelling systems, however, possess dilatant properties, evident in enhanced viscosity and gelling on application of external stress, and reversible melting with decrease in viscosity after removal of the stress[363-366], which is attributed to the ordering of the structure under the influence of a mechanical field[18,347]. Among such systems are aqueous polymethacrylic acid[347], poly(methyl methacrylate) in dimethyl phthalate[366], etc. The phenomenon of rheopexy—acceleration of gelation as the external stress is increased—is often observed in such systems.

The transition from solution to gel involves a broadening of the whole relaxation spectrum[327,328,347,366]. The system retains its shape if the lifetime of the cross-links exceeds the duration of the experiment[347]. Trapeznikov therefore proposed the presence of relaxation times of 10^4—10^6 s in a polymer—solvent system, corresponding to the observation times employed in practice, as a rheological criterion of a gel, enabling it to be distinguished from a solution[367].

2. Elastic, Strength, and Relaxation Properties of Gels

The principal rheological investigations of already formed gels, like those of the polymers themselves and their concentrated solutions, reduce to the study of the static and dynamic moduli of elasticity, the dependence of stress on deformation at a constant rate of shear, creep (i.e. the development of deformation with time at a constant stress followed by relaxation of the deformation), and relaxation of stress at constant deformation, enabling relaxation times and the relaxation spectrum of the system to be estimated.

The modulus of elasticity of a gel can be determined either by static methods (under tension[368], compression[368], or shear[325,326,331,332], on change in the dimensions of the specimen in a tube[369]) or by dynamic methods (from the rate of propagation of sound waves)[370]. Good agreement

between static and dynamic shear moduli indicates the absence from the gels of relaxation times of 0.001–100 s[371]. The modulus of elasticity either increases continuously with the duration of gelation (poly(vinyl chloride)[143], polyacrylonitrile[328]) or reaches a limiting value after a very long time[88]¶. The shear modulus is proportional to the square[235] or higher powers[143,145] of the concentration of polymer in the gel, but in several cases this relation is observed only up to a certain concentration[373], above which the concentration dependence of the modulus changes. This may correspond to a change in the gel structure with increasing concentration (Section IV). With small deformations and stresses the behaviour of gels obeys Hooke's law: i.e. the modulus of elasticity is constant[374]. Under higher stresses it increases with the stress[373].

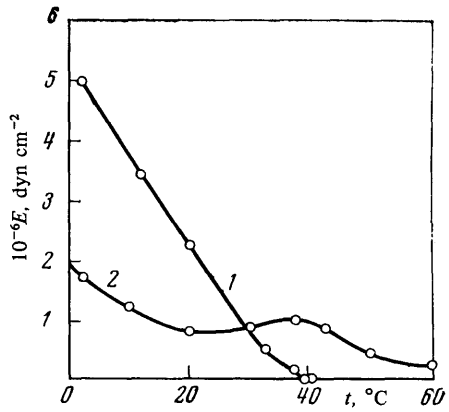


Figure 11. Temperature dependence of modulus of elasticity of gels of: 1) gelatin in water (φ_2 = 20%);[235] 2) polyvinyl alcohol in a mixture of water and glycerol (φ_2 = 10%).[373]

The temperature dependence of the shear modulus of gels indicates that in several cases their behaviour does not correspond to an entropy mechanism of elasticity. Fig. 11 shows that the shear modulus in gels of polyvinyl alcohol in aqueous glycerol increases with temperature over a considerable range (in conformity with the statistical theory of rubberlike elasticity), and only then does it decrease; whereas in gelatin gels the modulus of elasticity decreases with rise in temperature throughout the range investigated[235]. This decrease is due to the increasing rupture of cross-links with rise of temperature near the melting point of the gel, which is especially appreciable with gelatin, as the temperature range of the measurements is very limited. When a small number of chemical cross-links are introduced into a gelatin gel[375] or experiments are made under special conditions, such that the entropy mechanism of elasticity is not masked by the destruction of bonds[376-378], the shear modulus increases only slightly with rise in temperature.

¶ The modulus of elasticity, as well as other mechanical properties of gels, is determined by various aspects of their previous history: these properties differ for gels of the same concentration according as they have been obtained directly by cooling a solution or by concentrating a more dilute solution[372].

The strength properties of gels are most conveniently characterised by the limiting shearing strength[329,379], characterising the strength of the bonds forming the three-dimensional framework; rupture of these bonds precedes steady-state flow. The investigation of non-stationary régimes in concentrated solutions of polymers and gels of aluminium naphthenate has established several important laws governing these processes[379-381]. However, such a purely rheological approach is only beginning to be applied to polymer gels.

The creep of gels[382] under the influence of small shearing stresses was investigated by Rebinder and Ivanova-Chumakova, who proposed a simple method for determining the viscoelastic characteristics of gels[344,383,384].

In most gels part of the deformation is irreversible, with Newtonian flow (the viscosity of 10^6–10^9 P is independent of the applied stress). This means that gels are investigated under stresses exceeding the elastic limit, and that the flow involved in creep takes place with the structure unresolved. As the system cannot flow without the breakage of bonds forming the gel framework, however, a mechanism of chemical flow, i.e. with reorganisation of bonds under the influence of the load, must be envisaged for gels under these conditions[385,386]. Reorganisation and partial destruction of bonds in gels with rise in temperature and increase in stress also make it impossible to use reduced variable analysis in describing the creep of gels[387,388]: it is necessary to allow for reorganisation of the structure with variation in temperature, i.e. to displace the curves along not only the horizontal but also the vertical axis[389-391].

Investigations of the relaxation properties of gels by different workers have led to contradictory results. Deformation was found to be independent of frequency (between 1 and 1000 Hz) in dilute gels of gelatin (up to 20% concentration), but a frequency dependence appeared in concentrated gels[78]. The absence of long relaxation times in dilute gels was attributed to the presence of sparse local cross-links, which prevented displacement of the chains but did not ensure considerable intermolecular interaction. However, earlier[392-394] and later[395-399] investigations showed that stress relaxation occurs in extremely dilute gels (from 1% concentration) to a greater extent the higher the rate of the external constraint, and is described by the same equations as is stress relaxation in polymers and their concentrated solutions. Relaxation processes take place in gels not only by the reorganisation and interaction of chains but evidently mainly by a mechanism of destruction of old cross-links and formation of new ones under the influence of the applied stress[398]. The above discussion shows that the reorganisation of cross-links, i.e. of the gel structure, under the influence of an applied stress plays a decisive part in all mechanical properties of gels, which permits close connections to be established between such properties and the gel structure. Study of the general features of the reorganisation of the framework of gels and the mechanisms of such reorganisation is only beginning, and is extremely important for developing a theory of the deformation of all types of gels.

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Scientific views have developed appreciably since publication of the previous review on polymer gels in 1961,[26] as a consequence of the considerable progress made in investigating proteins and other natural polymers, as well as in the whole field of the physical chemistry of polymers. A deeper understanding of the properties of

gels has been gained primarily from the development of the supermolecular physics of polymers in all their states, as well as ideas on the structural reorganisation of a polymer under the influence of mechanical stress. The combination of molecular and colloid-chemical approaches has been another very characteristic feature of recent polymer chemistry and physics. In many cases the latter leads to a reinterpretation of concepts that have already become traditional, and also removes many of the contradictions which have accumulated in the investigation of gels, permitting an understanding of the occurrence of gels of different types. An important part has been played also by a deepening of our knowledge of the structure of the solvent present in a gel, and of the changes which it undergoes on the introduction of various types of additives. The general advances made in polymer science enable us to predict a rapid future development of our knowledge of the structure, properties, and possible applications of polymer gels.

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