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MODERN VIEWS ON GELATION IN POLYMER SOLUTIONS AND ON THE STRUCTURE OF GELS

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1. INTRODUCTION

The problem of gelation in polymer solutions is of great theoretical and practical interest. The practical importance of the study of gelation is due to the fact that it is necessary to obtain gels having definite physicochemical properties in several branches of industry (*e.g.* in the food, soap, paint, and other industries); but in several other

cases the formation of gels is, on the contrary, an undesirable phenomenon and to be avoided (in the manufacture of artificial fibres, adhesives, tanning solutions, etc.). Polymeric gels are interesting also from a theoretical point of view, since they represent a variety of three-dimensional structures possessing many of the properties of a solid, but containing very little solid material.

In spite of the great number of papers concerned with gelation[1-3], several problems still remain to be fully cleared up, including particularly questions of the mechanism of gelation, the nature of the bonds, the equilibrium state of gels, etc. The aim of the present paper is to examine the main present-day views on processes of gelation in polymer solutions. We will confine ourselves to an examination of gels formed when solutions set on cooling, without giving special consideration to gels obtained by the swelling of a polymer in some solvent.

2. GENERAL DEFINITION OF THE CONCEPT OF GELATION AND OF A GEL, AND FUNDAMENTAL CONDITIONS FOR GELATION

By the phenomenon of gelation is meant a process of continuous increase in viscosity of a polymer solution with time, depending on the nature of the polymer and the solvent and on the temperature, accompanied by a continuous growth of elastic properties, and leading to solidification of the whole system into a uniform non-fluid mass – a jelly or gel.

While it is quite easy to give a definition of the process of gelation or setting, based on the phenomenology of the process, the definition of the concept "gel" presents considerably greater difficulties. As early as 1926 Lloyd[4] began his paper on gels with the words: "The colloidal state – a gel – is a state which is easier to observe than to define". In its most general form a gel can be defined as a disperse system consisting of two components – polymer and solvent – uniformly distributed in a space, and exhibiting the mechanical properties of solids.

Polymer gels can be obtained both by the setting of solutions and by the swelling of a polymer in a solvent in which its solubility is limited. According to modern views a general condition for gel formation is the limited solubility of the polymer in the particular solvent. The work of Kargin *et.al.*[5] has shown the applicability of the phase rule to polymer solutions and has established that the formation of gels is associated with the separation of the system into two phases when the solubility of the polymer in a given solvent is limited. Consequently the condition of limited solubility is a necessary condition for gelation. This necessary condition – a partial diminution in the solubility of the polymer, or more correctly of its functional groups, in the given solvent[6] – can be achieved either by changing the temperature, by changing the nature of the solvent at a given temperature, or by making specific additions to the solution. Thus the first stage in gelation is supersaturation of the solution with respect to definite functional groups in the polymer chain. When solutions are supersaturated with substances of low molecular weight, the system usually begins to separate rapidly into two phases. A peculiarity of polymer solutions is that, when solubility is lost and supersaturation occurs, under certain conditions the system does not separate into two phases. The definition of a gel as a system with incomplete separation into layers, given by Papkov[7], is applicable here. The fact that loss of solubility does not lead to separation into layers is due to the precipitation of the polymer from the solution in microvolumes[8], the polymer molecules being linked to one another to a certain extent. We consider that such incomplete formation of layers occurs when the polymer molecule contains groups differing in chemical nature, usually polar and non-polar groups. In such a case the difference in partial solubility[9] of these groups, when present in a definite ratio, results in one part of the molecule being, as it were, in a dissolved state, while the other part tends to precipitate out of the solution. This obviously explains the fact that almost all known gels (gelatin, agar, poly(vinyl alcohol), cellulose nitrate, etc.) consist of molecules containing groups which are different in chemical nature.

The view that formation of intermolecular bonds in solutions of polymers during gelation occurs by the interaction of groups in the polymer which are sparingly soluble in the given solvent has been developed in papers by Lipatov[8,9] Bresler[10], and Morawetz[11], and can be accepted as fully proved. These ideas follow also from the papers by Kargin *et.al.*[5] mentioned above. The specific effect of the solubility of the polymer on the ability of a solution to set is shown also in the fact that gelation can be observed both when the temperature is lowered and when it is raised. Thus although the classical examples of polymeric gels – those of gelatin – are formed when the temperature of the solution is lowered, with solutions of cellulose nitrate in ethanol, in which the solubility falls rapidly with rise in temperature, gelation occurs on heating[12]. It can be stated, in conformity with the work of Kargin *et al.*[5] that, if the solubility diminishes as the temperature falls, gelation occurs on lowering the temperature, and conversely. With solutions of cellulose acetate in dibutylcarbitol benzene phosphonate, where the solubility diminishes on heating, gelation occurs on heating, but for solutions in the same solvent of cellulose acetate containing a certain proportion of propionate groups the temperature coefficient of solubility is positive, and gelation occurs on cooling[13].

However, a diminution in solubility of the polymer is not in itself sufficient for gelation to ensue. Another important condition is the achievement of a definite concentration in the solution, characteristic of each polymer–solvent system. The existence of a critical concentration is due to the fact that gelation occurs when the ratio of intramolecular and intermolecular bonds formed as the solubility decreases reaches a definite value. For dilute solutions it is known that the probability of formation of intramolecular bonds is independent of the concentration of the solution, whereas the number of intermolecular bonds rises sharply with increase in concentration. Thus the critical concentration at which gelation begins corresponds to the start of preferential formation of intermolecular bonds with a decrease in solubility. This concentration was roughly estimated by Ferry[2] for gelatin solutions on the assumption that the structure of the gel is a three-dimensional network formed by joining together the ends of the macromolecules. In spite of the admitted crudity of such a view, the value of 1% found by Ferry for the critical concentration corresponds in fact to the concentration of gelatin solutions at which gelation is possible.

Above we have considered the main cause of gelation to be a reduction in the solubility of a polymer in a given solvent. Gelation may also be produced, however, by introducing certain additives into polymer solutions. These questions have been elucidated in detail in papers by Zubov

et al.[14-16] In the presence of added compounds of multivalent elements gelation is most often due to the formation of bonds between the polymer molecules in the solution as a result of chemical reaction between the additive and some functional groups in the polymer (*e.g.* gelatin in the presence of alum[17], copolymers of methacrylic acid and methyl methacrylate in the presence of salts of bivalent metals[18], etc.). When stable chemical bonds are formed, gelation leads to irreversible changes in the system. Such systems can no longer be brought into solution by changing the temperature. When compounds of univalent elements are added, there is no possibility of chemical bonds being formed and only the usual type of intermolecular bonds are formed[18].

The solubility of a polymer can be easily varied by adding to the solutions small quantities of a poor solvent, which impair the dissolving power of the solvent. Such additions, too, can lead to gelation. For example, introduction of only 2% of water into solutions of poly(acrylonitrile) in dimethylformamide results in setting occurring even at room temperature, whereas in the absence of water these solutions set only at temperatures below 2°. [19]

The effect of the polydispersity of the polymer on the gelation of its solutions is also readily explained in terms of the general condition for gelation, namely partial loss of solubility. Polydispersity results from a difference in solubility between individual fractions of a polymer in a given solvent, in spite of their identical chemical composition. Since molecules having different molecular weights can take part in forming the three-dimensional structure of the gel, it is obvious that readily soluble fractions will make gelation more difficult. Detailed consideration of these questions has been given in papers by Lipatov[9] and Zubov[16]. Thus it has been shown[9] that a concentrated solution of cellulose acetate will take 24 h to set, whereas a solution of this material freed from readily soluble fractions forms a gel very rapidly. A similar effect is observed with gelatin solutions[16].

Finally, we must note the effect on gelation of the structure of the macromolecule itself. As will be shown below, gelation is observed to involve the formation of secondary structures from molecules which are arranged in a regular manner relative to one another. Walker[20] remarks that the capacity of a polymer for gelation in solution is related to its ability to crystallise. If a change in solubility of a polymer in a solvent involves too great an ordering of the molecular distribution, a precipitate comes down instead of a gel being formed. This explains, for example, the fact that the jellies formed on cooling polyethylene solutions[21] are quite distinct in character from ordinary jellies, *e.g.* of gelatin. An increase in the randomness of interacting groups along the chain leads to a diminution in the ordering of the molecules relative to one another, and decreases the tendency for a deposit to separate out, thus favouring gelation. Some regularity in the mutual arrangement of the molecules is necessary, however, since it favours the formation in the solution of the secondary structures which precede gelation. The structure of the macromolecule also determines its ability to gel because the latter depends on the flexibility of the macromolecule. The conformation of a polymer chain in solution depends on the flexibility of the chain and on its interaction with the solvent. In the case of flexible molecules the viscosity of dilute solutions will be lower, and that of concentrated solutions higher, in a thermodynamically poor solvent than in a good solvent[22]. With rigid molecules, according to Tager[22], the viscosity of solutions will be lower in a good solvent than in a poor solvent, since the uncoiled form of the chain in the poor solvent favours the formation of intermolecular bonds. Hence it follows that the critical concentation for gelation should be lower with rigid polymers than with flexible polymers [*e.g.* gelation in solutions of gelatin and of poly(methacrylic acid)[23]].

The fundamental conditions for gelation considered above also enable other features of the process, *e.g.* the rate of setting, to be understood. If gelation occurs when the temperature is lowered, the velocity of the process will, of course, decrease with rise in the latter; at a given temperature an increase in the rate of setting will be observed when the concentration of the solution is increased[24]. If, however, the concentration of the solution is equal to that of the gel, obtained by syneresis, gelation will occur instantaneously when the temperature is lowered[9].

The following conclusions concerning the fundamental conditions for gelation can be drawn from what has been said above. It occurs only when there is limited solubility of a polymer in a solvent. Therefore all factors affecting the solubility of the polymer also influence the process of gelation. However, gelation is not related solely to the loss of solubility. A necessary condition for it is the formation of a continuous spatial network of macromolecules interacting with one another. As a result of this, it is gelation and not precipitation which occurs when the solubility is decreased. Any additive in the solution which favours the formation of intermolecular bonds will promote gelation. Finally, the capacity for gelation is closely linked with the chain structure of the polymer molecules, which is a ncessary condition for the production of the continuous three-dimensional gel network covering the whole volume of the system.

3. THERMODYNAMICS OF GELATION

The setting of a gel resulting from a change in the external conditions is a spontaneous process accompanied by a decrease in the free energy of the system: $\Delta F < 0$. Since bonds are formed between individual macromolecules in the polymer in solution, producing relatively ordered secondary structures, the process of gelation involves both a decrease in the heat content and a decrease in the entropy of the system. The latter is enlarged also by the reduction in the flexibility of the chains due to the formation of intermolecular bonds, which results in a decrease in the number of possible configurations available to the macromolecule.

At the present time sufficient experimental evidence has accumulated to support the occurence of heat effects during gelation. Such results have been obtained by Lottermoser[25], Fischer[26], and Lipatov[27,28]. Recently this question has been resuscitated in the literature in connection with work[29] in which no heat effects were observed to accompany setting. We consider, however, that the assumptions underlying this work cannot be valid, although they start from a purely thermodynamic consideration of the question.

The experimental determination of heats of gelation involves several difficulties. It has been shown[30] that the magnitude of the heat effect accompanying setting depends on several factors, the most important being the homogeneity of the original polymer and its purity. Fractionation and careful purification of the polymer result in greater heat effects being observed during gelation and the gel passing into solution over a narrower temperature range on

heating than when these criteria are not observed. Another factor making it difficult to determine exact values of heats of setting is the possibility that bonds which differ both in nature and in stability are formed during the process. It is also necessary to remember that the process takes time to occur, and the evolution of heat occurs gradually[31]. In view of the experimental difficulties associated with the direct determination of heats of setting, other methods were employed.

Eldridge and Ferry[32] have estimated heats of gelation for gelatin gels. They deduced an equation linking the melting point of the gels (the temperature at which the gel passed into a solution on heating) with the concentration of the gel, its final form being

$$\log C = -\Delta H/RT + \text{const},$$

where ΔH is the heat of gelation, T the melting point, and C the concentration. This equation was derived by regarding gelation as analogous to processes of polycondensation of bi- and multi-functional monomers, which under certain conditions form a continuous spatial structure. ΔH is regarded as a heat of reaction:

2 moles of cross-linking points → 1 mole of cross-links.

The formation of cross-links is likened to a process of binary association:

$$m_1 + m_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} m.$$

In the case of gelation at low temperatures, the forward reaction takes place, so that $k_1 > k_2$ and $K = k_1/k_2 > 1$. When the temperature is raised the reverse reaction takes place, and $K < 1$, *i.e.* the value of K decreases with rise in temperature, and the equilibrium is displaced causing rupture of the bonds formed at the lower temperature. Values of ΔH = 73 and 220 kcal mole^{-1} were found for gels of gelatin which had been kept at 0° and 15° before melting. It is evident from these data that the conditions of preparation of the jelly and its aging have a considerable effect on the magnitude of ΔH, which these workers ascribe to differences in stability of the bonds which are formed. Thus the estimate of the heats of rupture of the structural lattice of the gel using the method suggested by Ferry is quite indefinite in character, which in our opinion is due to jellies being investigated while in a non-equilibrium condition.

If it is supposed, as was done in the work referred to, that the bonds which are formed are hydrogen bonds, it turns out that each cross-link is formed by 10–45 hydrogen bonds. This, of course, is physically impossible, and can only mean that, at the intersections of the three-dimensional network of the gel, there are secondary structures formed by the polymer molecules and having a definite degree of order.

Meerson and Lipatov[28] estimated the heats of fusion of the gels by using Flory's equation[33] for the heats of fusion of crystalline polymers in the presence of solvents. This method gave values of 61 kcal mole^{-1} for dilute gelatin gels and 90 kcal mole^{-1} for the concentrated gels. These values are somewhat lower than those found by Ferry[32], obviously because of the factors already discussed. A direct determination has been made[28] of the heat of fusion of a gel by determining its heat of solution in urea solution at 20° and the heat of mixing of the (polymer) solution with urea solution at 70°. The difference in the heats of solution at these temperatures gives the heat of fusion of the jelly, provided, of course, that the heats of solution of the gel and of mixing of the solutions are independent of temperature. The method suggested by Ferry[32] for determining heats of gelation has been also employed[34] for aqueous and hydrochloric-acid solutions of poly(methacrylic acid).

In view of all the work reported above, it is obvious that we can strictly speak of a definite melting point of a gel, or of a temperature at which it passes into solution, only in the case of dilute gels, in which rupture of the bonds in the structural network occurs quite rapidly. The passage of more concentrated gels into solution usually occurs over a certain range of temperature. Here both the heat of gelation and the temperature of the transition depend not only on the nature of the bonds in the gel but also on the conditions of gelation. During the aging of gels the heat of disintegration of the network structure increases and the temperature of fusion rises, as has been shown by Zubov and Kargin[14,15] in the case of gelatin gels and by Walter[35] for poly(vinyl chloride).

Gels are characterised by a lack of agreement between the temperatures at which they set and those at which they melt. According to Zubov[16], this is explained by the occurrence, during the aging of concentrated gels, of extremely slow processes of stress relaxation, which affect the gel structure as a whole. Another cause of variation in the transition temperatures of gels into solutions may be the increase in stability of intermolecular bonds occurring during aging[32], which, however, can be regarded as a result of the relaxation process.

The applicability of several thermodynamic relationships to the melting of gels and the occurrence of a heat effect in this process raise the possibility of regarding the melting of jellies as a phase transition. Several experimental data provide grounds for such a view. Thus the dependence of the specific volume of gels on temperature is characterised by the occurrence of a point of inflection coinciding with the melting point determined visually. In several cases such a curve has a shape characteristic of crystalline polymers[28]. The view that the melting of jellies involves a phase transition is developed by Boedtker and Doty[36] in a long paper concerned with gelation in gelatin. The concept of phase transitions occurring in gels on fusion has been developed also by Flory[37]. He regards the relationships which he has observed for the change in specific volume with temperature in the collagen–glycol and gelatin–water systems as criteria for the occurrence of a phase transition of the first kind. This conclusion is supported by the applicability to the fusion of gels of the equation for the melting points of crystalline polymers. The occurrence of changes in the volume of a gel on melting[38,39] also indicates the possibility of phase transitions.

In spite of this work, the question of the occurrence of phase transitions in the fusion of gels cannot be regarded as settled. It is quite obvious, however, that the melting of a gel cannot be compared with the fusion of a crystalline polymer, where the phase transition is accompanied by a sharp change in the degree of order of the system, the melting point and the heat of fusion being completely definite thermodynamic quantities. Consequently the melting of gels cannot be regarded as a phase transition of the first kind. On the other hand, it is clear that the disintegration of the structural network of a gel leads to a definite change in the heat content of the system and to a certain change in its degree of order. Therefore the question of the thermodynamic nature of the conversion of a gel into a solution requires still further investigation.

The question of the occurrence of phase transitions in gels is closely linked to the question, repeatedly discussed in the literature, as to whether a polymeric gel represents a one- or a two-phase system. The work of Kargin *et al.*[5] was the first to show clearly the applicability of the phase rule to polymer solutions, and it has been established that under certain conditions two phases are formed in solution, namely a solution of the polymer in the solvent and a solution of the solvent in the polymer, *i.e.* a gel. It is known from Lipatov's papers[9,40] that setting occurs *via* a series of successive stages, with the system finally undergoing syneresis, *i.e.* separation into two equilibrium phases, represented by the gel and a solution of the polymer above the gel. Syneresis has been shown[30] to yield a gel having the same composition as that obtained when the polymer swells in the solvent. Only a gel which can be obtained by independent paths from different sides, *i.e.* by swelling and by setting, can be in thermodynamic equilibrium. The gel formed when a system separates into two phases satisfies this condition, and is consequently an equilibrium gel. In this case, since we have a two-phase system consisting of two components with two degrees of freedom (temperature and pressure), it is obvious that the equilibrium gel is a single-phase, two-component system.

But how must we regard gels which, owing to the extreme slowness of the changes, do not exhibit syneresis on setting? Since the phase rule is inapplicable to non-equilibrium systems, the number of phases in such systems can be judged only indirectly. According to Papkov[7,41] a gel is formed when a single-phase system, a polymer solution, passes into a region of separation into layers. Below the critical solution point, when separation has not yet occurred, we obviously have a two-phase system. The concept of a two-phase structure for jellies has been developed also by Sharkov[42]. It can be concluded from the published results that a non-equilibrium gel is a two-phase system, but an equilibrium gel is a thermodynamically stable single-phase two-component system. Formation of equilibrium gels is accompanied by a definite change in the thermodynamic parameters characterising the system. However, the possibility of applying a series of thermodynamic relationships describing phase transitions to gels does not yet provide grounds for regarding the melting of gels as a phase transition of the first kind accompanied by a sharp change in the order of the system and characterised by rigorously defined thermodynamic parameters.

4. MECHANISM OF GELATION

The process of gelation, *i.e.* the transition from a solution to a jelly, can be arbitrarily divided into two stages. The first is characterised by a considerable increase in the viscosity of the system, but on the whole the system still retains the inherent properties of solutions. The second stage begins from the moment of the appearance of elasticity, *i.e.* the start of the development of the properties of a solid. Subsequently the elasticity gradually increases and reaches a limiting value, determined by the conditions of gelation. From this point of view gelation can obviously be described as a process of the gradual arrangement of the macromolecules in solution into secondary structures with subsequent interaction between the latter to form a continuous three-dimensional structure.

Papers published during recent years have examined the transition from solution to gel by analogy with the formation of three-dimensional structures in the polycondensation of bi- and multi-functional molecules or with the cross-linking of linear molecules. Such a view has a definite physical meaning. This question is discussed quantitatively in papers by Flory[43] and Stockmayer[44]. It is assumed in these papers that combination of the macromolecules with one another is initially accompanied by a change in viscosity, and then, at the gel point, all the molecules combine to form a single three-dimensional structure. This instant corresponds to the appearance of elastic properties. The position of the gel point is determined by the presence of the minimum number of intermolecular bonds which are sufficient for the formation of the three-dimensional structure. When the gel point is reached, further growth occurs in the number of intermolecular bonds in the system, leading to an increase in the strength of the network.

In spite of the great similarity between processes of gelation and the formation of three-dimensional structures during polycondensation, the Flory–Stockmayer theory can be employed only for a qualitative description of the former process. This is because gelation is accompanied by the formation of both intra- and inter-molecular bonds, and the character of the process depends on their relative proportions. Further, it is supposed that the bonds between the molecules are local in character: there are bonds between two active groups (*e.g.* hydrogen bonds). The knowledge now available concerning the structure of polymers in solution and in the solid phase, obtained thanks to the work of Kargin and his school, enables an explanation to be given also for the existence of bonds which are not localised at a single point. The existence of such non-localised bonds had been pointed out by Ferry[2].

An experimental demonstration of the two stages into which gelation can be divided has been given in the work of Lipatov and Lapin[45] and has been shown[46] by means of heating and cooling curves. The presence of two maxima on the curves when setting occurs was explained by the initial formation of weaker bonds followed by that of stronger bonds, actually responsible for gel formation. The presence of two types of bonds differing in strength has also been pointed out in other papers[2,28]. These results can be interpreted as due to the formation of secondary structures from macromolecules arranged in a definite fashion during the early stages of gelation. It is perfectly obvious that the creation of such structures, in the form of stable clusters or groups of molecules, is necessary for gelation from dilute solutions. The existence of such structures is confirmed by early work on the turbidity of solutions during setting[47,48] and by the work of Boedtker and Doty[36], who showed from light scattering measurements that molecular aggregates in gelatin solutions exist even at great dilutions, their size and number increasing continuously with increase in the concentration of the solution. It was shown that these aggregates do not break down even at great dilutions or when the solutions are slightly heated. It was also observed that the change in light scattering ceases appreciably before the structural network of the gel is formed. On this basis it was concluded that the initial stage of gelation involves the formation of aggregates, which then link together to form a continuous three-dimensional structure. The stability of the aggregates at great dilutions has been shown also by Beyer[49]. Electron-microscopic investigations[50] have provided a direct demonstration of the existence of secondary structures, in the form of globules or bundles of uncoiled chains, even in dilute solutions. It was shown that the presence of such secondary structures in

solutions was a consequence of the bundle structure of amorphous polymers. Thus these papers make it possible to establish some link between the structure of solid polymers and that of concentrated and dilute polymer solutions.

It is reasonable that the processes producing the secondary structures in solution (or aggregates according to Doty) should be affected by the same factors as those governing gelation. According to Doty[36] the formation of such aggregates involves a certain degree of order in the arrangement of the macromolecules in the aggregate. In this sense he speaks of an analogy between the processes of gelation and of crystallisation. Such an analogy, however, is completely without substance. The work of Kargin and Slonimskii[51,52] has firmly established the differences between crystallisation in high polymers and order–disorder processes, and has shown that even a very high degree of order in the molecular chains does not give grounds for regarding a polymer as crystalline. It is still less possible to speak of the existence of crystalline structures in polymer solutions and gels.

According to Doty[36], the second stage of gelation consists in the linking of the aggregates together in the course of their growth to form a three-dimensional structure. In conformity with this he considers that the melting of gels involves the simultaneous occurrence of two processes: (1) rupture of the bonds in the three-dimensional network of the gel, resulting in the aggregates being set free, and (2) rupture of the bonds between the molecules within the aggregates. Such a view is confirmed by the presence of molecular aggregates in solutions obtained by the melting of gels.

The nature of the bonds responsible for gelation has been discussed in the literature in particularly great detail in connection with gels of gelatin, owing to the complex chemical character of this material. In fact, the formation of different types of bonds – electrostatic, bonds between non-polar groups, bonds between polar groups, hydrogen bonds involving peptide groups in the chain, etc. – is possible in gelatin. It has been established that electrostatic forces play a negligible part in the setting process, since the temperature at which gelatin solutions set is independent of pH.[53]

The marked effect of such additives as urea and acetamide[54] on the melting point of gelatin gels, and the slight effect of introducing non-polar additives[15,16] led to the conclusion that intermolecular interaction in gelatin gels is due to the formation of bonds primarily between polar groups in the macromolecules[15]. According to another point of view[9,55] gelatin gels are formed by the interaction of macromolecules through their non-polar groups, since polar groups react with water, and the formation of bonds between them would presuppose that desolvation occurs, for which there is no evidence[31]. The formation of bonds between polar groups may be assumed even in a polar solvent, but this would require that the bonding energy of the polar groups of the macromolecules among themselves should be greater than the bonding energy of these groups with solvent molecules. These differences in viewpoint are associated with the extremely complicated chemical nature of gelatin. The formation of gelatin gels is probably due to various types of bonding, including bonds between several of the polar groups present in gelatin. In this connection particular interest attaches to an investigation[56] of the effect of various additives (salts of inorganic and organic acids) on the melting point of gelatin gels which have been chemically modified in a definite manner. It was shown that a chemical change in the gelatin molecules entailing bonding to polar groups (acetylation of amino-groups, nitration of guanidino-groups, sulphonation and acetylation of hydroxyl groups, and esterification of carboxyl groups) has no appreciable effect in changing the melting point of the gel of the modified gelatin. It was concluded from this that the above groups play no essential part in gelation. Therefore the action of the additives investigated is associated either with their effect on the non-polar parts of the molecule (in the case of additions of organic ions) or with that on the links between the peptide groups. It is assumed that formation of hydrogen bonds between peptide groups in different chains is the main cause of gelation in the case of gelatin.

Doty[36] also regards the formation of hydrogen bonds between gelatin molecules as the main cause of the formation of aggregates, but he assumes that in gelation the intersections of the network are not local bonds but ordered portions of the chains linked by hydrogen bonds. Thus an examination of existing views as to the mechanism of gelation in polymer solutions leads to the conclusion that this process consists in the formation of stable intermolecular bonds of both localised (*e.g.* hydrogen) and non-localised (*e.g.* van der Waals) types. Here the essential part in the formation of a three-dimensional network is played not by the mutual interaction of individual molecular chains but by the interaction of secondary structures – aggregates of molecules or bundles of molecular chains – existing in concentrated solutions.

5. DEGREE OF ORDERING OF MACROMOLECULES IN GELS

When considering the mechanism of gelation we have already remarked that a necessary condition for the process is the formation in solution of secondary structures, in which the polymer molecules are arranged in a definite manner relative to one another. In addition, we emphasised that such ordering cannot in any way be confused with crystallinity. The occurrence of highly ordered regions in supersaturated solutions leads, as already noted, to precipitation.

Furthermore X-rays have repeatedly demonstrated the presence of definite regions of ordered arrangement of macromolecules in gels, such data being given in the review by Ferry[2]. We feel that the cause of such regularity is the presence in solution of secondary structures, the existence of which has been demonstrated recently by Kargin *et al.*[57,58] They have established that these bundles of uncoiled molecules are stable structures, characterised by a quite definite degree of order in the arrangement of the polymer molecules in them. Kargin *et al.*[57] have put forward the hypothesis that amorphous polymers have a bundle structure. The ideas developed in these papers allow us to make a fresh approach to several aspects of the problem of gelation, and in particular to explain how equilibrium gels of identical structure can be obtained by swelling and by setting. Until recently it was supposed that molecules in solution are irregularly arranged relative to one another, and that in amorphous polymers also there is complete disorder in the mutual entanglement of the chains. On swelling, *i.e.* on penetration of solvent into the polymer, the entropy of mixing of the polymer with the solvent increases and the entropy of the polymer network decreases

owing to deformation of the chains and their transition to more extended conformations. At the instant at which these quantities are in equilibrium, the process of swelling ceases. Such a picture, which is valid for cross-linked polymers, cannot be extended to all polymers. In the discussion mentioned above it was obscure in what way, in the formation of the equilibrium gel by setting, transition occurs from the coiled configurations of molecules in solution to the uncoiled configurations with the formation of an extended network, similar to that obtained on swelling. Only with the development of ideas on the bundle structure of polymers does it become possible to explain these phenomena. Polymers in a condensed state are supposed[57] to represent a system of entangled bundles able under certain conditions, *e.g.* on stretching, to change their shape, to uncoil and to straighten out. On the basis of these ideas we may suppose that the swelling of a polymer involves rupture of the bonds between individual bundles of molecules, a change in their shape, and the establishment of a new arrangement of the bundles in the swollen polymer, with the individuality of the bundles to some extent preserved. On the other hand, since the molecular bundles may exist also in solution, it is easy to imagine that, on setting, bonds will be formed between them, leading to a structure similar to that obtained on swelling. On such a view we must remember that a change in the shape of the molecules with a change in the nature of the solvent will not always lead to the same effects in concentrated as in dilute solutions, since in the former the intermolecular interaction may greatly impede a change in shape of the molecules, as will also the entry of a molecule into a bundle. It may therefore be accepted that, when the solvent deteriorates, *i.e.* in the process of gelation, molecules are not displaced, as occurs in dilute solutions, but interaction between the chain bundles is intensified, leading ultimately to the production of a continuous three-dimensional network.

Papkov[41] regards the structure of a non-equilibrium gel consisting of two phases as analogous to that of an emulsion in which the low-viscosity phase (*i.e.* the solvent) forms spherical particles in the high-viscosity phase (*i.e.* the polymer). In the light of the ideas considered above, it is impossible to agree with such a view. The structure suggested by Papkov for a gel does not explain either the fact that a gel can be obtained by two independent paths, or the similarity in mechanical properties of jellies formed by intermolecular and by chemical bonds. Nor does this scheme explain the complex of relaxation properties of jellies, and takes no account of the possibility of obtaining single-phase equilibrium gels. Finally, these concepts disregard thixotropic systems, in which the bonds between the molecules are similar in nature to those in ordinary, thermally reversible gels.

Thus existing views as to the structures of amorphous polymers and of gels lead us to conclude that there is an appreciable degree of order in the arrangement of molecules in gels. This regularity is due to the existence in solution of stable secondary structures of the type of aggregates or bundles of molecules having a definite degree of order, which, however, cannot be compared with the order characteristic of crystalline polymers.

6. RELATIONSHIP BETWEEN STRUCTURE AND MECHANICAL PROPERTIES OF GELS

The views considered above as to the nature of gels are confirmed by existing knowledge of their mechanical properties.

The formation of three-dimensional network structures involves the creation of a sufficient number of stable intermolecular bonds. Consequently the physical properties of gels will depend on the number and nature of the intermolecular bonds, as well as on the nature of the polymer and the solvent. In their most general form the mechanical properties of polymer gels are analogous to those of cross-linked polymers, and are determined by the deformations of the portions of the chain molecules situated between intersections in the three-dimensional network of the gel. The elastic properties of gels are explained by a change in shape of portions of the chains on deformation, *i.e.* they have the character of rubberlike elasticity. The nature of deformations occurring in polymer gels has been studied in detail[14-16]. It has been shown that the elasticity of jellies involves a change in entropy. However, whereas in the case of polymers having a purely rubber-like elasticity a rise in temperature is accompanied by an increase in the equilibrium modulus of the system, with gels a change in temperature immediately leads to a change in the number and strength of the intermolecular bonds, as a result of which the rigidity of the system diminishes (with gels which melt on heating). The analogy between gels and the three-dimensional networks of cross-linked polymers gives us some idea of the effect of the number of bonds in the network on the mechanical properties of gels. These ideas are based on the kinetic theory of elasticity, which links the extent of deformations and the corresponding stresses with the temperature and the number of bonds in a network of flexible polymer chains[59]. However, the kinetic theory can give only a qualitative description of gels, since the three-dimensional network of a gel is more imperfect than a cross-linked polymer, owing to the greater number of intramolecular bonds formed on gelation in dilute solutions. In addition, the lower strength of bonds in gels leads to their rupture and redistribution, also disregarded by the kinetic theory. Further, whereas in cross-linked polymers the flexibility of the chains in the network is determined solely by their chemical nature and the temperature, in gels an important part is played also by the nature of the solvent, on which depend both the strength of the intermolecular bonds and the flexibility of chain segments which are not linked together.

Polymer gels are able to exhibit true elastic deformations, *i.e.* to obey Hooke's law right up to the melting point[60]. True elastic properties are associated with the presence of strong intermolecular bonds and with weak interaction between unlinked portions of the chains. Gels are always more elastic than solutions of equal concentration, since in the latter the possible elasticity is masked by flow. With respect to mechanical properties it is difficult to draw a sharp boundary line between a gel and a solution, since many solutions exhibit elastic properties below the limiting shear stress. An example of this is provided by thixotropic solutions, which possess a structure formed by unstable bonds which are broken on mechanical treatment. It is interesting that, at the start of gelation, immediately after the appearance of elasticity, all jellies possess thixotropic properties[61]. This points to a close relationship between thixotropic and ordinary (thermally-reversible) setting.

The presence of elastic properties allows gels to be characterised by their modulus of rigidity. Most papers on the mechanical properties of jellies have been concerned

with elucidating the dependence of this modulus on various factors. These questions have been investigated in detail by Zubov[16,15,54], Ferry[62,63], Sheppard[60], and Hirai[64,65]. The laws observed to govern the changes in mechanical properties confirm to a considerable extent the views of the structure of polymer gels which we have examined above. It is important to note here that the magnitude of the modulus of rigidity of a gel depends also on the method of preparation if it is not an equilibrium gel. Thus, at any instant before equilibrium is reached, the modulus of gels obtained from solutions by cooling is lower than that of a gel heated to the given temperature. This phenomenon is due to the slow establishment of equilibrium in gels with change in temperature. Whereas the cooling of a solution involves a slow process of the formation of bonds of different strengths with the selection of those characteristic of the given temperature, heating a gel formed at a lower temperature involves merely the rupture of those bonds which are unstable at the given temperature. A detailed investigation of the dependence of the mechanical properties of gelatin gels on the conditions under which they have been aged has been carried out by Rebinder and Ivanova-Chumakova[66].

We have discussed above the effect of various additives on gelation. Those additives which govern the process of setting also have a substantial effect on the mechanical properties of the gels[15,19,35,54,60,67,68]. The effect of adding a non-solvent on the rigidity of gels is governed by the fact that, when the solvent deteriorates, the total number and strength of the intermolecular bonds in the gel increase. On the other hand, successive replacement of the solvent in gels may be accompanied by a considerable increase in rigidity, obviously not due to a change in the number of bonds, since the volume of the gel remains unchanged during such replacement[69]. This is obviously due to a change in flexibility of the segments of the polymer chain between the intersections of the network, as the solvent deteriorates. On passing to a worse solvent these segments tend to contract, but this is prevented by the previously formed bonds in the network; as a result, these portions of the molecules are in a strained condition, which hinders their deformation.

The most interesting feature of the mechanical properties of gels is their relaxation behaviour, first studied thoroughly in the work of Zubov and Kargin already mentioned. The relaxation behaviour of gels differs from the behaviour of a polymer in a condensed state. There is a great difference in the character of the relaxation in dilute and in concentrated gels. The former obey Hooke's law over a wide range of rates of deformation, the magnitude of the deformation being independent of the time during which the forces have acted. This indicates that in dilute gels the free portions of the macromolecules between the joints in the network structure do not interact with one another. In contrast, concentrated gels exhibit a greater dependence of the extent of deformation on the rate of action of the forces the higher the concentration. In this case Hooke's law is no longer obeyed. Such behaviour is explained by an intensification of the intermolecular interaction of the portions of the chains situated between intersections in the three-dimensional network. A detailed characterisation of the properties of gels can be obtained also by investigating the relaxation of tension[61]. In the case of gelatin gels it has been shown that, under static conditions of investigation, the bonds in the gel do not break down under loads of short duration. But when the mechanical action is prolonged, a permanent set appears in gels, and appreciable stress relaxation is observed[66]. The relaxation of stresses at constant deformation and the presence of irreversible deformations can be due only to a relative displacement of the molecules of secondary structures forming the gels, which is possible only as a result of the rupture of the bonds between them. Obviously these effects are associated not so much with the relaxation of stresses by a change in shape of the chains, as with processes of relaxation of the bonds. The different rates of stress relaxation in gelatin gels under different conditions indicates the existence of bonds of different strengths. According to Ferry's data[63] the bonds in 6% gelatin gels are characterised by a set of relaxation times between 10^3 and 10^6 sec. Every temperature then has its own set of relaxation times, and a rise in temperature shifts the relaxation spectrum towards lower values. The concept of a set of bonds in gels is being developed at the present time also by Trapeznikov[70]. Stress relaxation in gels accompanied by the rupture of bonds between molecules and the resulting displacement of the latter is similar in character to the chemical relaxation of stress in cross-linked elastomers[71]. The relaxation properties of gels greatly depend on their methods of preparation. If the bonds are of great strength, they are characterised by great times of relaxation, and all factors promoting an increase in bond strength lengthen relaxation times.

An interesting feature of the relaxation behaviour of gels is that their rigidity remains unchanged during relaxation, *i.e.* that the total number of bonds does not change: in the place of the bonds which have been broken in the displacement of the molecules or structural units in the gel, new bonds of the same type are formed, but with different arrangements of the molecules. These bonds have the same distribution of relaxation times as those in the original gel[63].

Data on the mechanical properties of gels bring out their two peculiarities – the presence of reversible elastic deformations and their dependence on the conditions of formation of the gels, and the exhibition by gels of relaxation properties depending on the concentration of the gel. Data on the mechanical properties support the views of the structure of gels obtained in other ways, and enable these concepts to be considerably supplemented.

The main task in the study of concentrated solutions and their conversion into the gelatinous state is to investigate their structure in order to be able to control the properties of the solutions and gels, which is of great practical importance. The great advances made in the investigation of the structure of polymers in solution and in the condensed phase, and the discovery of the bundle structure of amorphous polymers, enable a fresh approach to this problem, which has not yet been completely solved, *i.e.* the structure of concentrated polymer solutions and gels. Although many questions have still to be cleared up, at the present time, conditions are suitable for a more complete investigation into the structure and properties of polymer gels, one of the most interesting systems formed by polymers.

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SODIUM NITROPRUSSIDE AND ITS USE IN ANALYSIS

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INTRODUCTION

Sodium nitroprusside, first prepared in 1850[1], has been used for over a century as a reagent in the qualitative and