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POLYMER GELS

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SUMMARY

The formation of various types of chemically and physically cross-linked gels is discussed. Modified mechanisms are proposed for the formation of permanently porous gels. Chemically cross-linked gels are suggested to arise mainly from locally high concentrations of pendant double bonds occurring as a result of incipient gel formation. In physically cross-linked systems, permanent porosity is suggested to be due to the formation of domains of mesomorphic phases. For gel formation to occur, molecules must participate in more than two such liquid crystalline domains.

INTRODUCTION

The ability of natural and synthetic polymers to form gels has been of considerable importance for the development of modern separation techniques. Many techniques, such as gel chromatography, various kinds of electrophoresis and membrane processes, are dependent on the structure of gels for their operation. In others, like affinity chromatography and ion exchange, the gels merely act as supports of the active groups. The development of gels has been rapid during the last two decades and has almost entirely been directed towards applications. As a consequence the understanding of the basic phenomena governing the structure of gels has suffered. In polymer science, the emphasis has been placed on gels formed from polymers cross-linked in undiluted form, such as rubbers and alkyds. These are well understood through the work of Flory¹ and others.

Gels are solids consisting of three-dimensional networks of polymers and a continuous liquid phase. The polymer framework gives the system its mechanical stability. It can be covalently bonded throughout ("chemically" cross-linked) or consist of long chain molecules united by secondary bonds ("physically" cross-linked), *e.g.*, in crystallites. Another way to categorize gels is by porosity, and the two main groups are then homogeneous and permanently porous (macroporous, macroreticular). The first group has relatively small pores and shrink when the solvent is removed. The second group can have very large pores and yet the liquid phase can be removed without collapse of the network. This terminology is not precise and many exceptions exist, *e.g.*, the agarose gels which have very large pores, are stiff and collapse when the continuous phase, water, is removed.

In the present paper we give an account of gel formation and gel structure as seen from the polymer scientist's point of view. Chemically and physically cross-linked gels are discussed, in particular, permanently porous gels for which mechanisms of formation are suggested.

CHEMICALLY CROSS-LINKED GELS

Homogeneous gels

Homogeneous gels are made by polymerization of monomers having a functionality higher than two, or by cross-linking of polymers. Both these processes can occur in solution or in the bulk phase. The numerous ways of making such gels or gel-forming substances have been reviewed, see, for example, ref. 2.

When in contact with a good solvent a homogeneous cross-linked polymer swells. The cross-links prevent the polymer from going into solution. Thermodynamically this can be expressed as the difference in Gibb's free energy between the swollen and the dry polymer network³:

$$\Delta G = \Delta G_m + \Delta G_{el} \quad (1)$$

The free energy of mixing, ΔG_m , is negative for a good solvent while the elastic free energy, ΔG_{el} , is positive and tends to contract the gel. When $\Delta G < 0$ the network swells until at least some polymers chains are fully extended and compensate the swelling pressure. For poorer solvents, $\Delta G_{el} > \Delta G_m$. The gel then contracts and solvent is exuded. This phenomenon is called syneresis and occurs because the polymer chains tend to change their conformation from an extended one to the most probable one, *i.e.*, where the conformational entropy is maximal. In a non-solvent, $\Delta G_m > 0$ and the polymer network collapses to give a non-porous solid.

A characteristic feature of the structure of homogeneous gels is that the polymer chains are separated and have a flexibility determined by the rotational freedom around the bonds of the chains and the distance between the cross-links. When the gel swells the chains separate and the segment concentration decreases. In the neighbourhood of the cross-links, separation is not possible without breaking covalent bonds. Thus microheterogeneities arise at the cross-links and also at entanglements. These heterogeneities probably account for the separation properties of homogeneous gels of the Sephadex type⁴.

Permanently porous gels

Many systems which yield gels with permanent porosity have been described. An early comprehensive review was given by Seidl *et al.*⁵. By far the most extensively studied system is the copolymerization of styrene and divinylbenzene (DVB) which was first developed for ion-exchange resins⁶ and later for gel chromatography by Moore⁷. Only the styrene-DVB system will be considered here.

Seidl *et al.*⁵ described three general ways to produce permanent porosity:

- (1) Polymerization in the presence of an inert polymer;
- (2) Polymerization in the presence of a solvent;
- (3) Polymerization in a solvent-non-solvent mixture.

In method 1 the inert polymer initially dissolved separates as microdroplets as

the polymerization proceeds. After the polymerization the inert polymer is extracted with a suitable solvent and the holes left constitute the porosity. The method does not give high porosity and is difficult to control.

In method 2 a solvent for the polymer and monomers is used to create the porosity. The following sequence of events can be distinguished. First, a polymer rich in pendant double bonds is formed since the first double bond in *p*-DVB copolymerizes readily⁸. At less than 10% conversion a gel is formed. Since the formation of a gel causes restriction in the mobility of the gel network, high local concentrations of double bonds will be formed along the polymer strands of the gel⁸. This causes polymerization to take place predominantly in the domains along the chains where the concentration of double bonds is highest. In consequence the initially formed network chains will form the basis of a framework as indicated in Fig. 1.

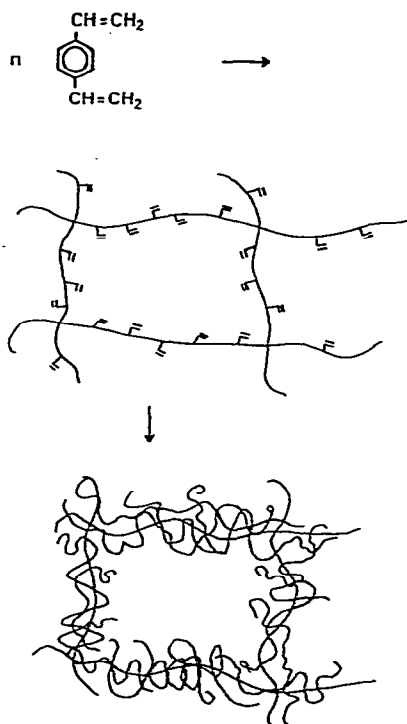


Fig. 1. Schematic representation of the processes leading to permanently porous chemically cross-linked gels.

As long as the concentration of double bonds is high in the framework, *i.e.*, the initial DVB concentration is high, the polymerization will predominantly take place there. This leads to a network increasingly cross-linked along the strands. The polymerization stops when the pendant double bonds for steric reasons can no longer participate in the reaction. This view is in accord with the observation of relatively large numbers of double bonds in porous gels⁹.

In method 3 we suggest that the following events take place. At low conversion a gel is formed⁹. Since the solvent still contains much monomer, ΔG is negative and the gel fills the volume of the drop. However, it is a homogeneous gel and collapses

when the solvent is removed⁹. As the polymerization progresses the solvent becomes less effective and ΔG_{e1} becomes of greater significance in the free energy expression. Before this happens, the polymer strands must have been stabilized to such an extent that they can support the gel structure, *i.e.*, they must have been cross-linked so that the chain mobility has been nullified. Further consumption of monomer reduces the ability of the solvent to dissolve the polymer and phase separation occurs. The monomer will then tend to dissolve in the polymer-rich phase and further polymerization will occur along the polymer strands already formed. The microspheres observed in electron microscopy are probably a result of the phase separation.

PHYSICALLY CROSS-LINKED GELS

Homogeneous gels

Many of the common thermoreversible gels belong to this class. Examples are gelatin, agar and carrageenan which form gels in water, polyacrylonitrile which gives gels together with polar solvents such as dimethyl sulphoxide and poly(vinyl chloride) (PVC), the plasticized varieties of which are nothing but thermoreversible gels. It is thought that similar phenomena are responsible for gel formation in all cases, namely the ability of the polymers to participate in the formation of ordered regions like crystallites. For a gel to be formed the molecules in the network must take part in more than two separate ordered regions. The forces holding the molecules together are secondary bonds acting cooperatively. These bonds can be broken by heating, without primary bond scission, *i.e.*, the gels can be melted.

The free energy of a solution of a polymer can be considered as the sum of contributions from segments of the polymer chain with different chemical composition or configuration

$$\Delta G_m = \Delta G_1 + \Delta G_2 + \Delta G_3 + \dots \quad (2)$$

where the indices refer to the different segments. Well above the gel melting point all the individual free energies are negative. As the temperature is lowered a point is reached where one of the segmental free energies becomes positive. The corresponding segments may have energetically more favourable conformations in crystallites while the total free energy of solution and those of other segments are still negative. If the concentration and the number per molecule of these segments are high enough a gel will form which is kept together by physical cross-links. Since the free energy of solution of the other segments is still negative, the chains between the cross-links will be extended from their most probable conformation.

Studies of gelation of PVC solutions in dioxane have shown that syndiotactic sequences of 10–12 vinyl chloride residues are responsible for gelation¹⁰. It has been shown by NMR spectroscopy that the number of such syndiotactic sequences is high enough to satisfy the condition of two per molecule¹⁰. For polyacrylonitrile, similar determinations have revealed that only 4–5 monomer residues are necessary for gel formation to occur¹¹.

In gelatin, amino acid sequences rich in amino acids are thought to be responsible for the initial gelation. Sequences less rich in amino acids help to increase the stability of the gels. The process is likely to be a partial reformation of collagen

triple helices¹². The sequences which cannot take part in helix formation keep the ordered regions apart since their free energies of mixing are still negative.

The formation of gels of carrageenan in water has been attributed to the occurrence of double helices¹³. In each molecule there are sequences capable of helix formation interspaced by kinks. They can be said to serve as joints between the ordered regions.

Permanently porous gels

Physically cross-linked gels having a permanently porous structure are often formed during wet-spinning and in membrane preparation. In both these processes a viscous polymer solution is coagulated, and under certain conditions a porous three-dimensional network is formed.

In good solvents only the free energy of segments with longer regular sequences can become positive ($\Delta G_1 > 0$ in eqn. 2). When this occurs elastic gels may be formed if the conditions mentioned above are fulfilled. In polymer solutions prepared from solvent–non-solvent mixtures other segmental free energies can also become positive ($\Delta G_2 > 0$ in eqn. 2). However, the total free energy of mixing can still be negative. This could lead to both gelation and the formation of a liquid crystalline phase.

In the light of the above discussion it becomes necessary to assign different interaction parameter (χ) values to different segments. Assuming that the segments can be treated as separate entities, the free energy can be expressed by Flory–Huggins theory. This theory states that, for a random coil polymer, the limit for incidence of phase separation is $\chi = 0.5$ at infinite molecular weight, while rigid rods having $X = 100$ separate at $\chi = 0.10$ ¹⁴. Thus a separation into a mesomorphic phase will occur in a solvent which is good for a random coil polymer.

The gelation process is, like other crystallization processes, influenced by the

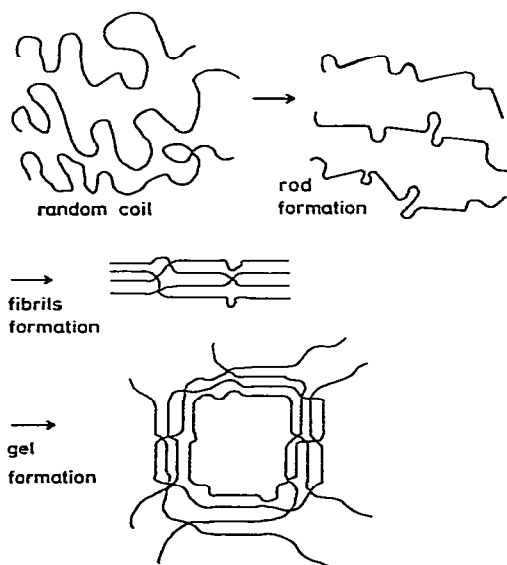


Fig. 2. Schematic representation of the processes leading to permanently porous physically cross-linked gels.

degree of supersaturation, while the formation of a liquid crystalline phase is, like other liquid-liquid phase separations, dependent on the non-solvent content. The processes leading to formation of permanently porous gels¹¹ during slow cooling of polymer solutions could thus schematically be described in the following manner (Fig. 2). First the polymer molecules change conformation from random coils to rod-like molecules. The latter then form a liquid crystalline phase, which will grow to give stable fibrils. In the last step a gel is formed due to the low degree of supersaturation in these solutions. The gel will be stabilized by the fibrils and this will prevent the collapse of the gel structure during drying. Such a process leads to the formation of a permanently porous gel.

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