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Madeleine D Jabourov, Katsuyoshi Nishinari and Simon B. Ross-Murphy
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1 Introduction

A number of high polymer systems can assemble to form networks and gels and this assembly can occur by a variety of mechanisms. Some of these involve chemical treatments and processes, others are largely physical in nature – it is on the latter that this volume is focused. In this introductory chapter we consider the nature of polymer gels and networks, the processes of assembly, their characterization by physical methods and the coverage of succeeding chapters.

1.1 Gels from colloidal and polymer networks: a brief survey

Traditional colloidal gels were first investigated by Thomas Graham in the Philosophical Transactions of the Royal Society (Graham, 1861). Graham proposed a definition of substances according to their diffusive power. Colloidal substances (from the Greek κολλα, ‘glue’) are slowly diffusing substances, held together in solution by what he termed ‘feeble forces’. In the classification of these substances Graham included hydrated silicic acid, hydrated alumina, starch, gelatin, albumen and gum.

Graham continued his discourse, saying ‘opposed to the colloidal, is the crystalline condition, the distinction is no doubt of one of intimate molecular constitution’, although the means of characterizing the latter were not available at that time. This very profound introduction to the colloidal state also includes this following intuitive statement: ‘another eminently characteristic quality of colloids is their mutability’, that is to say their ability to change. He writes: ‘Their existence is a continued metastasis’, i.e. again capable of change, which immediately points towards the current fully accepted difficulties in characterizing this particular state of the matter. He was also the first to recognize the specificity of the colloidal state and even went as far as suggesting that ‘it is the source of vitality’ revealing the mystery of life!

Efforts to analyse the colloidal state appear again in 1899, in a paper by W. B. Hardy with the subtitle ‘The Structure of Colloidal Matter and the Mechanism of Setting and of Coagulation’. He addressed in particular the question of the effect of the fixing reagents used in cell observation:

> I would start the discussion with no statement as to the nature of cell-protoplasm other than that it is, as Dujardin described it, ‘glutinous’. Now this glutinous character is a special characteristic of that state of matter to which Graham applied the word ‘colloidal’. This statement holds without modification whether the initial stage, that is the soluble colloid, be entirely fluid (colloidal

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> solution), entirely solid (jelly), or a mixture of the two; or whether the physical change is or is not accompanied by chemical change.

He recalls also that:

> Graham's nomenclature is as follows: The fluid state, colloidal solution, is the 'sol', the solid state the 'gel'. The fluid constituent is indicated by a prefix. Thus an aqueous solution of gelatin is a 'hydrosol', and on setting it becomes a 'hydrogel'.

This nomenclature is still largely valid nowadays, other extensions having been introduced. Gelatin, in some ways the paradigm hydrogel, and which derives its name directly from 'gel', is produced by hydrolysis of collagen, so gelatin gels were probably recognized by early man during cooking, much before their properties were understood.

Gelation was initially regarded in the same light for supersaturated solutions of inorganic compounds or natural polymers, although now the two are regarded very differently. Natural rubber gave the first estimate of molecular mass (referred to informally, and in the early literature, as 'molecular weight') in the thousands of daltons, but these were then largely dismissed and so posed the question of the nature of such molecules. Paul J. Flory wrote: 'The gap between molecules of ordinary size and those of hundreds or thousands times as large was too great to be bridged in a single leap' (Flory, 1953). Indeed, recognition of polymer molecules (macromolecules) came much later, when Hermann Staudinger, against the views of many of his contemporaries, asserted the existence of covalently bound long chains (Mülhaupt, 2004). Rubber, gelatin and cellulose were all considered to belong to this category. The gels described in this volume mostly involve such polymeric chains. Covalently bound polymer networks became very important in polymer science, since, depending upon conditions, they can form 'rubber-like' elastomers – they often show high elasticity – rigid resins or foams. According to Treloar (1975) such elastomer systems, for example, have been studied for many years, going back to the work of Gough and Joule in the nineteenth century. In excess of solvent such a polymer network no longer dissolves; instead it simply swells – often, but not exclusively, since this depends on the polymer–solvent system – to fill the volume of its container. The solvent can be replaced by another fluid inside the network, giving rise to macroscopic changes of gel volume either by swelling or by shrinking

Covalently linked networks are permanent, since the junctions can be assumed to be formed irreversibly; in physical networks the junctions are sometimes irreversible even though they do not involve covalent linkages (Ca alginates or, heat-set protein gels), but they can also sometimes associate or dissociate reversibly under thermodynamic (temperature, pH, ionic strength) or mechanical action (shear, elongation), depending on their species and mode of formation. In fact any definition of physical gels which simply implies shear or temperature reversibility is far too narrow. As we will see below, some of the systems of interest to us *are* reversible when they are subject to, for example, stirring ('shear'), others are temperature reversible, but some are neither of these. Many papers, particularly some theoretical papers, seem not to have grasped this essential facet.

That said, the widely cited definition by Dorothy Jordan Lloyd that 'the colloidal condition, the gel, is one which is easier to recognise than to define' (Jordan Lloyd, 1926) still reflects the unclear description. An early, more formal classification of the gel state was noted by Hermans (1949), but still stresses the traditional colloidal viewpoint. According to Hermans' definition:

- Gels should be coherent two-component systems formed by solid substances finely dispersed or dissolved in a solvent.
- They should exhibit solid-like behaviour.
- The dispersed component and the solvent should extend continuously throughout the whole system (bicontinuous systems).

In an earlier review (Djabourov, 1988), four different structures were illustrated: aggregates of colloidal particles, with crystalline or amorphous structures; frameworks of rod-like particles as in supersaturated solutions; polymer gels with long linear chains held together by physical bonds such as 'crystalline junction zones'; and covalent bonds.

1.2 Structural characteristics and their study

At a Royal Society of Chemistry Faraday Division Meeting, Flory (1974) proposed a structural classification of gels which has some features in common with Hermans' definition, but with more emphasis on specifically polymeric systems:

- Well-ordered lamellar structure, including gel mesophases
- Covalent polymeric networks, completely disordered
- Polymer networks formed through physical aggregation, predominantly disordered, but with regions of local order
- Particular, disordered structures.

In the present volume we are concerned with aspects of all of these classes, although, as we have already stated, the second of these, the so-called chemical gels, although very important, falls naturally outside the definition of a physical gel. Instead we will be concerned with the other three types. Incidentally, the term 'physical gel' itself has not been in existence for that long: although it is difficult to establish quite who first coined the term, it seems to go back to the early 1970s, to Pierre-Gilles de Gennes.

At a later Faraday Division Meeting, Andrew Keller, another distinguished polymer scientist, noted (Keller, 1995) that

> there is no simple and unique definition of the gel state. Its main constituent is a fluid, yet it retains its shape, which is a characteristic feature of the solid state matter. It can support large strains to a high elastic limit, which, however, a real solid cannot do. Everyday one can experience that a jelly wobbles! The retention of shape implies a connectedness of the system which, in view of the fact that the major component is a fluid, means that there is a connective pathway along the non-fluid component which is the existence of a 'network'.

Consequently he coined a further definition in which gels were 'fluid containing self supporting disperse systems where the non-fluid connecting elements are not confined to individual chain molecules but can also be larger assemblies of molecules, finely divided struts or even membranes of the appropriate solid phase'.

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Despite the above definitions, we need to clarify that many of the systems described as ‘gels’, such as shower gels and pain relief or topical gels, are often not gels even in terms of the various descriptions above. For example, in the cosmetic and pharmaceutical area, the term ‘hydrogel’ is widely employed. The ‘hydro’ part of this again shows that the solvent is water or electrolyte, but the ‘gel’ part, by contrast, does not always require that the underlying structures are of the types of network defined above. Instead, in some of these application areas, this term has been applied rather more broadly to just ‘simple’ viscous solutions. The importance of this distinction is introduced below, and detailed in Chapters 2, 3 and 4. Noting how widely the term is applied in the external literature, we will still use the term ‘hydrogel’ in this volume, but underline the necessary caveat that we are using it implicitly in a more restricted sense than some workers in these application areas.

1.2.1 Solids versus liquids

What should be clear from almost all of the definitions given above is that a gel has some solid or solid-like characteristics, but the field is not made easier by the number of different terms employed. These include hydrogel, as already noted, microgel, nanogel, strong gel, weak gel, fluid gel, topical gel and liquid gel.

A further question must be considered: if a gel is solid-like, then what constitutes a solid? This is not as straightforward a distinction as might at first be thought. For example, some materials, such as pitch or bitumen, appear to be solids, but are actually flowing, although their rate of flow is obviously extremely small. In the famous pitch drop experiment, for example, one drop falls approximately every decade.[1] At the same time, some unfortunate jumping off a very high river bridge dies not of drowning but of multiple fractures, since over very short times water responds like a solid. This underlies the reality that almost all materials are actually ‘viscoelastic’ – they combine both liquid (viscous) and solid (elastic) properties, and which of these dominates tends to depend on factors such as temperature (and pressure) and the duration of observation. In practice most conscious human activities correspond to time scales from, say, 0.1 s up to tens of seconds, so specialist instruments that sample over much shorter or much longer time scales (Chapter 2) tend to be much better at making distinctions such as ‘solid’ versus ‘liquid’.

In fact the transition from liquid to solid – the sol–gel transition – has been quite extensively studied. This is examined in Chapter 3, including a discussion of the best way to determine the characteristics of the transition. In food applications, a very traditional area of use for gels, there are many methods recommended for beginners when preparing jams, marmalades or creamy desserts, for example, to produce soft creams or wobbling solids rather than a viscous, sticky, unpleasant, lumpy texture. Every country has its own recipes, because gel textures are appreciated in food preparation everywhere.

For a long while it was thought that simply inverting a tube was an appropriate laboratory technique. Indeed, even today this approach is sometimes still used, not

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[1] http://en.wikipedia.org/wiki/Pitch_drop_experiment

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least because it is both cheap and easy. Slightly more sophisticated methods, which involve capillary tubes or falling ball methods, have subsequently been proposed. However, except for quick screening of systems, these approaches are little exploited nowadays, and the science of rheology – now understood as the study of the mechanical behaviour of liquids and solids – has been exploited instead.

In fact there have been a number of attempts to define the nature of a gel in more formal 'rheological' terms, including by the late John Ferry (1980) and more recently by Burchard and Ross-Murphy (1990), Almdal *et al*. (1993) and Nishinari (2009). All of these definitions are in terms of the mechanical (rheological) properties of the materials in question, and the response of a gel to deformation (for example shear) and time, as detailed in later chapters.

However, the easiest of these defnitions to explain is that of Ferry, who requires that a gel is not able to sustain a steady-state flow. In other words, when it is subjected to a steady flow-rate experiment, for example stirring at a constant rate, it will tend to fracture or rupture, as we would expect for a solid, rather than to flow like a liquid. Unfortunately this definition excludes some systems of interest to us, and so appears to be too narrow. Two later approaches (Burchard and Ross-Murphy, 1990; Almdal *et al*., 1993) try to represent gel characteristics in terms of response of the material over time.

The recent article by Nishinari (2009) re-addresses the rheological definition of a gel and its various arguments and counter-arguments. In the end he cites te Nijenhuis (1997), who was obliged to conclude, along the lines of Jordan Lloyd, that 'a gel is a gel, as long as one cannot prove that it is not a gel'. Nevertheless he makes the important point that a gel can be defined both by its mechanical behaviour and by its structural features. Succeeding sections will try to maintain this structure–property linkage.

1.2.2 Multidisciplinary nature of gel studies

The implicit structural complexity in all these definitions should already have established to the reader's satisfaction that the study of gels is a highly multidisciplinary activity. Indeed we can enumerate the disciplines of direct relevance to the study of physical gels and of their formation, gelation, as follows:

- Gels are an aspect of macromolecular science: polymeric chains are needed to create a network.
- Gels are an aspect of colloid science: aggregation and association of small particles (or macromolecules such as globular proteins) can lead to physical and colloidal gels.
- Mathematical treatments of networks are needed to describe their topology. The network itself may become a mathematical abstraction (like self-avoiding walks), while issues of criticality (gelation and the gel point) are related to other problems in statistical physics.
- Mechanical behaviour: rubber elasticity is expected for networks from flexible chains. When the network includes rod-like chain elements or more rigid connecting elements, things become more complicated. Although the matrix is a fluid, we may consider an analogy with composite materials, where the network is the filler.

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- Thermodynamics: in chemical networks, swelling behaviour is related to polymer–solvent interaction properties. In physical gels, partial crystallization, phase separation, glass transition, conformational changes and solubility limitations are also related to thermodynamics.
- A range of spectroscopic and other characterization techniques must be used to measure both static and dynamic characteristics of networks: structure, size of the junctions, their spatial distribution, connectedness and time-dependent properties.
- The wide range of technological applications gives rise to specific investigations related to the functional properties of gels: their texture in food materials, controlled-release drug delivery capacity for biomedical applications, adhesion on various surfaces and the production of new materials.

Overall, then, this book describes structure–property relationships for the class of materials known as physical gels. These are formed by a sequence of local processes or mechanisms that create a partial and/or localized aggregation of the polymers in solution. For reasons of relevance (and space) we discard from our scrutiny other types of polymeric gels, including the chemical gels already mentioned, hybrid gels containing both organic polymers and inorganic particles, and purely inorganic gels. However, since some of these were also included in the Flory classification, we need to mention, albeit briefly, their characteristics and relations with the systems of direct interest here.

1.3 Non-physical gels

This somewhat humorous title reflects not that the excluded gel types do not exist, but simply that they lie outside the scope of this volume. Many have been covered in depth elsewhere, and for the interested reader we include at the end of this chapter a brief bibliography, in addition to the more specific list of references.

1.3.1 Chemical gels

Chemical networks can form either in the course of polymerization (for example, in the formation of a branched macromolecule from small molecule precursors during step-addition polymerization) or by the cross- or end-linking of previously formed macromolecules, either in solution or in the melt ('curing' or vulcanization in the nomenclature of rubber technology). Cross-linking methodology and technological practice have been fully reported in the literature and justify the numerous developments of synthetic polymers from organic chemistry.

Chemical networks have very characteristic properties, the most relevant being rubber elasticity (provided the system is above its glass transition temperature) and swelling in 'solvents'. These properties are influenced both by the number of chemical junctions and their spatial distribution, which can be uniform, random or clustered. The contribution of cross-links is sometimes difficult to establish, however, both because of problems controlling the chemical reaction(s) and because of the natural entanglements of chains in solution. In addition, so-called 'network defects' such as chain ends or closed loops do not generally contribute to connectivity and so to macroscopic properties. Network topology is regarded as a major factor influencing the elasticity of networks, since the number of *elastically effective* junctions of the network is often significantly different from the *total number* of junctions. The determination of the number of cross-links active in the network relies on models, whereas the stoichiometric number of cross-links can, in principle, be measured by analytical means (such as spectroscopy or calorimetry). In physical gels, these difficulties are even more pronounced: such factors as the course of the thermal process, the non-equilibrium state and the slow kinetics of reorganization of labile networks induce substantial changes in macroscopic properties. For this reason, the basic properties of chemically cross-linked networks are outlined in Chapter 4 since they provide some of the necessary background for understanding physical gels.

1.3.2 Hybrid organic–inorganic materials

A new area has opened up with the field of hybrid organic–inorganic materials. The formation of chemical bonds between organic and inorganic components allows molecular composites with novel properties to be produced. We take as an example hybrid networks containing clay particles. Clays are layered aluminosilicates (typically silica tetrahedra bonded to alumina octahedra) present in sheet-like structures with charge compensating counterions (such as Li^+ , Na^+ , K^+ or Ca^{++}) located in the inter-layer spaces. One important consequence of this charged nature is that clays are generally hydrophilic. The compatibility between organic polymers and inorganic hosts results in systems exhibiting so-called 'intercalated' or 'exfoliated' morphologies. In intercalated structures, the organic component is inserted between the layers of the clay in such a way that the inter-layer spacing is expanded. In exfoliated structures, the layers of the clay have been completely separated and are randomly distributed throughout the organic matrix; the type of layer 'delamination' determines the properties of the clay nanocomposites.

For example, Haraguchi and Takehisa (2002) were able to prepare a new type of hydrogel based on poly(N-isopropylacrylamide) (poly(NIPAm)), polymerized *in situ* in the presence of exfoliated, uniformly dispersed clay particles. The free radical polymerization was initiated from the clay surface, without the use of an organic cross-linker, so the clay sheet itself acts as a large cross-linker. Here it was thought that initiator was adsorbed on to the surface of the clay particles, and the monomer and catalyst were in the surrounding liquid. The properties of these gels are very different from those of the polymer cross-linked with a conventional organic cross-linker. Compared to the latter, the change of mechanical properties of the hybrid gel is impressive. For example, in the stress–strain curve, the hybrid gel can reach a maximum elongation of 1000% before fracture, and its behaviour is almost completely reversible, whereas some unswollen chemical gels are relatively brittle. Other hybrids have been developed by intercalation of biopolymers in clays, providing new nanocomposite materials, although this topic again falls outside the scope of this volume.

1.3.3 Inorganic gels

The synthesis of solid materials via ‘soft chemistry’ has been widely developed over the last two decades. These syntheses involve sol–gel chemistry based on inorganic polymerization of molecular precursors. The sol–gel process is a wet-chemical technique for the fabrication of metal oxide materials, starting either from a chemical solution (‘sol’ is short for ‘solution’) or from colloidal particles, to produce an integrated network (a ‘gel’). Typical precursors are alkoxides $M(OR)_z$, where M is a metal with valency z (Si, Ti, Zr, Al, Sn, . . .) and OR is an alkoxide corresponding to a deprotonated alcohol which undergoes hydrolysis and polycondensation (step-addition) reactions to form a system composed of solid particles. The sol evolves towards a continuous inorganic network, composed of particles with sizes ranging from 1 nm to 1 μm, dispersed in a solvent containing a liquid phase.

Sol–gel syntheses developed mainly from 1980 but are nowadays very widely used. The approach is interesting in that it is a cheap, low-temperature technique that allows for fine control of a product’s chemical composition. The process can be used for producing monolithic ceramics, glasses, fibres, membranes, aerogels or powders (e.g. microspheres or nanospheres), and it can be fabricated as very thin films of metal oxides for various purposes. Making thin films requires an advanced knowledge of the rheology of the sol–gel transition in order to control the thickness and regularity of the film with precision. Several rheological studies can be found involving the sol–gel transition in silica gels from tetraethoxysilane (TEOS) (Devreux *et al.*, 1993) or from tetramethoxysilane (TMOS) (Martin *et al.*, 1987). Sol–gel transitions exhibiting similarities with the polymerization of organic molecules have been explored in the context of a unified description of gelation phenomena (see Chapter 3). Other than this, such inorganic gels will not be discussed further in this book.

However, physical gels of a wide variety of other types will be covered. As outlined above, these gels can be classified according to their mechanism of network formation. Recent experimental studies not only allow a much better understanding of gel structures at a very local scale (~1 nm) but enable rheological measurements of gels to be carried out under defined small- and large-deformation regimes. Because the number of gelling systems has increased following a series of innovations, it is necessary to both compare and categorize results for current systems. However, it is now possible to reveal the unique ‘fingerprint’ of some of these systems to rationalize the origin of their properties. This remains the overall objective of this book.

1.4 Physical gels

Throughout this book we identify several mechanisms leading to physical gelation, depending on the polymer and on the solvent. In volume terms, the major component in physical gels is the solvent, and in most of the physical gels presented in this book the solvent is aqueous. However, in a few other systems the choice of appropriate organic solvent plays a very important role in gelation and often helps modify the structure of polymer aggregates (Chapter 8).

Water and electrolyte solutions are often good solvents for biopolymers. However, after chemical modification via inclusion, grafting or substitution of non-polar (hydrophobic) groups, the solubility of such modified polymers may be limited, so that the aqueous solvent becomes poorer, especially with increasing temperature. With electrically charged polymers (polyelectrolytes), solubility is also reduced when water contains large amounts of salt (high ionic strength). The overall mechanism of physical gelation often lies in this subtle interplay between solubility and aggregation. The 'sol state' is a true solution. Then, with a combination of several factors including temperature, pH, polymer concentration, polymer molecular mass and ionic strength, there is a reduction in this ability to solubilize the polymer. This alone would normally produce a precipitate, a two-phase liquid-droplet morphology or even crystallization. However, in gels there is still connectivity within polymer-rich domains or phases. The mechanisms reported below have been identified as being among the features that are characteristic and give rise to the formation of physical gels.

Some of these structures at different distance scales are shown in Figures 1.1 and 1.2. Figure 1.1 introduces the differences between chemical, physical and colloidal networks, drawn to the same scales. Figure 1.2 illustrates the various mechanisms leading to physical gel structures:

1. Conformational changes of the polymer (e.g. the coil–helix transition) which give rise to more rigid domains. In this category we find the coil–triple helix transition in gelatin (Figure 1.2a), the aggregation of helices in certain carrageenans (Figure 1.2b) and the double helices in agarose, and the 'egg-box' structure in alginate gels (Figure 1.2c). The first two cases are driven by lowering the temperature; the last two are induced by temperature changes and/or specific ionic content.
2. Denaturation of globular proteins under conditions where the protein remains essentially globular induces aggregation, so producing colloidal type networks formed with branched structures (Figure 1.2d) or linear ones (Figure 1.2e). These consist of particulate networks including the casein networks formed in milk clotting or cheese-making. Such aggregation is usually irreversible, but shares some characteristics with the phase separation of model colloidal systems. Since the assembly can involve mutual hiding of hydrophobic groups exposed during denaturation, it also has features in common with the systems immediately below.

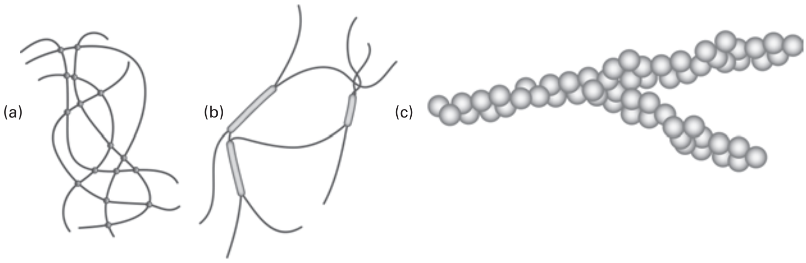

Figure 1.1 Types of network structure: (a) point junctions (chemically cross-linked); (b) junction zone systems; (c) colloidal network strands. These are not drawn to scale, since in (a) and (b) the strands are typically <0.3 nm in thickness, whereas in (c) this dimension can be >2 nm.

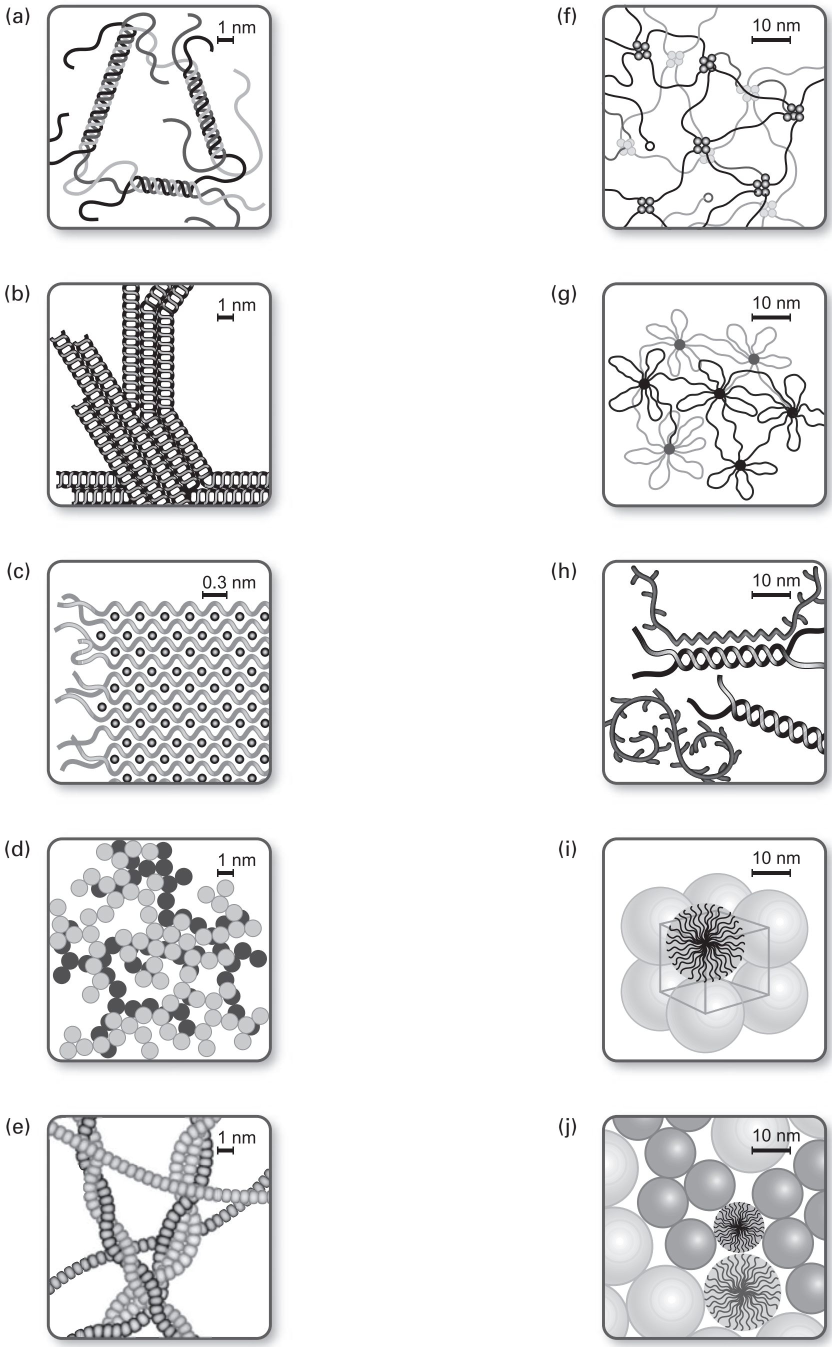

Figure 1.2 Mechanisms of network formation, and the observed structures in physical gel systems: (a) helical association (gelatin, agarose); (b) helical formation in charged polysaccharides such as carrageenans; (c) egg-box complexation in Ca^{2+} alginate gels; (d) colloidal aggregation of proteins close to the isoelectric point; (e) fibrillar aggregation of proteins in amyloid type gels at low pH; (f) hydrophobic effect in telechelic polymer aggregation; (g) flowers in amphiphilic block copolymer aggregation; (h) synergetic interactions between two polysaccharides; (i) colloidal crystal with spherical micelles; (j) mixtures of similar spherical micelles in ternary systems (colloidal glass).