

Reversible Polymeric Gels and Related Systems

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Paul S. Russo

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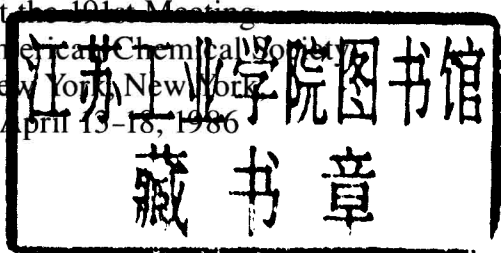
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Reversible Polymeric Gels and Related Systems

Paul S. Russo, EDITOR
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Reversible Polymeric Gels and Related Systems

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Foreword

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

Preface

ONE OF THE UNIQUE CHARACTERISTICS of macromolecules is the physical control they can exert upon less complex systems such as simple fluids. Nowhere is this more evident than in gels, where a macromolecular component, usually present in minor amounts, solidifies a liquid system. This remarkable transformation is only achieved by molecules or assemblies that possess a great span *and* a mechanism of associating with similar molecules to produce a three-dimensional, space-filling structure. The associations may be covalent (chemical gels) or reversible (physical gels). The structures and underlying mechanisms of reversible gelation are varied and not fully understood in most cases. However, substantial progress is being made, in part due to powerful techniques such as cold-stage electron microscopy, video-enhanced optical microscopy, and rheo-optical methods. Greater sophistication in data analysis and theoretical interpretation permits conventional methods, such as dynamic light scattering, to make greater contributions than were once possible. The resurgent interest in reversible gelation is evident among scientists of practically every discipline. Even as biologists display increased interest in the elegant reversible gels that nature has employed for eons, chemists and engineers dealing with synthetic polymers have come to realize the opportunities afforded by reversibly gelling systems for novel materials and devices.

The symposium from which this book was developed brought together a diverse group of researchers involved in reversible polymer gels. During the preparation of the symposium, it became evident that not only reversible gels, but also related systems such as transient gels, semidilute solutions, and permanent gels, were of interest to some researchers planning to attend. Speakers included physical and organic chemists, theoretical physicists, biochemists and biophysical chemists, and materials scientists and engineers from industrial and academic laboratories. The diversity in the audience was even greater. It is a testimony to the need for cross-disciplinary approaches and thought processes in gel research that most participants attended from start to finish, even though the symposium—like the book—was arranged approximately by subdiscipline, and despite strong competing symposia.

This book should appeal to scientists who, like most gel researchers, have no formal training in gels per se but encounter them as interesting extensions of more traditional systems. The book has a reservoir of good

ideas and techniques from a variety of disciplines and will be a success if it enhances the interchange of ideas from one subdiscipline to another. The overview chapter, Chapter 1, looks at the nature of gels in general and reversible gels in particular. References, a solid definition of the term "gel", a proposed gel classification scheme, and a prospectus for future research appear in this chapter. We hope that this chapter will be useful to the newcomer while providing fresh viewpoints and information for the veteran gel researcher. Chapters 2-8 concern synthetic systems in nonaqueous media. Subjects run the gamut from fundamental science in support of an important commercial gel process to theory, experiments involving semidilute solutions, and new information about other important systems. Chapter 9 is a thorough and fascinating study of a small molecule that assembles into structures large enough to gel. Chapters 10-12 focus on gels made from rodlike polymers. A clearer understanding of gelation phenomena will be required to perfect high-performance materials and superstructures made from such macromolecules. Chapters 13 and 14 give clear accounts of the state of knowledge about gelation of two important biomolecules that are also rather stiff chains: DNA, which displays some extraordinary transitions that may be related to its recently discovered reversible gelation, and gelatin, the classic reversible gel. These chapters mark the transition to aqueous systems. Chapter 15 presents kinetic theory pertaining to one of nature's most elegant networks, the cytoskeleton. It is encouraging that such a complex system can be modeled in tractable form. Chapters 16-18 deal with a promising copolymer for biomedical applications. Chapter 19 demonstrates the use of spin resonance for determination of ionic and water environments in gel systems.

I was fortunate to have many helpers while I arranged the symposium and edited this book. In particular, I thank Juanita Miller for her efficient and organized handling of the considerable correspondence associated with both the symposium and this book. My cochair of the symposium, Paul Dubin of Indiana-Purdue University at Indianapolis, was a vital source of helpful suggestions and advice. I thank all the reviewers for their careful, prompt, and constructive evaluations of the articles. Finally, I thank all the contributors for their patience, cooperation, and attention to detail.

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Chapter 1

A Perspective on Reversible Gels and Related Systems

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The features common to reversible polymer gels of many types are identified and discussed. The nature of the gel state is carefully defined, and a novel classification scheme based on morphology, rather than chemical or mechanistic considerations, is proposed. The article also serves as an overview to some of the more commonly used techniques used in the study of gels, and as an introduction to some of the current trends in reversible gel research. Some speculations regarding future trends in reversible gel research are presented.

Of all the physical states, there is something especially elusive about gels. Systems which gel reversibly are particularly difficult to understand, for the requirement is that an enormous transformation of physical state must occur, usually involving only a small portion of the system. Yet an astounding variety of mechanisms can result in reversible gelation, and it seems that a general understanding of reversible gels will not soon be achieved. Perhaps the greatest universality is presently found in the objectives of gel researchers and the obstacles to meeting them (1). The would-be gel researcher must first confirm positively that the system is a gel. Even this isn't always trivial. Next, the conditions under which reversible gelation occurs must be carefully mapped out. Recent controversies show that this matter is often complex, too. After these preliminaries, a structural analysis of the gel is appropriate. Next, it is often of considerable interest to undertake the kinetic study of how the structure forms during gelation—a question which is often the most difficult of all. Finally, we may add such practical concerns as the commercial utility or biological function of the gel.

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Several factors conspire against research into the above issues. The viscoelastic nature of gels can exhibit long-term and sample history effects. It is often necessary to account for the delicate interplay between non-equilibrium phenomena and seemingly equilibrium structure. Conveniently measureable transitions--such as visual clearing--may or may not be actually connected to true melting. Weak optical contrast can impede conventional optical microscopy for morphological analysis, even in systems where the structural elements are otherwise large enough. Also, unlike many conventional solids, the mechanical weakness of gels can complicate electron microscopic investigations. Accordingly, gel structure and its development can often only be inferred from indirect observations.

The foregoing problems surface as central themes for the many diverse studies in this collection. However, each study has its own "flavor", derived in part from the system itself but also from the traditions and lore of a specific scientific discipline, there being no science devoted exclusively to the study of gels. It is interesting to consider the backgrounds of our contributors. Included are polymer/colloid physical chemists, biophysical chemists, physicists, materials scientists and engineers, and at least part-time synthetic chemists. On a global scale, the field is even more diverse. Most are led to gel problems, not as a primary area of interest, but as an extension of other efforts. Occasionally, this diversity of interests and backgrounds seems to have led to misunderstandings, as workers with different objectives and training have paid more or less attention to particular aspects of a given problem. For example, much of the current interest in polyethylene gels derives from gel spinning operations for the production of commercially important ultrahigh modulus fibers (2,3). Perhaps it was the focus on fiber spinning which led to the belief (4) that stirring was a prerequisite for gelation. Exhaustive studies have now shown that this is not the case (5). Occasionally, problems of language can interfere with a clear picture. For example, terms such as "adsorption entanglement" (gel) are probably best avoided. In this paper, we shall endeavor to be as precise about the term "gel" as possible.

Turning to a more general view of the interplay between various areas of research, we find synthetic polymer gel problems being attacked on at least two fronts. A battalion of researchers with roots in the dilute solution characterization of polymers and colloids using methods such as light scattering, dynamic birefringence, sedimentation, viscosity, etc., (6) is allied with materials scientists and engineers, armed with electron microscopes, rheological equipment, dynamic mechanical testers, and the like. Since the target gel objectives of this battle are neither conventional dilute solutions nor materials in the usual sense, measurement techniques are often stretched to their limits. Little wonder that clever new adaptations are so actively sought (7). In the biological theater, cytologists are allied with chemists, biochemists, and physicists in an assault on difficult structure/function problems. The added dimension of performing "in vivo" experiments has resulted in powerful, noninvasive and sensitive techniques, such as video microscopy

(see below). Also, it is in the biological sciences, where gel electrophoresis is so widespread, that gels serve as a research tool. As a result, preparative techniques for making the (covalently crosslinked) acrylamide gels are very highly refined, and this has enabled beautifully clever and reproducible experiments on the thermodynamic nature of the gel state (8-13). Much of what is learned should carry over to reversible gels, and it seems that the opportunities for new devices (14) based on gel transitions abound. In sum, the study of reversible gels and related systems exemplifies interdisciplinary science at its best, uniting as it does individuals with true expertise in diverse specialty areas.

The remainder of this chapter is devoted first to elaborating on the terminology and common issues of reversible gel research, secondly to identifying and comparing some of the strategies that contributors from diverse fields have found successful, and lastly to speculation about future trends of research in reversible gels and related systems.

Fundamental Considerations

The Ferry Definition. Abuse of the word "gel" is a persistent problem, despite the clarifying efforts of prominent authors (15,16). A particularly common error is the reference to any highly viscous solution as a gel. Thus, it will be convenient to begin with a precise statement of what a gel is. A satisfactory and succinct definition was given by Ferry many years ago (16):

A gel "is a substantially diluted system which exhibits no steady state flow".

Implicit in this simple definition are some important limitations. For example, gels are restricted to liquid-bearing colloidal systems--dispersions of one ultrafine material in a liquid. Thus, frozen solutions, or even frozen gels (defined as a gel where the liquid component has solidified on the molecular scale), are not gels. Neither, for our purposes, are dried gels, even if the drying is accomplished without perturbing the network structure. The Ferry definition clearly identifies the gel state as a macroscopic solid, but difficult issues of time and physical scale are required to make this judgement. For example, in order to determine whether a solution is a gel, one might turn it on its side and observe whether it flows. But how long should one be prepared to wait? How large must the sample be? Certainly, large enough that capillarity could not account for any observed lack of flow, but not so large that the gel structure would disintegrate under its own weight.

Analogous problems exist for practically every conceivable alternative test. In the commonly used "ball drop" method (17), a chemically inert sphere is placed on top of the gel, and its motion under gravitational influence observed. But for how long? How large must the sphere be? Large enough that it is retained by the reticular gel structure, but not so large that its weight destroys the gel. Many workers would agree that rheological measurement is the soundest method for identifying

gels. For example, if we place a dilute suspension suspected to be a gel between two horizontal parallel plates and apply a weak static shear strain by displacing the upper plate a small and fixed distance while holding the lower plate still, we expect the true gel to exert a counterbalancing force. Ideally, the force required of us to maintain the displacement would be constant, but how long are we willing to wait to ensure that it is? And how small must the shear displacement be to ensure that the gel structure is not perturbed by the measurement? The difficulty of these questions is emphasized by the results of studies on covalently crosslinked networks (18). In such systems, long-time relaxation processes associated with entanglement release are often found, but a residual force associated with the elasticity of chain segments between covalent crosslinks does remain almost indefinitely. The temporary force associated with the release of entanglements demonstrates that even these gels, which are undoubtedly permanent on any chemically significant time scale, have some temporary character, which can be perturbed by the measurement itself. Thus, rheological measurement substitutes the human sense of vision used in simple "flow" or "ball-drop" experiments, which might be augmented by a microscope, cathetometer, or other motion-sensing mechanism, with the sense of touch, as enhanced by the rheometer. Nevertheless, the potential for ambiguity remains.

Comparison to More Common Physical States. From the foregoing, one may deduce that restraint in the rigorous application of any definition of the gel state is appropriate. In fact, there is nothing new about this. The same problems exist in characterizing liquids and solids. Ordinary glass is thought to be a fluid on the appropriate time scale, but tossing a rock at a windowpane has a distinctly different result from dropping one into a lake, which in turn is rather different from skimming a stone across a smooth pond. Similarly, ice is both solid enough to skate upon, and liquid enough to form glacial "rivers", depending on physical scale (19). The only new feature of gelling systems is that we are less accustomed to "typical" time and physical scales. We require a standard.

Lack of steady flow of a liquid-bearing colloidal solution requires the existence of a space-filling, three-dimensional structure. As we might select a perfect crystal as a canonical solid, or liquid argon as a prototypical liquid, we can choose the covalently crosslinked network, without any entanglements, to represent the ideal gel state. Then an appropriate time scale for reversible gels would be the lifetime of a typical crosslink bond: if subjected to conditions that would cause flow in a pure liquid but which at the same time do not disrupt the gel structure, a permanent gel should not exhibit steady flow over a period of several years. Regarding physical scale, the system should be large enough that capillary forces would not impede flow but small enough to avoid collapse. Where these time and physical scales are inapplicable or inconvenient (i.e., for gels *in vivo*) it can be tested, at least in principle, whether a portion (the structural portion) of the system is immobile on a time scale appropriate for the system and research at hand.

When discussing a new gel it is exceedingly important that full details of the observation that led to describing the system as a gel be given, including: physical scale; method of determining flow, and, especially, duration of the observation.

When is the gel formed? As if it were not difficult enough to decide whether a system is a true gel under just one set of conditions, it is often valuable to determine a map ("phase diagram" is not always appropriate, implying as it does equilibrium structure) showing how conditions may be varied and gelation still be obtained. Some of the major factors are concentration, temperature, and chain length. For ionic gels, pH, ionic strength, even ion type, can be important. Biopolymer gels often involve several components, and their mutual synergism must be charted (20). The detailed sample history is sometimes important, certainly more often for gels than for most simpler colloidal solutions. For example, in order for the spinodal decomposition mechanism of phase separation (21,22), which has been considered as a potential gelation mechanism (23, and references therein), to dominate over nucleation and growth, very rapid quenching may be required for any solution away from the critical composition.

A Classification Scheme for Gels: Fishnet & Lattice Gels

Provided that gelation has been confirmed and properly mapped, it is appropriate to turn to morphological considerations. General and excellent schemes for classifying gels have been proposed (15,24). These classification schemes are based on the chemical nature and interactions of the building blocks making up various types of gels. For example, stereoregular homopolymers may fall into one category; covalently bonded gels into another, etc. This is a very useful approach, and what follows is not meant to replace it so much as to offer a different viewpoint. In the present scheme, there are two very broad categories of structure—"fishnet" and "lattice", which can, in fact, be achieved by a variety of mechanisms. Thus, the viewpoint offered below is strongly tied to the end structure of the gel, and only indirectly to chemical properties which produce them. The various structures are defined in the text, but use is also made of simple drawings. It is hoped that others will adopt the wider use of simple pictorial diagrams for the description of gel structures.

Some consideration of the mechanisms which can lead to the various structures is appropriate, even though this is not the basis of the classification scheme. In this connection, it may be noted that mechanisms are often the least-known aspect of gelation. Accordingly, in this paper we will not just limit discussion to the most commonly considered mechanisms, but will also include reasonable hypothesized ones, for which there may be little experimental evidence so far.

Fishnet Gels. By analogy with typical covalent gels, reversible gel structures are frequently discussed in terms of "crosslinks"

which join "network strands". In reversible gels, the crosslinks must be the result of molecular association, but the details vary. The necessary condition is that a polymer chain, on average, pass through two or more "domains of association", resulting in a network. The structure within these domains--i.e., within the crosslink--depends primarily on the crystallizability of the polymer and is the subject of much current interest. The simplest case is that of easily crystallizable stereoregular chains where the relationship between gelation and crystallization has been documented thoroughly and a plausible mechanism of gelation has been put forth (5,24).

Polymers that are not crystallizable in the bulk phase, or only very weakly crystallizable, are not so well understood. This category includes such polymers as atactic polystyrene (25-29) or poly(vinylchloride) (30,31 and references therein). A closely related problem is the gelation of non-block copolymers (5), which share with atactic polymers the feature that chemically and conformationally homogeneous sequences may be relatively short, so that when two or more chains interact, large crystalline domains are prevented from forming.

Let us explore just two noncrystalline systems, in order to gauge the complexity of the situation. For example, in poly(vinylchloride) it has been proposed that gelation occurs by molecular entanglement and hydrogen bonding, while crystal formation occurs only later (30). This result is based on: determinations of the heat of gelation via the Eldridge-Ferry relationship (32) in various solvents with different H-bonding character; partially on the observed difference between the temperature of melting as measured by falling ball methods and the temperature of a thermodynamic transition associated with crystal melting, as measured by differential scanning calorimetry (DSC); and, finally, on the observation that DSC melting endotherms were absent (or undetectably weak) in young gels, appearing slowly over a period of several hours, well after gelation. Before generalizing these results, it should be remembered that poly(vinylchloride) samples differ from source to source.

A rather different picture emerges from the extensive studies of ethylene copolymer gels, where DSC endotherms are coincident with the ball drop melting temperatures (5). It is argued that this shows that crystallization is a requirement for gelation. Indeed, it is unlikely that the agreement between the DSC and "ball drop" melting temperatures in (5) is fortuitous--i.e., that the some supposed initial, non-crystalline gel structure and the final crystallite structure have identical melting points. Thus, is likely that, in the ethylene copolymer gels, the equilibrium gel has a crystalline crosslink. However, this does not prove that crystallization is a necessary condition for gelation. There remains the possibility that the gel is first established by another mechanism, such as aggregation, and only later converts to a form stabilized by crystalline junctions (27), perhaps at the expense of the initial gel structure, thereby rendering its earlier existence undetectable in a ball drop or DSC melting experiment.

In the two systems just considered, gelation is taken to occur from a one-phase solution. However, under some circumstances, there is the possibility that liquid-liquid phase separation precedes crystallization, and that a gel forms as a result of this process. A crystallization process may or may not be superimposed on this phase separation at a later time, and the crystals may or may not further stabilize the gel. One may surmise that the detailed nature of the crosslink is sometimes a very difficult problem. The crosslink may be a well-formed crystallite, or it may be a much more nebulous "aggregate", or it may even transform from the latter to the former. One tactic which may help in these complex systems is to focus on microgel particles, using the powerful tools of dilute solution analysis. An interesting example of this approach appears in this book (31). However, it is not necessary for a classification scheme to dwell excessively these details.

The fundamental feature shared by all the above systems is the very existence of crosslinks--nevermind their structure--which are separated by flexible polymer strands. The crosslink is the "strong point" of the structure, with the strand providing the elasticity, quite like typical covalent gels. ALL networks of this type, whether reversible or covalent, will be referred to as fishnet gels. These systems obviously bear some structural resemblance to typical rubberlike networks, especially when the crosslink occupies a relatively small portion of the available volume. As a striking example of the utility of this relationship, the maximum draw ratio of polyethylene films prepared by drying gels has been successfully accounted for by modifying the classical rubberlike theory to account for the initial solvent content (3).

Lattice Gels. The customary division of gel structure into strong crosslink and loose strand is often too restrictive. The requirement for gelation is more fundamentally that a permanent, space filling structure exist. The familiar concepts of "crosslinks" and "strands" are supplemental, not basic. We shall refer to those space-filling structures in which a clean division of structure into crosslinks and strands is inappropriate as "lattice gels". For example, a lattice structure could be evolved during an attempt, perhaps incomplete, by the system to separate into two phases, especially by a nucleation-free mechanism (spinodal decomposition). Although a crystallization process may be superimposed upon the spinodal decomposition, this is not really necessary, as sometimes supposed (24). For example, the creation of a polymer-rich phase might generate regions containing entanglements of sufficiently long lifetime to qualify as a gel structure, or even "glassy" regions. This hypothesis is discussed relative to rodlike polymer gels elsewhere in this book (23). Lattice gels might also be made by the assembly of small subunits, involving specific or non-specific interactions between the structural components, and it is possible that spinodal decomposition might occur as a prelude to this sort of process (96; see below). Lastly, we place all gels made from rigid fibrillar structures into this category, including covalently linked gels of rodlike polymers (33). Lattice gels obviously do not bear the formal resemblance