Introduction

The gel point (GP) marks the transition of a material from liquid to solid. The transition is caused by the growth of structure in the material, a structure that correlates molecular or supramolecular motion over large distances. At GP, the correlation length diverges to infinite size. This appearance of long-range connectivity is most easily seen in a rheological experiment (1).

The growth of connected structure is called *gelation* and its opposite, the decay of connectivity, is called *reverse gelation*. Depending on connectivity mechanism, the wide variety of gels can be grouped into two classes (2,3), the threedimensionally connected networks and all the others for which the connectivity mechanism is less clearly defined. This second group of gels goes under many different names such as "jamming," "soft glass," "colloidal glass," "self-assembly," "granular gel" to mention a few. For lack of a specific term, here we call this second group the *glassy gels* since they often involve nonequilibrium states. As a common property of both classes of gels, the material structure immobilizes as it assumes a state of minimal internal energy that would get disturbed by flow. GP is marked by the divergence of regions of immobile structure to infinite size. Below GP connectivity, the material is able to flow and to relax while, beyond the gel point, a yield stress needs to be overcome before flow may happen.

Since a polymer at its gel point is in a critical state (4–9), it commonly is called a *critical gel* (10) to distinguish it from the various materials that are commonly called gel. It is interesting to explore the properties of the critical gel and use these as reference for describing the properties in the vicinity of the gel point. The critical gel affords universal rheological properties that are intermediate between liquid and solid, including the temperature shift factors that are also in between (11). It combines extreme ductility and fragility when subjected to large strain. Its

Encyclopedia of Polymer Science and Technology. Copyright John Wiley & Sons, Inc. All rights reserved.

high adhesion strength (tackiness) is also an expression of the intermediate state; the critical gel still maintains the wetting properties of the liquid (low molecular weight polymer) while starting to gain the cohesive strength of the solid. The adhesion behavior must be accounted for when designing experiments with gels. It also suggests future applications of gels as adhesives.

The information most needed can be summed up in the following questions:

- (1) When does GP occur?
- (2) How soft or stiff is the material at GP?
- (3) How fast does the material pass through GP?

These questions can be answered with the knowledge of the properties at GP. The simplicity and universality of the GP behavior, as shown below, suggests the use of the critical gel as reference state for developing soft materials.

Rheological Properties of the Critical Gel

The evolution of equilibrium mechanical properties during gelation is schematically shown in Figure 1 (using the example of chemical gelation). The steady shear viscosity of the liquid state grows as the connectivity increases. In the approach to GP, the steady shear viscosity diverges (ie, an infinite time would be necessary for the flow to reach steady state). Beyond GP, the equilibrium modulus starts to grow. At GP, the viscosity is infinite while the equilibrium modulus is still zero



Fig. 1. Evolution of mechanical properties of a cross-linking polymer as a function of extent of cross-linking p (schematic). Representative properties are the steady shear viscosity for the liquid state (sol) and the equilibrium modulus for the solid state (gel). All viscoelastic liquid states are in between the Newtonian liquid (p = 0) and the critical gel ($p = p_c$). Equivalently, all viscoelastic solids are in between the critical gel and the Hookean solid (p = 1).

because the stress in a deformed critical gel can still relax completely. This shows that the conventional equations for a liquid (characterized by a steady shear viscosity) or for a solid (characterized by an equilibrium modulus) do not apply at GP. The critical gel has its own rheological behavior (1). The critical gel

- a. requires infinite time to relax and
- b. relaxes in a broad distribution of shorter modes which are self-similar.

This expresses itself in slow power law dynamics for both the linear relaxation modulus G(t) and the relaxation time spectrum $H(\lambda)$ (12–14)

$$G(t) = St^{-n_{\rm c}}; \qquad H(\lambda) = \frac{S\lambda^{-n_{\rm c}}}{\Gamma(n_{\rm c})} \quad \text{for} \quad \lambda_0 < t < \infty \tag{1}$$

This rheological pattern seems to be a universal rheological property, since it occurs with both network gels and glassy gels at GP. Experiments with a large variety of chemically or physically gelling materials show this self-similar behavior without exception. The gamma function $\Gamma(n_c)$, arises naturally in the conversion of G(t) into $H(\lambda)$. The two material parameters are the stiffnes S and the relaxation exponent n_c . Subscript c is used here to identify the critical state at the gel point. λ_0 is a crossover time to small-scale dynamics of the building blocks of the critical gel.

In comparison, a power law behavior has been predicted for molecules of selfsimilar (fractal) structure (15,16), suggesting that the critical gel is self-similar over a wide range of length scales (10,17). It also has been shown, without use of an analogy, that the onset of rigidity in a randomly cross-linked system is a continuous phase transition (18); at the transition, the correlation length diverges and the system is necessarily self-similar. The scaling behavior is then an automatic consequence of statistical thermodynamics (qv). Several theories have been proposed for the critical gel behavior (19–22).

The relaxation exponent n_c may assume values in the range $0 < n_c < 1$ (21). Its value cannot be predicted since a systematic study of the effect of molecular architecture on the value of the relaxation exponent is still missing. Typical experimental values are as follows:

- $n_{\rm c} \cong 0.5$ for end-linking networks with balanced stoichiometry (12,14,23)
- $n_{\rm c} \cong 0.5-0.7$ for end-linking networks with imbalanced stoichiometry (12,13,24)
- $n_{\rm c} \cong 0.7$ for epoxies (25)
- $n_{\rm c} \cong 0.8$ for PVC plastisol (26)
- $n_{\rm c} \cong 0.3$ for radiation cross-linked polyethylene (27)
- $n_{\rm c} \cong 0.5$ for micellar block polyelectrolytes (28)

The gel strength *S* depends on the value of n_c . A large value of *S* is always associated with a small value of n_c . Very little information is available about n_c of glassy gels.

The dynamic modulus of the critical gel, as described by equation 1, is also a power law:

$$G^*(\omega, p_c) = \Gamma(1 - n_c) S(i\omega) n_c$$
⁽²⁾

The real (the storage modulus G') and imaginary (loss modulus G'') parts are related as

$$G'(\omega, p_{\rm c}) = \frac{G''(\omega, p_{\rm c})}{\tan(\frac{n_{\rm c}\pi}{2})} = \Gamma(1 - n_{\rm c})S\omega^n \cos\left(\frac{n_{\rm c}\pi}{2}\right)$$
(3)

The phase shift δ as defined by the loss tangent tan $\delta = G''/G'$, is proportional to the slope of the dynamic modulus at GP (13):

$$\delta_{\rm c} = \frac{n_{\rm c}\pi}{2} \tag{4}$$

Introduced into a general constitutive equation for linear Viscoelasticity (qv) (29,30), the above relaxation modulus results in the constitutive equation for critical gels, the Winter-Chambon gel equation: (12,13)

$$\tau(t) = S \int_{-\infty}^{t} dt' (t - t')^{-n_c} \dot{\gamma}(t')$$
(5)

The gel equation predicts all known rheological properties of critical gels, such as infinite viscosity and zero equilibrium modulus, as long as the applied strain is small. For large strains, a suitable strain measure must be introduced (12). Large strain behavior and breaking of the structure (reverse gelation by mechanical field) is not included in this equation. The breaking of critical gels (31) is a topic which needs to be investigated more closely in the future.

Chemical Gel Point

Chemically cross-linking polymers belong to the group of network gels. Molecules cross-link into large clusters through covalent bonds. The independent variable of the cross-linking process is the extent of reaction, p, which can be understood as bond probability. The polymer reaches the GP at a critical extent of the cross-linking reaction, $p \rightarrow p_c$. At GP, the second moment of the cluster size distribution diverges (7) and the molecular weight distribution is infinitely broad $(M_w/M_n \rightarrow \infty)$ as molecules range from the smallest unreacted oligomer to the infinite cluster. The molecular motions are correlated over large distances but the critical gel has no intrinsic size scale. The liquid polymer before the GP, $p < p_c$, is called a *sol* because it is soluble in good solvents. The solid polymer beyond the GP, $p_c < p$, called a *gel* is not soluble any more, even in a good solvent. However, unattached molecules (sol fraction) are still extractable from the gel.

Prediction of the Chemical Gel Point. The classical mean field theories (32-34) are able to predict the critical conversion p_c quite accurately (35,36). The

Vol. 10

predictions are mainly based on the assumptions that all functional groups of the same type are equally reactive, all groups react independently of one another, and no intramolecular reactions occur in finite species. The threshold p_c depends on the geometry of the network-forming species. Special cases follow.

Case 1. Homopolymerization of similar *f*-functional molecules:

$$p_{\rm c} = \frac{1}{f - 1} \tag{6}$$

The same relation is found for the end-linking of molecules of low functionality (f = 3 or 4) and for the vulcanization of long molecular chains. The average number of cross-linking sites along the chain is defined as

$$f = \frac{\sum_{i} f_{i}^{2} n_{f}}{\sum_{i} f_{i} n_{f}} \tag{7}$$

with n_f being the number of molecules of functionality f_i .

Case 2. Cross-linking of *f*-functional molecules A_f with *g*-functional molecules B_g , which are mixed at a molar ratio

$$r = \frac{f(\mathbf{A}_f)}{g(\mathbf{B}_g)}$$

reaches the gel point at a conversion

$$p_{A,c} = [r(f-1)(g-1)]^{-1/2}$$
(8)

with $p_{\rm B} = rp_{\rm A}$. For the formation of a gel, the stoichiometric ratio must be chosen between a lower and upper critical value:

$$r_1 = [(f-1)(g-1)]^{-1}$$
 and $r_u = 1/r_1$ (9)

Otherwise the reaction stops before reaching the gel point. The relations in equation 9 follow from equation 8 when considering species A_f or species B_g fully reacted, respectively.

Instead of the extent of reaction, the *stoichiometric ratio* is often chosen as independent variable of a chemical gelation experiment. Consider a system that consists of cross-linker A (average functionality f = 3 or f = 4, etc) and chain extender B (functionality g = 2). Assuming that the reaction is always brought to completion, the degree of cross-linking would depend on the stoichiometric ratio r (ratio of cross-linker sites to chain extender sites). The stoichiometry dependence of equilibrium mechanical properties is sketched in Figure 2. The cross-link density is a maximum for balanced stoichiometry. The viscosity diverges at a lower and an upper critical ratio r_1 and r_u of equation 9. Solid behavior is found everywhere at intermediate stoichiometry $r_1 < r < r_u$. Critical gels are formed at $r = r_1$ and $r = r_u$.





Fig. 2. Steady-state mechanical properties (schematic) of cross-linking polymers with different stoichiometric ratios r, defined as ratio of cross-linking sites of two reacting polymers. The reaction is presumably brought to completion. Steady critical gel behavior is found at the lower and the upper critical values, r_1 and r_u .

Physical Gel Point

Physical gels are able to form sample-spanning, supermolecular structures. Connectivity has been found with a wide range of mechanisms which have been reviewed extensively by te Nijenhuis (37), Larson (38), and Nishinari (39). Physical gels come as both network materials (associative networks) and glassy gels. Such glassy gels can energetically associate into a sample-spanning structure, by repulsion as well as by attraction, leading to nonequilibrum states (soft glasses) (3,28). In analogy to chemical gelation, the physical gelation is defined by the growth of physically connected aggregates and the physical gel point is reached when the correlation length of molecular (or supramolecular) motion diverges to infinity. For temperature-dependent connectivity these materials are called *thermoreversible* (40); however, other variables might determine the connectivity such as pH value, concentration of connecting component, charge density, or stress level.

The principal differences between chemical and physical gels lie in the lifetime and the functionality of the junctions. Chemical bonds are considered to be permanent while the physical junctions have finite lifetimes. Physical junctions are constantly created and destroyed, however, at very low rates so that the network appears to be permanently connected if the time of observation is shorter than the lifetime of the physical network. For longer times of loading, the material flows and is characterized as a liquid even beyond its gel point. The analogy between chemical and physical gelation applies very well to systems with longliving bonds. It becomes less defined when renewal of physical bonds occurs on the time scale of observation and the system behaves as a liquid. In this case, a characteristic renewal time, λ_{pg} , of the physical bonds determines long-time ordering processes and rheology of a physical gel.

The analogy between physical and chemical gelation applies only to time scales shorter than the characteristic renewal time. Equation 1 changes into

$$G(t) = S_{\rm c} t^{-n_{\rm c}} \quad \text{for} \quad \lambda_0 < t < \lambda_{\rm pg} \tag{10}$$

Physical gels typically have a yield stress beyond which the structure gets broken and liquid behavior sets in. Below the yield stress, the physical gel is a solid at experimental times shorter than the renewal time and it is a liquid at experimental times longer than the renewal time.

Range of the Power Law

The power law of the critical gel of a cross-linking polydimethylsiloxane (PDMS) was found for G' and G'' to extend over a frequency range of more than five decades (13,14), the entire experimental range. A lower frequency limit is given by the correlation length, which is the linear size of a typical cluster of the self-similar structure. This correlation length diverges at GP and the lower frequency limit of the power law could theoretically be extended to zero. However, a practical lower frequency limit is given by the finite sample size, ie, at a scale of observation that exceeds the size of the sample in the rheometer. The upper frequency limit of the power law behavior very much depends on the small scale structure of the critical gel.

For chemical gelation, the upper frequency limit (and the corresponding lower time limit, λ_0 , of eqs. 1 and 10) typically depends on the following two molecular sizes:

- (1) *Size of the chains between cross-links*: The randomly coiled chains exhibit self-similar behavior and the transition from the self-similar critical gel to the self-similar chain (between network junctions) is difficult to detect experimentally.
- (2) *Glass length*: At very high frequency, the scale of observation decreases below the lower scaling length of the polymer called the *glass length*. The *glass length* is given by the size of the network element that determines the transition to glassy behavior at low temperature. This smallest network element depends on the specific molecular structure. It could be the distance between cross-links or the length of a chain unit. At this small-length scale, vitrification becomes important and deviation from equilibrium self-similar behavior is expected. In this description of chemical gelation, it is tacitly assumed that the scale of observation is sufficiently larger than the glass length. The details of the molecular structure are neglected by neglecting the high frequency transition to the glass behavior of the chemical networks.

Physical critical gels typically have a very limited power law region. The slow dynamics is governed by the transition to flow behavior as an expression of the finite lifetime of the physical junctions. The faster dynamics undergoes transition to the dynamics of the structural building blocks. These building blocks are typically quite large in physical gels so that their dynamics can be seen at already low frequency. Between these two phenomena, little may remain of the self-similar dynamics of the critical gel. General relations are difficult to find because of the large variety of connectivity mechanisms, especially is glassy gels. Nonequilibrium states make the power law parameters path-dependent, ie they depend on the history of the glassy gel formation.

Vicinity of the Gel Point

The power law region seems to stretch out and then contract again, having its widest range at GP. The slope gradually decreases during gelation. This phenomenon is visible on cross-linking of PDMS (13,14), and it is very pronounced for radiation cross-linking of polyethylene (27). It is found in physical gels (26,28,41–44) as well as in chemical gels.

The longest relaxation time λ_{max} first grows to infinity and then decays again. In the vicinity of GP, this may be expressed in power laws (45):

$$\lambda_{\max} \sim \begin{cases} (p - p_{\rm c})^{-s/(1 - n_{\rm c})} & \text{for} \quad p < p_{\rm c} \\ (p_{\rm c} - p)^{-z/n_{\rm c}} & \text{for} \quad p_{\rm c} < p \end{cases}$$
(11)

These equations hold for small introduce absolute value signs $|p - p_c|$, ie, in the vicinity of GP. Materials near GP are often called *nearly critical gels*. The exponents depend not only on the dynamic critical exponent (relaxation exponent n_c) but also on the dynamic exponents *s* and *z* for the viscosity $\eta \sim (p_c - p)^{-s}$ and the equilibrium modulus $G_e \sim (p - p_c)^z$. If one, in addition, assumes symmetry of the diverging λ_{max} near the gel point

$$\frac{s}{1-n_{\rm c}} = \frac{z}{n_{\rm c}} \tag{12}$$

then the critical exponents are related as (45,46)

$$n_{\rm c} = \frac{s}{s+z} \tag{13}$$

Into these relations one may introduce specific values (s, z) from percolation theory or from branching theory and determine the corresponding values for n_c . The wide range of values for the relaxation exponent $0 < n_c < 1$ lets us expect that the dynamic exponents s and z are nonuniversal. Since s and z can be predicted from theory (47), n_c values can be calculated from equation 13. This result, however, relies on the symmetry hypothesis, which does not seem to be generally valid, at least not for highly entangled polybutadienes (48).

The slow dynamics of a system, for which the relaxation time goes through a singularity, can be described with a discrete relaxation time spectrum with a

Vol. 10

longest relaxation time $\lambda_{\max}(p)$ that diverges at GP:

$$G(t,p) = G_{\rm e} + \frac{S}{n \ \Gamma(n) \lambda_{\rm max}^n} \sum_{i=1}^{\infty} \exp\left(-\frac{t i^{1/n}}{\lambda_{\rm max}}\right) \tag{14}$$

Its four parameters $G_{\rm e}$, S, $\lambda_{\rm max}$, and n all depend on the bond probability p. In the liquid below GP and at GP, the equilibrium modulus is equal to zero, $G_{\rm e} = 0$. For n = 0.5 and $G_{\rm e} = 0$, this spectrum reduces to the well-known Rouse spectrum. It is remarkable that depending on the value of $\lambda_{\rm max}$, the Rouse spectrum describes a viscoelastic liquid that includes the Newtonian liquid ($\lambda_{\rm max} \rightarrow 0$) and the critical gel ($\lambda_{\rm max} \rightarrow \infty$) as limiting cases.

Alternatively to equation 14, a cutoff function $F(t, \lambda_{\text{max}})$ may be applied to the equation of the critical gel, equation 1:

$$G(t,p) = G_{\rm e} + St^{-n}F(t,\lambda_{\rm max})$$
⁽¹⁵⁾

The model reduces to the power law at the gel point $F(t, \lambda_{\max}) \rightarrow 1$ for $\lambda_{\max} \rightarrow \infty$. The stretched exponential cutoff function (49)

$$F(t, \lambda_{\text{max}}) = e^{-(t/\lambda_{\text{max}})^{\beta}} \quad \text{with} \quad 0 < \beta < 1$$
(16)

was found to give good results with a curing epoxy (50).

Measurements of Instant of Gelation

Equilibrium Rheological Measurements. The appearance of an equilibrium modulus or the divergence of the steady shear viscosity might be used to estimate the position of the gel point by extrapolation. Extrapolation is necessary because these measurements fail in the close vicinity of GP. Measurement of the equilibrium modulus (51,52) is extremely difficult because its value remains below the detection limit for a considerable time and it, theoretically, requires an infinite time to perform the measurement. The diverging steady shear viscosity (53–55) indicates the location of GP. The simplicity of this experiment may lead to neglect of the severe shortcomings that can be summed up as follows:

- (1) GP is found by extrapolation of an experiment which never can reach steady state since the longest relaxation time diverges at GP.
- (2) The network structure near GP is very fragile and most probably gets broken during the viscosity measurement, causing an apparent delay in gelation or may induce reverse gelation.

For these reasons, steady-state measurements give only an apparent gel point. The real and the apparent gel point might be close together, but additional experiments will be needed for confirming such an assumption.

Transient Rheological Measurement. The nature of the critical gel suggests transient measurements, which are possible even if the longest relaxation



Fig. 3. Evolution of relaxation modulus of a cross-linking polymer as shown with five samples of increased cross-link density. Parameter is the reaction time distance from the gel point $(t - t_c)$. The values are calculated from dynamic mechanical data (13). The power law relaxation is limiting behavior for the liquid and the solid. One of the samples is very close to the critical gel. However, at very long times it deviates from the power law behavior. It is still a fluid.

time diverges. A typical evolution of the relaxation modulus is shown in Figure 3. The power law is distinguished from the other states by being a straight line. It shows that the entire relaxation time spectrum is affected by the gel transition. It is surprising to find that intermediate relaxation modes, which are accessible to experiment, are affected by the diverging longest relaxation time in a way that makes it possible to distinguish between a sol and a gel (1,13,14). It is not necessary to measure the diverging longest relaxation time; measurement of intermediate relaxation modes suffice for detecting the gel point in many different ways. Three examples are as follows:

- (1) the loss tangent tan $\delta = G''/G'$ of the critical gel is independent of the frequency of the dynamic experiment. GP is detected by the intersect of tan δ curves (see Fig. 4). A multifrequency experiment has been designed for detecting the GP based on this approach (56).
- (2) For start-up of shear flow at constant rate, the transient viscosity grows in a power law with time. This might be utilized for detecting GP. The total strain must be kept small because, near GP, stress relaxation is infinitely slow and shear modification cannot be avoided even at extremely low rates of deformation.
- (3) It is especially simple to detect the instant of gelation of a material whose critical relaxation exponent n_c is known. For any frequency (within the power law region) and any temperature, in a small amplitude oscillatory shear experiment at constant ω_0 , GP is reached at the instant at which functions $G'(\omega_0, t)/\cos(n_c\pi/2)$ and $G''(\omega_0, t)/\sin(n_c\pi/2)$ intersect (see eq. 3).



Fig. 4. Loss tangent of a chemically cross-linking polybutadiene as function of reaction time (48). Data were taken at several frequencies. The GP is marked by the instant at which the loss tangent is independent of frequency. All data are taken at low frequencies where the self-similar behavior prevails.

In the special case of $n_c = 0.5$, this relation simplifies even further. It should be noted that an intersect of G' and G'' is not necessarily indicating a gel point in spite of many published claims to the contrary.

With dynamic mechanical experiments, the instant of gelation can be measured as precisely as the accuracy of the rheometer permits, a significant advantage over extrapolation methods. An additional advantage is that the strain is kept small and shear modification of the molecular structure is avoided. The main limitation is the experimental time that tends to get long as low probing frequency is chosen. Rapidly gelling materials do not give sufficient time to the experimentalist to perform mechanical spectroscopy near the gel point.

Nonrheological Methods. Dynamic light scattering has been developed as nondestructive and real-time determination of GP for both chemical and physical systems (57–59). Time-resolved dynamic light scattering not only allows one to determine the gelation threshold but also to investigate critical dynamics near the gelation threshold. At GP, a power law appears in the intensity–time correlation function. Specific features originate from some unique aspects of gels: nonergodicity, frozen inhomogeneities, in addition to the divergence of the connectivity correlation.

Specific Methods for Chemical Gelation. The predictability of the threshold p_c suggests that GP can be found by monitoring the degree of cross-linking until it has reached the theoretical p_c value. However, the degree of cross-linking is difficult to measure accurately. Side reactions that parallel the cross-linking reaction (60,61) might interfere with the measurement. For practical purposes, these difficulties are avoided by saying that the polymer is before the gel point (sol state) if it can be completely dissolved in a good solvent and beyond the gel Vol. 10

point (gel state) if it cannot be dissolved completely. Numerous solution swelling experiments have confirmed that the rheologically observed GP coincides with the transition from a completely soluble state to an insoluble state (13,14,23).

Applications

For many applications in polymer processing, it is sufficient to know when the liquid-solid transition occurs for the purpose of avoiding it. For example, shaping must occur before the gel point while the polymer is still able to flow and the stress can relax to zero. Polymers around the gel point are used in a broad spectrum of applications such as gel processing, reactive processing (gel as intermediate state), and the development of new polymeric materials (adhesives, absorbents, porous catalysts, vibration dampers, membranes, colloidal glasses). They are also important outside the polymer field, for example, in food technology or in blood clotting.

BIBLIOGRAPHY

"Gel Point" in *EPSE* 2nd ed., Suppl. Vol., pp. 343–352, by H. H. Winter, University of Massachusetts, Amherst, Mass.

- 1. H. H. Winter and M. Mours, Adv. Polym. Sci. 134, 165–234 (1997).
- 2. P. S. Russo, *Reversible Polymer Gels and Related Systems* (ACS Symposium Series No. 350), American Chemical Society, Washington, D.C., 1987.
- D. Bonn, H. Kellay, H. Tanaka, G. Wegdam, and J. Meunier, *Langmuir* 15, 7534–7536 (1999).
- 4. A. Coniglio and H. E. Stanley, Phys. Rev. Lett. 42, 518 (1979).
- 5. A. Coniglio, H. E. Stanley, and W. Klein, Phys. Rev. B 25, 6805 (1982).
- 6. P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, 1979.
- 7. D. Staufer, A. Coniglio, and M. Adam, Adv. Polym. Sci. 44, 103 (1982).
- 8. D. Stauffer, Introduction to Percolation Theory, Taylor & Francis, Philadelphia, 1985.
- 9. H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford Press, New York, 1985.
- 10. T. Vilgis and H. H. Winter, Progr. Colloid Polym. Sci. 26, 494-500 (1988).
- 11. A. Izuka, H. H. Winter, and T. Hashimoto, Macromolecules 27, 6883-6888 (1994).
- 12. H. H. Winter and F. Chambon, J. Rheol. 30, 367–382 (1986).
- 13. F. Chambon and H. H. Winter, J. Rheol. 31, 683-697 (1987).
- 14. F. Chambon and H. H. Winter, Polym. Bull. 13, 499-503 (1985).
- 15. M. Muthukumar, J. Chem. Phys. 83, 3161 (1985).
- 16. M. E. Cates, J. Phys. 46, 1059 (1985).
- 17. M. Muthukumar and H. H. Winter, Macromolecules 19, 1284-1285 (1986).
- 18. P. Goldbart and N. Goldenfeld, Phys. Rev. Lett. 58, 2676 (1987).
- 19. W. Hess, T. Vilgis, and H. H. Winter, *Macromolecules* **21**, 2536–2542 (1988).
- 20. J. E. Martin, D. Adolf, and J. P. Wilcoxon, Phys. Rev. Lett. 61, 2620-2623 (1988).
- 21. M. Muthukumar, Macromolecules 22, 4656 (1989).
- R. H. Colby, M. Rubinstein, J. R. Gillmor, and T. H. Mourey, *Macromolecules* 25, 7180 (1992).
- F. Chambon, Z. S. Petrovic, W. J. MacKnight, and H. H. Winter, *Macromolecules* 19, 2146 (1986).

- 24. D. Durand, M. Delsanti, M. Adam, and J. M. Luck, Europhys. Lett. 3, 297 (1987).
- 25. D. Adolf, J. E. Martin, J. P. Wilcoxon, Macromolecules 23, 527-531 (1990).
- 26. K. te Nijenhuis and H. H. Winter, Macromolecules 22, 411 (1989).
- 27. E. M. Valles, J. M. Carella, H. H. Winter, and M. Baumgärtel, *Rheol Acta* **29**, 535–542 (1990).
- 28. S. R. Bhatia and A. Mourchid, Langmuir 18, 6469-6472 (2002).
- J. D. Ferry, Viscoelastic Properties of Polymers, 3rd ed., John Wiley & Sons, Inc., New York, 1980.
- R. B. Bird, R. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*, Vol. 1, John Wiley & Sons, New York, 1987.
- 31. S. K. Venkataraman and H. H. Winter, Rheol. Acta 29, 423-432 (1990).
- 32. P. J. Flory, J. Am. Chem. Soc. 63, 3083 (1941); J. Phys. Chem. 46, 132 (1942).
- 33. W. H. Stockmayer, J. Chem. Phys. 11, 45-55 (1943).
- 34. W. H. Stockmayer, J. Chem. Phys. 11, 45 (1944).
- 35. C. W. Macosko and D. R. Miller Macromolecules 9, 199 (1976).
- 36. K. Dusek and D. Patterson, J. Polym Sci A 26, 1209 (1986).
- 37. K. te Nijenhuis, Adv. Polym. Sci. 130, 1-252 (1997).
- R. Larson, The Structure and Rheology of Complex Fluids, Oxford University Press, Oxford, 1999.
- 39. K. Nishinari, Rep. Progr. Polym. Phys. 43 (special issue), 163-192 (2000).
- J. M. Guenet, Thermoreversible Gelation of Polymers and Biopolymers, Academic Press, New York, 1992.
- 41. L. Li and Y. Aoki, Macromolecules 30, 7835-7841 (1997).
- H. Soenen, H. Berghmans, H. H. Winter, and N. Overbergh, *Polymer* 38, 5653–5660 (1997).
- 43. B. D. Chin and H. H. Winter, Rheol. Acta 41, 265 (2002).
- 44. R. H. Horst and H. H. Winter, Macromolecules 33, 7538-7543 (2000).
- 45. H. H. Winter, Progr. Colloid Polym. Sci. 75, 104-110 (1987).
- 46. Martin and co-workers, 1989.
- 47. C. P. Lusignan, T. H. Mourey, J. C. Wilson, and R. H. Colby, *Phys. Rev. E* 60, 5657 (1999).
- 48. M. Mours and H. H. Winter, Macromolecules 29, 7221-7229 (1996).
- 49. C. Friedrich and L. Heymann, J. Rheol. 32, 235 (1988).
- 50. D. Adolf and J. E. Martin, Macromolecules 23, 3700 (1990).
- 51. R. J. Farris and C. Lee, Polym. Eng. Sci. 23, 586 (1983).
- 52. M. Adam, M. Delsanti, and D. Durand, *Macromolecules* 18, 2285 (1985).
- 53. S. Lipshitz and C. W. Macosko, Polym. Eng. Sci. 16, 803 (1976).
- 54. J. M. Castro, C. W. Macosko, and S. J. Perry, Polym. Commun. 25 (1984).
- 55. S. A. Bidstrup, Ph.D. dissertation, University of Minnesota, 1986.
- E. E. Holly, S. K. Venkataraman, F. Chambon, and H. H. Winter, J. Non-Newtonion Fluid Mech. 27, 17–26. (1988).
- 57. P. Lang and W. Burchard, Macromolecules 24, 814-815 (1991).
- 58. M. Shibayama and T. Norisuye, Bull. Chem. Soc. Jpn. 75(4), 641-659 (2002).
- 59. J. E. Martin, *Phys. Rev. A* **36**, 3415 (1987); J. E. Martin and K. D. Keefer, *Phys. Rev. A* **34**, 4988–4992 (1987).
- 60. C. W. Macosko and J. C. Saam, ACS Polym. Prepr. 26, 48 (1985).
- 61. A. Fisher and M. Gottlieb, In Proc. of Networks 86, Elsinor, Denmark, Aug. 1986.
- 62. J. E. Martin, J. P. Wilcoxon, and D. Adolf, Phys. Rev. A 36, 1803 (1987).

H. HENNING WINTER University of Massachusetts Vol. 10 GENETIC METHODS OF POLYMER SYNTHESIS 145

GELATIN. See Volume 6.

GELS. See Hydrogels.

GENE-DELIVERY POLYMERS. See Volume 6.