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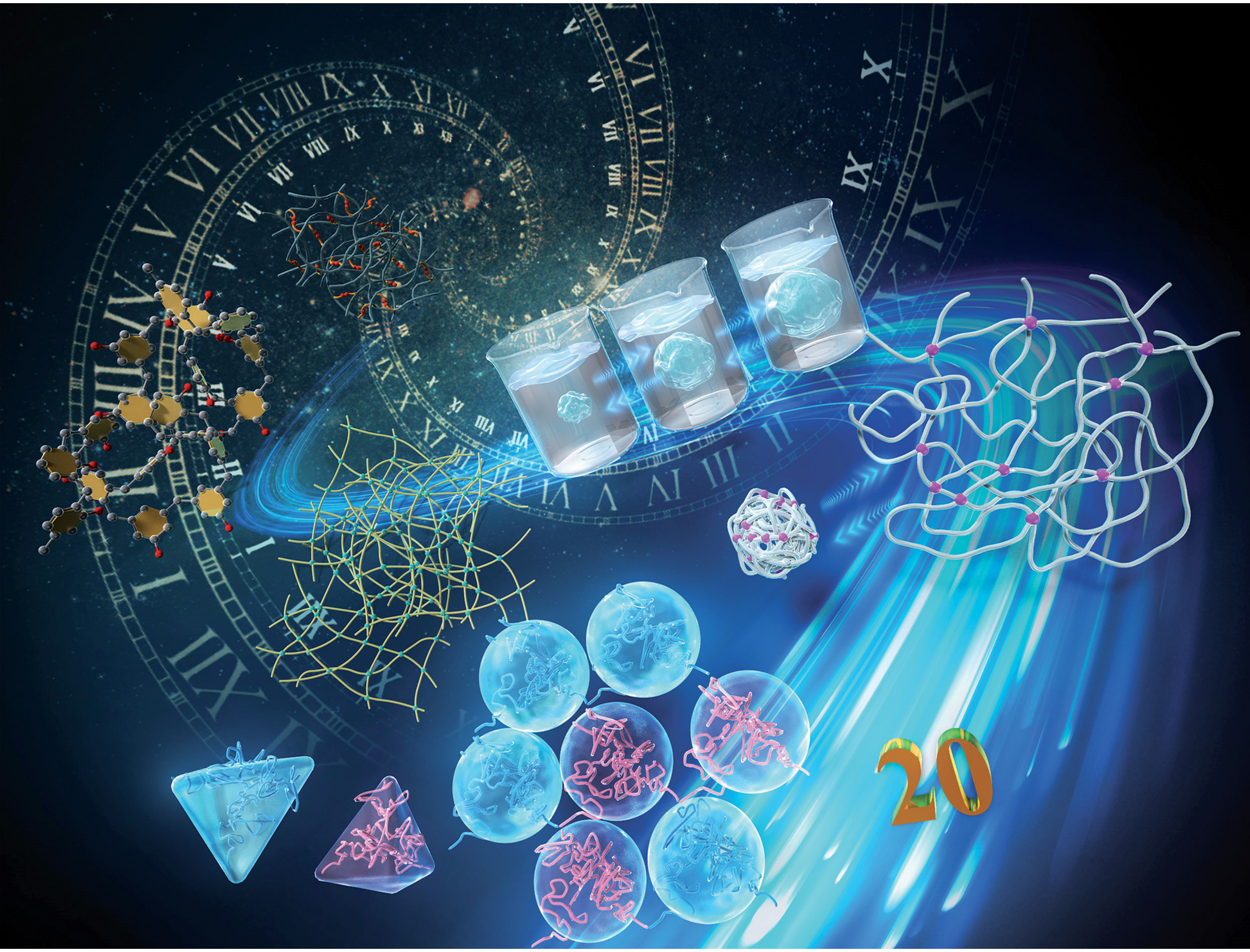

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Physics of polymer gels: Toyoichi Tanaka and after†

Mitsuhiro Shibayama

This review revisits the works of Toyoichi Tanaka on the physics of polymer gels and discusses their scientific significance with the keywords of volume phase transition, structure, dynamics, kinetics and inhomogeneities, followed by some recent topics including defect-free homogeneous gels. Then, the modern physics of polymer gels will be considered from the viewpoints of cross-linking, networking, and percolation, along with the scope of future directions of polymer gels and polymer networks.

1 Introduction

Polymer gels are ubiquitous and are found in many places and situations in daily life. They are interesting materials owing to their unique physical properties and various functions, such as swelling and shrinking, elastic and viscoelastic properties, and environmental responsiveness. Polymer gels have been intriguing in many fields, such as chemistry, physics, materials science, pharmacy, biology, food science, and so on, for more than half a century. They consist of cross-linked polymer chain networks and a large amount of solvent. In spite of this simple combination, polymer gels have been a difficult system to study in physics because of their topological nature, *e.g.*, random cross-linking and imperfect networking.

The late MIT physics professor Toyoichi Tanaka was a leading authority on the physics of polymer gels. Tanaka brought about a revolution in the physics of polymer gels. He sublimated chaotic gels, with disparate molecular weight distributions of the strands between the cross-links and with the mesh of the polymer network being full of defects, into beautiful physical objects that can be described by mathematical equations. In particular, his discovery of the "volume phase transition (VPT)"[1] shed new light on polymer science: analogous to the liquid–vapor transition of water, a VPT is a dramatic change in the volume of a gel in response to an infinitesimal change in one of the intensive properties, such as temperature (T), solvent composition, salt concentration and pH, as well as light, pressure (P), and magnetic field. Since a VPT is a macroscopic manifestation of molecular-level changes in polymer conformation, one can study various phenomena occurring at the molecular level by simply observing a size and/or shape change of the gel. Here, the cross-links connecting polymer chains play a major role. The discovery and the concepts of the VPT strongly influenced not only polymer science, but also disciplines such as soft-matter physics, biophysics, and bioengineering, as well as various applications, *e.g.*, chemo-mechanical actuators, sensors, water absorbents, and other engineering and industrial applications.

On the occasion of the 20th anniversary of *Soft Matter*, a review on the physics of polymer gels is presented. Fig. 1 shows the publication and citation statistics of *Soft Matter* in the period of 2005–2024 with the keyword of topic = polymer gel (Web of Science, as of Aug. 24, 2024). There are 987 publications with an H-index of 87. Typical subjects include double network hydrogels,[2] stimuli-responsive polymer gels,[3] friction and lubrication of hydrogels,[4] and so on. Note that research on polymer gels was already at a blossoming stage and developing rapidly at the time of the first issue of *Soft Matter*. Fig. 2 shows

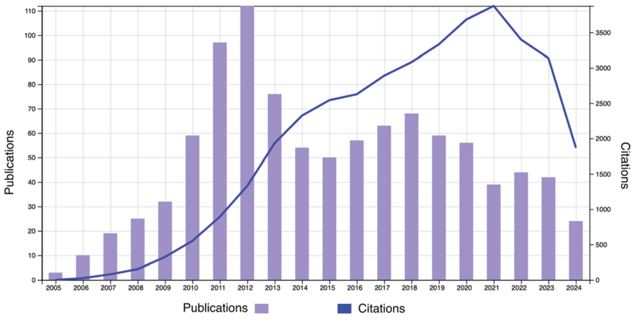

Fig. 1 Publication and citation statistics of *Soft Matter* with the topic of "polymer gel" (2005–2024). (Web of Science, as of Aug. 24, 2024.)

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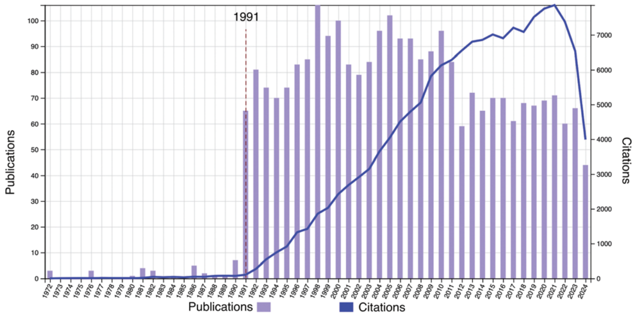


Fig. 2 Publication and citation statistics of *Macromolecules* with the topic of "polymer gel" (1972–2024). (Web of Science, as of Aug. 24, 2024.)

the publication and citation statistics of *Macromolecules* (an ACS journal) in the period of 1972–2024 with the same keyword. It is quite surprising to notice that there is a discrete jump in the publications together with a steep increase in citations starting at the year of 1991. More surprisingly, the same trend is also found in the statistics of *Physical Review Letters* (*PRL*; an APS journal), *Journal of Chemical Physics* (an AIP journal), and *Polymer* (Elsevier) exactly in the same year (see Fig. S1–S3 in the ESI†)! We may now have a naive question: why did such a discrete jump in publications happen in 1991?

This review consists of the following: in Section 2, we overview the representative achievements of Toyoichi Tanaka, emphasizing their physical significance and influence in sciences. Here, we try to answer the above question. In Section 3, macroscopic as well as microscopic views of the VPT are reviewed. In Section 4, "Gel inhomogeneities", which had not been explicitly reported in the works of Tanaka, are demonstrated based on shrinking kinetics, structure, and dynamics. Here, the frozen inhomogeneities are characterized *via* small-angle neutron scattering (SANS), and a decomposition method using dynamic light scattering (DLS) to separate the two types of concentration fluctuations, *i.e.*, dynamic and static (frozen) concentration fluctuations, is reviewed. In Section 5, recent advances in polymer gels, *i.e.*, quantitative understanding of polymer networks and gels consisting of defect-free ideal networks, the so-called "Tetra-PEG gels", are reviewed as "Toward realization of ideal polymer networks". Finally, future directions of the physics of polymer gels are considered in Section 6.

2 Physics driven by T. Tanaka

2.1 VPT: from theoretical prediction to experimental verification

Dušek and Patterson wrote a paper on solvent release from polymer gels due to poor solvation or high crosslink density and discussed the possibility that the composition dependence of the chemical potential of the solvent might exhibit minima and maxima that would predict phase separation.[5] This was the first theoretical paper predicting the VPT, and they also indicated that "it would be difficult to attain the conditions necessary for the transition in the free-swelling case, but that it should be possible for a gel under tension". As a matter of fact, the experimental verification of this theoretical prediction had to wait until 1978.[1]

In 1977, Tanaka and colleagues at the Massachusetts Institute of Technology (MIT) found in light scattering experiments that acrylamide hydrogel has a critical point at −17 °C and that it undergoes phase separation.[6] Note that this is due not to water freezing but to phase separation. In 1978, as part of their cataract research, Tanaka *et al.* were experimenting with acrylamide gel particles in acetone–water mixtures to study cloudiness (phase separation or critical phenomena). One day, when they left the gels in various solvent compositions overnight, they found that cloudiness did not occur, and instead, the gels split into two types, swollen and shrunken, depending on the solvent composition. This was a historical discovery of the volume phase transition (VPT) of gels.[1] However, reproducibility could not be achieved. After much trial and error, he realized that the gels that underwent the volumetric phase transition were aged gels that had been stored in a refrigerator and had been partially hydrolyzed, and that charged groups were necessary for the VPT.[7] That is, in order to realize a VPT, it is necessary to introduce a strong repulsive term in the free energy of the gel, such as electrostatic interaction and the Donnan potential, so as to compete with the attractive interaction favoring gel shrinking.[1]

2.2 Representative achievements of Toyoichi Tanaka

Toyoichi Tanaka studied biophysics at the University of Tokyo under the auspices of Prof. A. Wada, where he conducted experimental and theoretical works on coil-globule transition.[8,9] He was also involved in instrumentation and experimental works with dynamic light scattering (DLS).[10] DLS is a technique that is commonly used to determine the size and size distribution of small particles in suspension or polymers in solution by taking the time correlation of the scattered intensity.[11] He moved to MIT and began his gel research in the Benedek Lab in the Department of Physics. One of the themes was the study of cataracts, which is where the lens (intraocular lens) becomes cloudy, using the DLS technique, a specialty of Professor Benedek's. In the same year, he discovered that gels scatter light and fluctuate with time, leading to the development of a theory of gel fluctuation and its experimental demonstration. This was the birth of the cooperative diffusion theory of gels.[12]

Not only theoretical works but also experimental works on polymer gels were energetically conducted by Tanaka and his group until his tragic passing in 2001. T. Tanaka wrote 10 papers in *Nature*, 7 in *Proceedings of the National Academy of Sciences* (*PNAS*), 3 in *Science*, 16 in *PRL*, and many in other journals and books, of which representative works are listed in Table 1: the cooperative diffusion theory (the so-called THB theory; 1973),[12] critical phenomena in gels (divergence of light scattering intensity at the critical temperature; 1977),[6] the volume phase transition (VPT) of gels (1978,[1] 1981[7]), kinetics of gel swelling (the Tanaka-Fillmore (TF) theory; the first theoretical prediction of the relaxation time of gel swelling being the inverse square of the gel size; 1979),[13] collapse of gels

Table 1 Representative achievements of Toyoichi Tanaka

Year	Item	Ref.
1973	Cooperative diffusion theory and DLS (THB theory)[12]	*J. Chem. Phys.*
1977	Critical phenomena[6]	*PRL*
1978	Volume phase transition (VPT)[1]	*PRL*
1979	Kinetics of gel swelling (TF theory)[13]	*PRL*
1981	Volume phase transition[7]	*Sci. Am.*
1982	Gel in an electric field[14]	*Science*
1984	VPT of PNIPAM gel[15]	*Nature*
1985	Critical kinetics of VPT[16]	*PRL*
1987	Instability pattern[17]	*Nature*
1989	Universality class[18]	*J. Chem. Phys.*
1990	Light-induced VPT[19]	*Nature*
1991	Friction of gel[20]	*Science*
1991	VPT induced by hydrogen bonds[21]	*Nature*
1991	Saccharide-sensitive VPT[22]	*Nature*
1992	Neutron scattering studies of gels[23,24]	*J. Chem. Phys.*
1992	Multiphases[25]	*Nature*
1992	Patterns in shrinking gels[26]	*Nature*
1992	Super absorbency[27]	*Nature*
1993	Responsive gels: volume transitions[28]	*Adv. Polym. Sci.*
1994	Nonrandomness in proteins[29]	*PNAS*
1999	First-order VPT in polyampholytic gels[30]	*PRL*
1999	Reversible molecular adsorption[31]	*Science*
2000	Gel catalyst[32]	*PNAS*
2000	Molecular imprinting[33]	*PRL*

in an electric field (1982),[14] the VPT of poly(*N*-isopropylacrylamide) (PNIPAM) gel (1984),[15] critical kinetics near the VPT (1985),[16] instability patterns in gels (mechanical instability of gels at the phase transition; 1987),[17] the universality class of gels (1989),[18] visible-light-induced VPTs (1990),[19] friction of gels (reversible decrease of gel-solvent friction at the VPT temperature; 1991),[20] hydrogen-bond-induced VPTs (1991),[21] saccharide-sensitive VPTs (1991),[22] small-angle neutron scattering (SANS) studies on critical phenomena (1992)[23] and microphase separation (1992),[24] multiphases (existence of not only swollen and shrunken phases but also many intermediate phases; 1992),[25] patterns in shrinking gels (1992),[26] super absorbency (1992),[27] a review of the VPT (1993),[28] protein sequences (thermodynamic procedure to synthesize heteropolymers that can renature to recognize a given target molecule; 1994),[29] first-order phase transitions and evidence for frustrations in polyampholytic gels (1999),[30] reversible molecular adsorption (1999),[31] gel catalysts (2000),[32] and molecular imprinting (2000).[33] They cover biophysics, physics, and physical chemistry. These papers, at least those published before 1991, inspired the subsequent rush in research, as was evidenced by the publication statistics (Fig. 2 and Fig. S1–S3, ESI†). In particular, the THB theory (1973),[12] the volume phase transition (VPT) (1978),[1] and the VPT of PNIPAM gel (1984)[15] were extremely influential.

Fig. 3 shows the publications (1973–2001) and citations (1973–2024) of Toyoichi Tanaka, which started the work of the THB theory in 1973. It clearly shows a sharp increase in the citations around the year 1991, shown by a dashed line, and a marked correlation between the statistics in Fig. 2 and in Fig. 3. This eloquently answers the question posed in Fig. 2. Further evidence can be found in Fig. S4 (ESI†) (publication and citation statistics with the keywords of “volume phase transition AND polymer gels”).

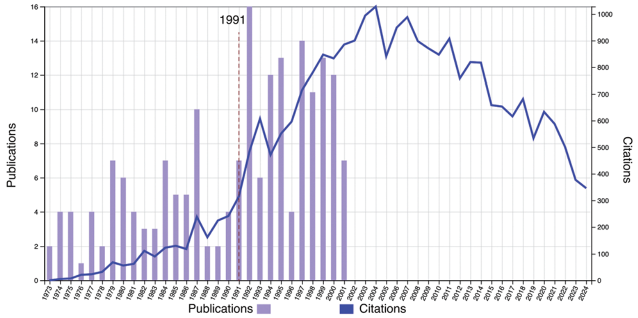


Fig. 3 Publication and citation statistics with the topic of “Toyoichi Tanaka AND MIT AND 1973–2001 ” (1973–2024). (Web of Science, as of Jan. 7, 2025.)

Tanaka’s achievements can be categorized into the following three fields: (1) research of the origin of the helix–coil transition (–1973), (2) the physics of gels – discovery of the VPT and related phenomena (1973–1993), and (3) the physics of proteins – basic principles of biological functions (1994–2000). Although (1) and (3) are, respectively, the starting point of Dr Tanaka’s research and the very science and life science he was aiming for, this review exclusively focuses on (2), *i.e.*, the physics of polymer gels. Comprehensive reviews on the VPT are found in monographs.[34,35]

2.3 The THB theory and TF theory

The comprehensive theory titled “Spectrum of light scattered from viscoelastic gels”[12] proposed by Tanaka–Hocker–Benedek (the THB theory) changed the perception of gels from phenomenological objects to theoretically predictable materials. This theory is based on the theory of elasticity.[36] They described the equation of motion for gel networks with the displacement vector, $\mathbf{u}(\mathbf{r}, t)$, which represents the displacement of a point $\mathbf{r} \equiv (x, y, z)$ in the network from its equilibrium location at time t, and derived the differential equation,

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = \nabla \cdot \tilde{\sigma} - f \frac{\partial \mathbf{u}}{\partial t} \tag{1}$$

Here, ρ is the mass density of the small volume element, $\tilde{\sigma}$ is the stress tensor ($\equiv \sigma_{ik}$) and f is the friction factor. By conducting the operation on the divergence, they obtained the starting equation for the motion of gels:

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = G\Delta \mathbf{u} + \left(K + \frac{1}{3}G\right)\nabla(\nabla \cdot \mathbf{u}) - f\left(\frac{\partial \mathbf{u}}{\partial t}\right) \tag{2}$$

Here, K is the bulk modulus and G is the shear modulus.

The derived equation is

$$\frac{\partial \mathbf{u}}{\partial t} = D \frac{\partial^2 \mathbf{u}}{\partial z^2} \tag{3}$$

which is formally the same as the diffusion equation of molecules, and D is the diffusion coefficient, defined by

$$D \equiv \frac{1}{f}\left(K + \frac{4}{3}G\right) \quad (\text{longitudinal diffusion, } \mathbf{u} \parallel z) \tag{4}$$

and

$$D \equiv \frac{G}{f} \quad (\text{transverse diffusion, } \mathbf{u} \perp z) \tag{5}$$

Eqn (3) ensures that the gel dynamics can be described with the conventional diffusion equation, although the phenomena are quite different.

Fig. 4 schematically shows the difference in (a) diffusion of ink dye molecules on a filter paper and (b) swelling of a piece of gel. Note that in the case of (a) each dye molecule diffuses independently, while in (b) the gel is allowed to swell only while keeping its shape. This is the essential difference between the two, which originates from the absence/presence of connectivity, respectively, for ink dye and gel.

2.3.1 DLS. DLS is a powerful tool for studying concentration fluctuations in soft matter.[11] The time correlation function for the scattered electric field $g^{(1)}(\mathbf{q}, t)$ is derived from eqn (3), and is proportional to the Fourier transform $u(\mathbf{q}, t)$ of the displacement $u(\mathbf{r}, t)$, and is given by

$$g^{(1)}(\mathbf{q}, t) \equiv \frac{\langle E(\mathbf{q}, t)E(\mathbf{q}, 0)\rangle}{\langle E(\mathbf{q}, 0)\rangle^2} \propto \langle u(\mathbf{q}, t)u(\mathbf{q}, 0)\rangle \propto \exp(-\Gamma t) \tag{6}$$

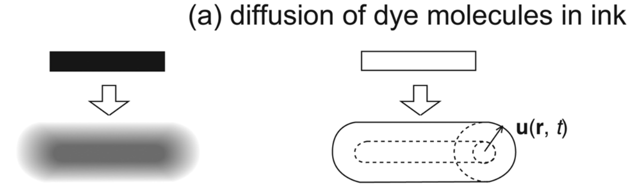
Here, $\mathbf{q}$ is the scattering vector and Γ is the relaxation rate defined by $\Gamma = Dq^2$.

The time correlation function of the scattered intensity is given by

$$g^{(2)}(\mathbf{q}, t) - 1 = |g^{(1)}(\mathbf{q}, t)|^2 = \exp(-2\Gamma t) \tag{7}$$

Tanaka *et al.* obtained the diffusion coefficient (eqn (4)) of polyacrylamide hydrogels *via* two methods; one using DLS with eqn (7), $D = D_{\text{DLS}}$, and the other *via* a macroscopic static measurement of the frictional and elastic constants, $D = D_{\text{macro}}$. Both were in good agreement with each other, $D_{\text{DLS}} \approx D_{\text{macro}}$,[12] which proved the validity of the THB theory beyond doubt.

2.3.2 Swelling kinetics: the TF theory. Since the driving force of the displacement of polymer chains is Brownian motion, the solution of the equation of motion (eqn (2)) is the diffusion equation (eqn (3)). On the other hand, in the case of the swelling kinetics of gels, the driving force is the osmotic pressure difference between the inside and outside of the gel and the effect of chain connectivity needs to be taken into account (as was schematically shown in Fig. 4).


(a) diffusion of dye molecules in ink

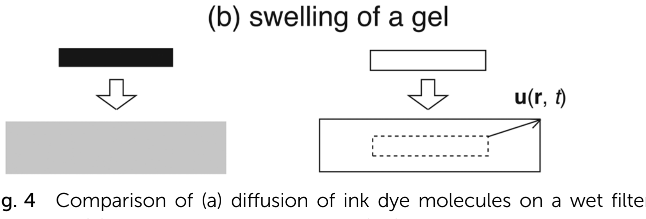

(b) swelling of a gel

Fig. 4 Comparison of (a) diffusion of ink dye molecules on a wet filter paper and (b) swelling of a piece of gel. **u**(**r**, *t*) is the displacement vector.

By solving the equation of motion of gels with the initial and boundary conditions of spherical gels in the spherical coordinate,[13] the swelling equation was derived:

$$\frac{\partial u_r}{\partial t} = D\frac{\partial}{\partial r}\left\{\frac{1}{r^2}\left[\frac{\partial}{\partial r}(r^2 u_r)\right]\right\} \tag{8}$$

Here, D is the diffusion coefficient defined in eqn (4). The size change of a gel in the swelling process is given by:

$$\begin{aligned}\frac{\Delta a(t)}{\Delta a} &\equiv \frac{a(t) - a_0}{a(\infty) - a_0} = \frac{6}{\pi^2}\sum_{n=1}^{\infty} n^{-2}\exp\left(-\frac{n^2 t}{\tau}\right) \\ &\simeq \frac{6}{\pi^2}\exp\left(-\frac{t}{\tau}\right) \quad (t/\tau < 0.5)\end{aligned} \tag{9}$$

where a_0 and $a(t = \infty)$ are the gel radius before swelling (*i.e.*, $a(t = 0) = a_0$) and the final radius at swelling equilibrium, $a(t = \infty) = a_\infty \equiv a$, respectively, and τ is the characteristic relaxation time of swelling given by

$$\tau = \frac{a^2}{\pi^2 D} \tag{10}$$

The time course of swelling for acrylamide hydrogels[13] is shown in Fig. 5. The experimental results[13] agreed well with the theoretical prediction, and the characteristic relaxation time τ and the diffusion coefficient of gel swelling $D(= D_{\text{sw}})$ were evaluated. It was confirmed that τ is proportional to the square of the gel size a^2 (the inset of Fig. 5) as predicted by the theory (eqn (10)). In other words, the swelling rate $1/\tau$ becomes slower with the square of the gel size. This was a serious fundamental problem in the application of gels to gel actuators, which require rapid response. This problem has been solved by the novel design of gels, *i.e.*, comb-type grafted hydrogels.[37]

2.4 PNIPAM gels and responsive gels

Hirokawa and Tanaka discovered a VPT in nonionic gels, *i.e.*, PNIPAM hydrogels.[15] Here, the VPT is simply controlled by one of the easiest intensive variables, *i.e.*, temperature, and the transition temperature is close to human body temperature. This sensational report on PNIPAM gels developed explosively in many fields both in fundamental science and also in applied science/engineering, namely in smart gels responsive not only to temperature, pH, and salt, but also to light and other external stimuli. Research on PNIPAM was reviewed by Schild[38] and recently by Halperin.[39]

2.5 Thermodynamics of the VPT

Tanaka explained the VPT of polymer gels in terms of mean field theory based on the extension of Flory's theory.[40] Here, the free energy of a gel consists of mixing enthalpy, mixing entropy, and elasticity terms. He derived the osmotic pressure of the gel

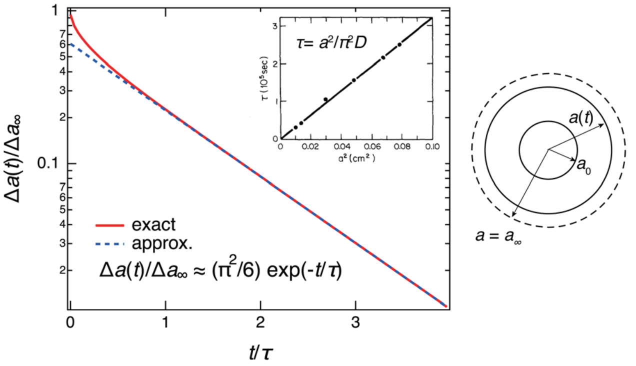


Fig. 5 Theoretical prediction of gel swelling kinetics (red-solid line, exact; blue-dashed line, predicted) and experimental results for acrylamide hydrogels with different final radii, $a \equiv a_\infty$. The definition of the symbols is shown on the right. The inset shows the experimental results on polyacrylamide hydrogels. (Replotted and modified from Fig. 4 and 6 in ref. 13.)

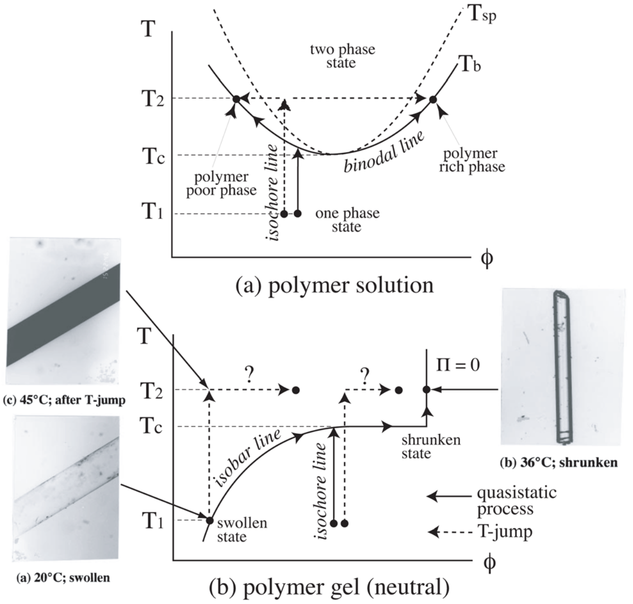


Fig. 6 Phase diagrams of (a) polymer solutions and (b) polymer gels (neutral/noncharged), and optical photographs of cylindrical gels. (Modified from parts of Fig. 1 in ref. 49).

and discussed its Taylor expansion with respect to the polymer fraction ϕ. The second virial coefficient becomes negative, corresponding to the discrete transition. This theory effectively reproduced the VPT.[1,28] Hirotsu *et al.* studied the VPT of weakly charged poly(NIPAM-*co*-acrylic acid) copolymer gels P(NIPAM/AAc) and explained the VPT with the mean field theory.[41] However, it should be noted here that there are some criticisms related to the mean-field assumption, namely the nonrandomness of the polymer–solvent interaction and hydrophobic interactions, the use of unrealistic values of the interaction parameter χ, and so on, in particular in the case of temperature induced VPTs (*e.g.*, PNIPAM hydrogels).[38,39] Hence, this issue has not been fully solved.[42,43]

2.6 Smart gels inspired by the VPT

The discovery of the VPT for temperature-responsive PNIPAM gels and its applications in smart gels seem to be other reasons why there was such a jump-wise increase in the publications. The smart gels[44] referred to here are gel actuators (chemo-mechanical, electro-mechanical, photo-induced, *etc.*), gel sensors (pH, enzyme and antigen-responsive hydrogels,[45] *etc.*), stimuli-responsive buckling gel films,[46] shape-morphing materials,[47] *etc.* Since there are a number of reviews in this regard, we focus on the structure and dynamics of the VPT in this review.

3 Macroscopic and microscopic views of the VPT

3.1 Phase diagrams: polymer gels *vs.* polymer solutions

Fig. 6 shows a comparison between phase diagrams of (a) polymer solutions and (b) polymer gels. Unlike polymer solutions, a polymer gel is an open system with its surrounding medium, *e.g.*, water. This is why a gel can change its size so as to balance the chemical potentials in and out of the gel. This is realized by setting the osmotic pressure, Π, to 0. The photographs in Fig. 6b show the case of a cylindrical PNIPAM gel of submillimeter thickness. When the temperature is changed much slower than the relaxation rate of the gel, the gel can change its size along the isobar line and reaches a transparent shrunken state or a swollen state *vice versa* ((a) → (b) or (b) → (a)) without phase separation. However, when the temperature is changed much faster, the gel cannot reach a new equilibrium state, resulting in phase separation (turbid gel) ((a) → (c)). This is followed by slow structural relaxation and results in a transparent shrunken gel, as shown in the photographs ((c) → (b)).[48] This example demonstrates a marked difference between polymer solutions and polymer gels. The VPT has been applied to many fields, such as drug delivery systems, sensors and actuators. For example, Miyata *et al.* demonstrated antigen-responsive hydrogels.[45]

3.2 Microscopic view of VPT: SANS

Small-angle neutron scattering (SANS) is a very powerful tool to study the structure of polymer gels because of various advantages: (i) large scattering contrast between hydrogenous polymer networks and deuterated solvent, (ii) a suitable target spatial range for gel mesh size, (iii) sensitivity to network inhomogeneities, and so on.[50] The difference between continuous and discrete shrinking transitions of polymer gels was clearly elucidated *via* SANS experiments.

Fig. 7(A) shows the swelling/shrinking curves of PNIPAM (homopolymer) gel and P(NIPAM/AAc) copolymer gels, where d and d_0 are the gel diameters at observation and in the reference state (*i.e.*, at preparation; $T_{\text{prep}} \approx 22$ °C), respectively, and d/d_0 is the linear swelling ratio. When increasing the temperature, the homopolymer gel underwent a continuous or a slightly discrete VPT, as shown by the squares, while the copolymer gel underwent a discontinuous transition, shown by circles. The

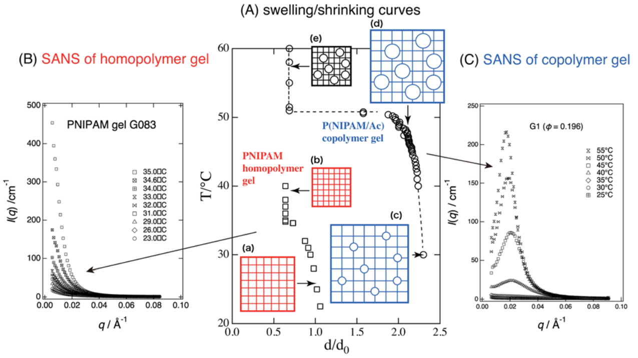


Fig. 7 Swelling/shrinking curves (T *vs.* d/d_0) (A), and SANS profiles for PNIPAM (homopolymer) gel (B) and P(NIPAM/AAc) (copolymer) gel (C). Homopolymer gels undergo a continuous VPT, while copolymer gels undergo a discrete VPT. SANS of the former shows critical divergence at $T_{\mathrm{PNIPAM}} \approx 32$ °C, while the latter shows a marked peak at $T > T_{\mathrm{PNIPAM}}$. The cartoons of square grids and circles show PNIPAM networks and ionized chain regions associated with AAc comonomers, respectively. The cartoons indicate that the size of the gel (grids) becomes smaller *via* hydrophobic contraction and the circles become larger *via* electrostatic repulsion, with changing T. (Modified from parts of Fig. 2 in ref. 49.)

reason for the difference could not be elucidated *via* macroscopic observations, such as visual or optical microscopy.

Fig. 7(B) (homopolymer gel) shows divergence of the scattered intensity with increasing T, indicating critical fluctuations ((a) → (b)).[23] On the other hand, Fig. 7(C) (copolymer gel) shows a first-order discrete transition accompanied by microphase separation ((c) → (d) → (e)).[24] Here, the microphase separation was induced by antagonistic interactions: the hydrophobic interaction of the PNIPAM network chains (shown by the lattice; inward favored) *vs.* the Donnan potential originating from the charged acrylic acid groups (shown by circles; outward favored). This is the first demonstration and evidence of a microscopic view of a discrete volume phase transition.

4 Gel inhomogeneities

Tanaka did not explicitly discuss inhomogeneities of gels in his works, but he recognized them through experimental observations, such as patterns in shrinking gels.[26] The existence of inhomogeneities in gels was already reported in the 1970s *via* static light scattering (SLS)[51] and later *via* DLS, small-angle X-ray scattering (SAXS), and SANS.[52–55] Geissler *et al.* proposed empirical equations for SANS and SAXS of gels in swollen poly(dimethylsiloxane) gels:[55]

$$I(q) = \frac{I_{\mathrm{L}}(0)}{1+\xi^2} + I_{\mathrm{G}}(0)\exp\left(-\frac{\Xi^2 q^2}{2}\right) \tag{11}$$

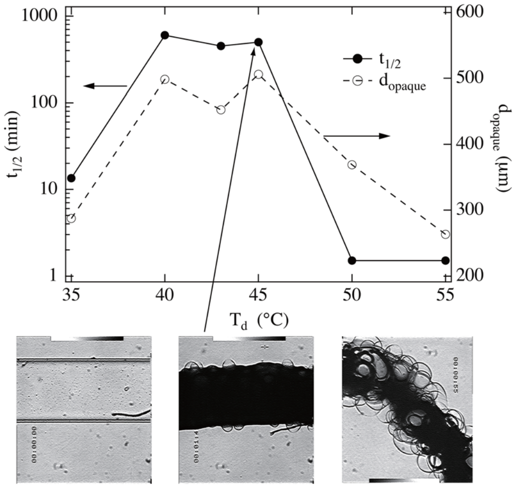
where ξ is the correlation length in the solution-like part of the gel, and Ξ is the size of solid-like domains, *e.g.*, highly cross-linked parts in the network. $I_{\mathrm{L}}(0)$ and $I_{\mathrm{G}}(0)$ are the corresponding prefactors. Later, the inhomogeneities were theoretically explained by Panyukov and Rabin (hereafter we call this the PR theory) as frozen inhomogeneities[56,57] formed during the gelation/cross-linking process.

4.1 Shrinking kinetics

Since gel inhomogeneities are introduced during the gelation process, the structure and properties strongly depend on how the gel is prepared, *e.g.*, the temperature T_{prep} and concentration C_{prep} at gel preparation. Certainly, the gel structure also depends on these at observation, *i.e.*, T_{obs} and C_{obs}. Hence, in order to describe the gel structure, two sets of parameters are required, *i.e.*, (T_{obs}, C_{prep}) and (T_{prep}, C_{prep}), as discussed for the PR theory.[56,57]

Fig. 8 demonstrates the shrinking kinetics and morphology of PNIPAM gels prepared at 20 °C and when jumping to different destination temperatures, T_{d}.[58] This figure shows that the shrinking kinetics strongly depend on T_{d}. If $T_{\mathrm{d}} \approx T_{\mathrm{PNIPAM}}$, the shrinking half time $t_{1/2}$ is around 20 min. It dramatically increases to 600 min for $40 \leq T_{\mathrm{d}} \leq 45$ °C, whereas it becomes much faster for $T_{\mathrm{d}} \geq 50$ °C. Interestingly, this change is well-correlated with the gel diameter d_{opaque} at which the gel becomes opaque (an indication of macroscopic phase separation). This means that the gel shrinking is slowed down (quenched) by macroscopic phase separation (the middle photograph). On the other hand, if the T_{d} is much higher than T_{PNIPAM}, the gel does not have time to macrophase-separate and shrinks to the desired shrunken state. Here, bubbles are formed, as shown in the right photograph (Fig. 8(c)). This photograph also indicates that gels are, in general, inhomogeneously prepared with water-rich and -poor domains.

Note that skin formation is believed to be one of the reasons that delay gel shrinking.[59] However, this is a competition between thermal diffusion *vs.* structural relaxation of the gel network. As discussed for eqn (10), the latter is strongly dependent on the size of the gel. In the case of the gel shrinking kinetics treated in this work, the gel diameter is submillimeter, where the thermal diffusion (T-jump) is much faster than the time for skin formation.



(a) initial stage $t = 0$ **(b) after T-jump to $T_{\mathrm{d}} = 45$ °C** **(c) after T-jump to $T_{\mathrm{d}} = 55$ °C**

Fig. 8 Shrinking kinetics of PNIPAM gels with T-jumps to different temperatures, T_{d}.[58] (Upper) $t_{1/2}$ (left) and d_{opaque} (right) *vs.* T_{d}. (Lower) Optical photographs of the gel (a) in the initial state, and after T-jumping to (b) $T_{\mathrm{d}} = 45$ °C and (c) to $T_{\mathrm{d}} = 55$ °C. (Modified from parts of Fig. 3 in ref. 49.)

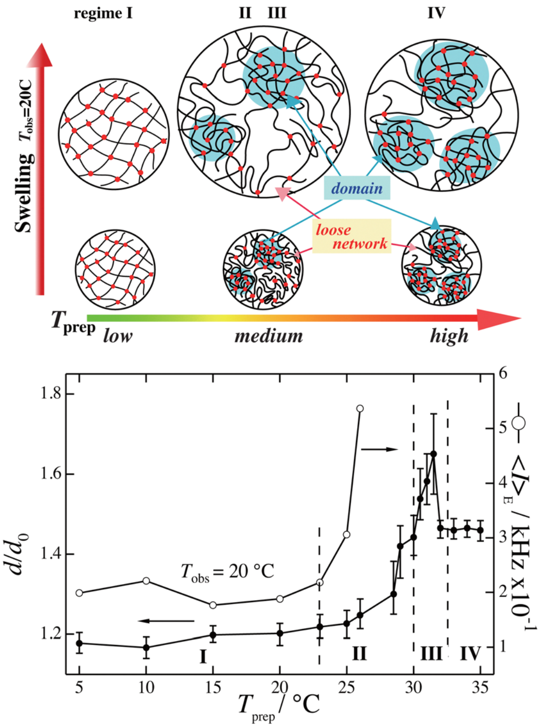


Fig. 9 (Top) Gel inhomogeneity model for PNIPAM gels prepared at different temperatures T_{prep} and observed at T_{obs} = 20 °C. (Bottom) Linear swelling ratio d/d_0 *vs.* T_{prep} (left; filled circles) and light scattering intensity $\langle I \rangle_E$ *vs.* T_{prep} (right; open circles).[60] (Modified from parts of Fig. 4 in ref. 49.)

The molecular picture of the distinct difference between the fast and slow response of gel shrinking relates to the connectivity. This leads to cooperative motion as discussed in Fig. 4. That is, due to chain connectivity, it takes a certain period of time, τ_{equib} to reach equilibrium, but if the temperature change is much faster than τ_{equib}, the structure is frozen. In comparison with polymer gels, PNIPAM solutions (not gels) instantaneously undergo phase separation or precipitation at T_{PNIPAM} irrespective of the rate of temperature change. This instant response is due to the absence of cross-linkers and each polymer chain can behave independently (not collectively as in the case of polymer gels).

Fig. 9 shows the preparation temperature, T_{prep}, dependence of the linear swelling ratio, d/d_0, of PNIPAM gels observed at T_{obs} = 20 °C.[60] As shown in the figure, d/d_0 strongly depends on T_{prep} and dramatically increases when approaching $T_{PNIPAM} \approx$ 32 °C. The right axis shows the light scattering intensity, $\langle I \rangle_E$, which also increases with T_{prep}, where $\langle I \rangle_E$ is the ensemble average scattering intensity as defined below. The changes in the gel network structure are schematically shown in the top of Fig. 9, indicating that gels prepared near T_{PNIPAM} are more inhomogeneous than those prepared at lower temperatures. This is an example of the case of PNIPAM hydrogels, but such inhomogeneities are commonly observed in polymer gels.

4.2 Structure and dynamics

In the late 1970s, de Gennes anticipated the importance of the two new techniques in polymer physics, "neutron diffraction" and "light scattering", in the preface of his book "Scaling Concepts in Polymer Physics."[61] These refer to SANS and DLS, respectively. Certainly, developments of DLS studies of polymer gels are owed to Tanaka. Later, the concept of inhomogeneities were taken into account in DLS analyses both theoretically and experimentally.[62–64] On the other hand, SANS of gels developed rather phenomenologically until the PR theory was proposed.[56,57] In this section, both SANS and DLS studies on polymer gels are overviewed.

4.2.1 Gel research with SANS. SANS became one of the most powerful tools for investigations of the structure of polymer gels because of the following reasons:[50] (1) it is not necessary to deuterate the polymer component, but the major component, *i.e.*, the solvent, can be simply substituted with a deuterated solvent in most cases to enhance the scattering contrast, as well as to reduce the strong contribution of incoherent scattering from hydrogenous components.[65] (2) A variety of labeling methods,[50] such as labeled networks, labeled paths, labeled chains, and labeled cross-links, can be chosen depending on the purpose of the study. (3) Reference samples, such as non-cross-linked polymer solutions, are easily available to study the effects of cross-links. (4) Versatile sample environments, such as gel deformation, shearing, rheometry and high pressure, are available because of the strong neutron penetration power.[48]

As a result of many experimental works and discussions, the following SANS function is commonly used to analyze the scattering functions of polymer gels:[66]

$$I(q) = I_{soln} + I_{excess} \approx I_{OZ}(q) + I_{DB}(q) \tag{12}$$

$$I_{OZ}(q) = \frac{I_{OZ}(0)}{1+\xi^2} \tag{13}$$

$$I_{DB}(q) = \frac{I_{DB}(0)}{(1+\Xi^2)^2} \tag{14}$$

where $I_{OZ}(q)$ is the scattering function of polymer solutions and ξ is the correlation length, meaning the screening length of a semidilute solution (the blob length). This equation is the Ornstein–Zernike equation.[67] On the other hand, $I_{DB}(q)$ is the excess scattering arising from gel inhomogeneities. This equation is the so-called Debye–Bueche equation, representing two-phase structures with the characteristic inhomogeneity length Ξ.[68] Ξ is related to the chord lengths of the A domain (*e.g.*, the cross-link-rich domain) l_A and of the B matrix (*e.g.*, the cross-link-poor matrix) l_B (or *vice versa*), respectively, as follows:[69]

$$l = l_A + l_B = \left(\frac{1}{\phi_B} + \frac{1}{\phi_A}\right)\Xi \tag{15}$$

$$l_A = \frac{\Xi}{\phi_B}, \quad l_B = \frac{\Xi}{\phi_A} \tag{16}$$

where ϕ_A and ϕ_B are the volume fraction of the cross-link-rich domain and cross-link-poor matrix, respectively. The validity of eqn (12) is supported by the theory of Panyukov and Rabin.[56,57] A review of SANS works for polymer gels can be found in ref. 50 and 66, where other topics, such as deformation and contrast variation, are also discussed.

4.2.2 Gel research with DLS.

Starting from the THB theory, dynamic light scattering (DLS) studies have also been a common tool to study the structure of polymer gels. In the case of polymer solutions, the scattering intensity is independent of the sampling position (ergodic system). In the case of polymer gels, on the other hand, the scattering intensity strongly depends on the sampling position.[62,64] This is because gels are nonergodic systems in which the time average is not equal to the ensemble average:

$$\langle I\rangle_{\mathrm{E}} \neq \langle I\rangle_{\mathrm{T}} \tag{17}$$

Hence, in order to describe polymer gels, two types of average scattering intensities have to be defined, *i.e.*, the time average scattering intensity $\langle I_p\rangle_{\mathrm{T}}$, and ensemble average scattering intensity $\langle I\rangle_{\mathrm{E}}$. Here, $\langle I_p\rangle_{\mathrm{T}}$ is the scattering intensity of a long-term average at a sample position p, and $\langle I\rangle_{\mathrm{E}}$ is an ensemble average of $\langle I_p\rangle_{\mathrm{T}}$ as given by

$$\langle I\rangle_{\mathrm{E}} \equiv \langle\langle I_p\rangle_{\mathrm{T}}\rangle_{\mathrm{E}} = \frac{1}{N}\sum_{p}^{N}\langle I_p\rangle_{\mathrm{T}} \tag{18}$$

Here, p is the sampling position and N is the number of sampling positions.

The scattering intensity $\langle I_p\rangle_{\mathrm{T}}$ is given by

$$\langle I_p\rangle_{\mathrm{T}} = \langle I_{\mathrm{F}}\rangle_{\mathrm{T}} + I_{\mathrm{C},p} \tag{19}$$

where the subscript F means the fluctuating (dynamic) component.

The scattering field now consists of a dynamic component $E_{\mathrm{F}}(t)$ and a static component $E_{\mathrm{C},p}$, and the latter is sample-position (p)-dependent, as is written by

$$E_p(t) = E_{\mathrm{F}}(t) + E_{\mathrm{C},p} \tag{20}$$

Here, the time correlation functions of these two fluctuations correspond to the respective intensities, I_{F} and I_{C}:

$$\left\langle E_{\mathrm{F}}^{*}(t)E_{\mathrm{F}}(t)\right\rangle_{\mathrm{T}} = \left\langle E_{\mathrm{F}}^{*}(t)E_{\mathrm{F}}(t)\right\rangle_{\mathrm{E}} \equiv I_{\mathrm{F}} \tag{21}$$

$$\left\langle E_{\mathrm{C},p}^{*}E_{\mathrm{C},p}\right\rangle_{\mathrm{T}} \equiv I_{\mathrm{C},p}, \quad \left\langle I_{\mathrm{C},p}\right\rangle_{\mathrm{E}} \equiv I_{\mathrm{C}} \tag{22}$$

The time correlation function for the dynamic fluctuations is the same as that given by Tanaka, *i.e.*, eqn (6) and (7). On the other hand, that for nonergodic systems is now given by[64]

$$\langle g_p^{(2)}(\mathbf{q},t)\rangle_{\mathrm{T}} - 1 = X_p^{2}|g^{(1)}(\mathbf{q},t)|^{2} + 2X_p(1-X_p)|g^{(1)}(\mathbf{q},t)| \tag{23}$$

where

$$X_p = \frac{I_{\mathrm{F}}}{\langle I_p\rangle_{\mathrm{T}}} \tag{24}$$

DLS analyses can be done by simply fitting the correlation function, $\langle g_p^{(2)}(q,\tau)\rangle_{\mathrm{T}}$, by using eqn (7). However, it is more convenient to use the following equation:

$$\langle g_p^{(2)}(q,\tau)\rangle_{\mathrm{T}} - 1 = \sigma_{\mathrm{I},p}^{2}\exp(-2D_{\mathrm{A},p}q^{2}\tau) \tag{25}$$

where $D_{\mathrm{A},p}$ ($D \leq D_{\mathrm{A},p} \leq 2D$) is the apparent diffusion coefficient at position p. This is because the difference between D and $2D$ is not easy to distinguish in the fitting process. $\sigma_{\mathrm{I},p}^{2}$ is the initial amplitude of the correlation function given by

$$\sigma_{\mathrm{I},p}^{2} = \langle g_p^{(2)}(\tau = 0)\rangle_{\mathrm{T}} - 1 = X_p(2 - X_p) \tag{26}$$

By taking the $\tau = 0$ limit of the equation, one obtains $D_{\mathrm{A},p}$:

$$D_{\mathrm{A},p} = -\frac{1}{2q^{2}}\lim_{\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}\ln\left\{\left\langle g_p^{(2)}(q,\tau)\right\rangle_{\mathrm{T}} - 1\right\}. \tag{27}$$

Here, the relationship among $D_{\mathrm{A},p}$, X_p, and $\sigma_{\mathrm{I},p}$ is given by

$$D_{\mathrm{A},p} = \frac{X_p}{\sigma_{\mathrm{I},p}^{2}}D = \frac{D}{2 - X_p} \tag{28}$$

On the other hand, $\langle I_p\rangle_{\mathrm{T}}$ has its lower bound $\langle I_{\mathrm{F}}\rangle_{\mathrm{T}}$. Since $\langle I_p\rangle_{\mathrm{T}}$ is the scattering intensity corresponding to the thermal fluctuations, its lower bound is proportional to the absolute temperature T.

The distribution of $\langle I_p\rangle_{\mathrm{T}}$ is given by

$$P\left(\langle I_p\rangle_{\mathrm{T}}\right) \approx H\left[\langle I_p\rangle_{\mathrm{T}} - \langle I_{\mathrm{F}}\rangle_{\mathrm{T}}\right]\exp\left\{-\frac{\langle I_p\rangle_{\mathrm{T}} - \langle I_{\mathrm{F}}\rangle_{\mathrm{T}}}{\langle I\rangle_{\mathrm{E}} - \langle I_{\mathrm{F}}\rangle_{\mathrm{T}}}\right\} \tag{29}$$

Here, $H(x)$ is the Heaviside step function; $H(x) = 1$, $(x \geq 0)$, $H(x) = 0$, $(x < 0)$.

From eqn (24) and (28), one obtains

$$\frac{\langle I_p\rangle_{\mathrm{T}}}{D_{\mathrm{A},p}} = \frac{2}{D}\langle I_p\rangle_{\mathrm{T}} - \frac{\langle I_{\mathrm{F}}\rangle_{\mathrm{T}}}{D} \tag{30}$$

This equation is useful to decompose the scattering intensity (and/or the concentration fluctuations) to the static and dynamic components and to evaluate the diffusion coefficient D (= D_{DLS}).[70,71]

Fig. 10 shows an example of the decomposition plot of polymer gels: (a) the scattering intensity variations with sample position, *i.e.*, speckle patterns, typical for polymer gels; (b) two correlation functions for solution-like and solid-like parts in a gel; (c) the distribution function of the apparent diffusion coefficient D_{A}, which is a decreasing function of $\langle I_p\rangle_{\mathrm{T}}$ with a lower cutoff $\langle I_{\mathrm{F}}\rangle_{\mathrm{T}}$; and (d) the decomposition plot from which D(= D_{DLS}), $\langle I_{\mathrm{F}}\rangle_{\mathrm{T}}$, and $\langle I_{\mathrm{E}}\rangle_{\mathrm{T}}$ can be evaluated.[71]

DLS has made long strides in incorporating the concept of inhomogeneities, and provides various pieces of information: the mesh size, the sol–gel transition point,[71–73] the separation of static/dynamic concentration fluctuations,[70,71] probe diffusion,[74,75] *etc.*

4.3 Classification of gel inhomogeneities

Polymer gels inherently contain various types of inhomogeneities that are introduced during gel preparation stages, such as the polymerization/cross-linking stage, or kinetically trapped in the sol–gel transition stage. Shibayama discussed gel inhomogeneities[76] and classified gel inhomogeneities into spatial, topological, connectivity, and mobility inhomogeneities.[71] Fig. 11 schematically shows gel inhomogeneities.[71] The upper row shows the concentration fluctuations of polymer solutions (left) and polymer gels (right), where

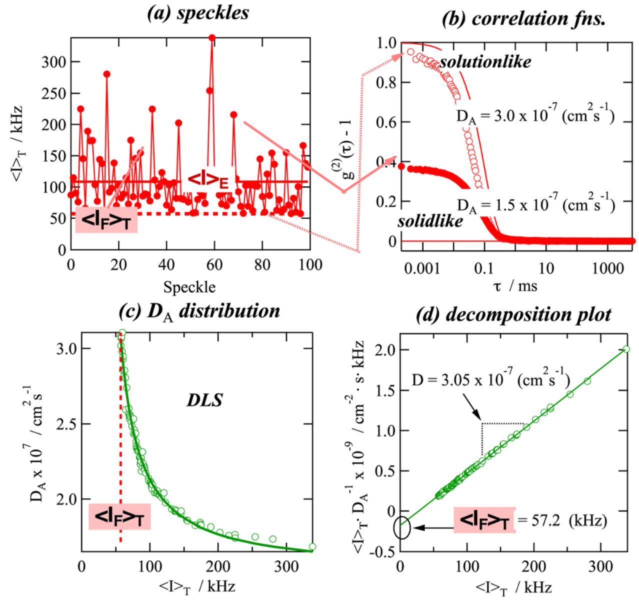


Fig. 10 DLS decomposition plot. (a) Speckles, (b) correlation functions, (c) D_A distribution, and (d) decomposition plot. (Reprinted with permission from ref. 71. Copyright 2006 Chemical Society of Japan.)

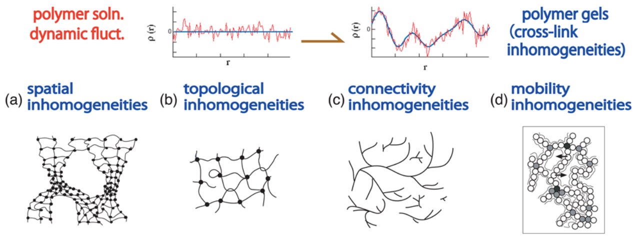


Fig. 11 Various types of inhomogeneities. (Upper row) Schematics of concentration fluctuations: (left) polymer solutions and (right) polymer gels where frozen inhomogeneities (blue) are introduced by cross-linking, superimposed onto thermal fluctuations (red). (Lower row; from left to right) (a) Spatial, (b) topological, (c) connectivity, and (d) mobility inhomogeneities.

frozen inhomogeneities (blue line) are superimposed on dynamic fluctuations (red line). The lower row shows the types of inhomogeneities, *i.e.*, spatial, topological, connectivity, and mobility inhomogeneities (from left to right). These various inhomogeneities can be investigated *via* SANS, swelling/shrinking experiments, DLS, and light scattering intensity speckles, respectively. A recent review by Seiffert followed up the literature of SANS as well as small-angle X-ray scattering (SAXS) and static and dynamic light scattering.[77]

5 Toward realization of ideal polymer networks

5.1 Tetra-PEG gels

Gels are believed to be inherently inhomogeneous because cross-linking is an inevitable process of gel preparation. Many researchers have tried to prepare defect-free homogeneous gels, but have failed. In 2008, Sakai *et al.* succeeded in fabrication of near-ideal polymer gels with monodisperse mesh sizes, called tetra-PEG gels.[78] The tetra-PEG gels were prepared by cross-end-coupling of *N*-hydroxysuccinimidyl (NHS)-terminated tetra-PEG macromers and amine-terminated tetra-PEG macromers. The typical molecular weights M_w of commercially available PEG macromers are 5 kDa to 40 kDa. These tetra-PEG macromers were separately dissolved in neutral buffered water. By simply mixing the two aqueous solutions with vigorous stirring, gelation occurred.

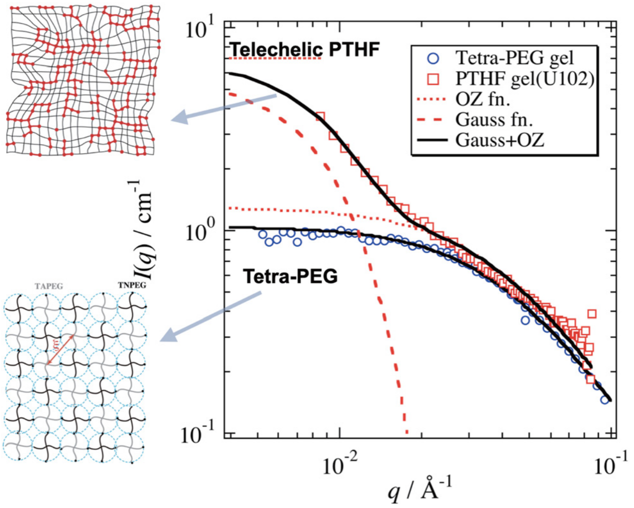


Fig. 12 SANS functions of a conventional PTHF gel and tetra-PEG gel. Solid lines are fitted with eqn (11) with/without a Gaussian component for the PTHF gel and tetra-PEG, respectively. The cartoons on the right schematically show the network structures. (Modified from Fig. 3 of ref. 66.)

Fig. 12 shows the SANS functions of a poly(tetrahydrofuran) (PTHF) network gel and tetra-PEG gel. The former consisted of end-linked PTHF networks having a fairly narrow molecular weight distribution, with a polydispersity index of 1.20.[79] Even though it was regarded as a unimodal model polymer network, its SANS function had a strong forward scattering, which was fitted with eqn (11). On the other hand, the SANS function of tetra-PEG did not show such a forward scattering[80,81] and was simply fitted with the Ornstein–Zernike function $I_{OZ}(q)$ in eqn (13). In the review paper of the structure–mechanical properties of tough hydrogels,[66] the difference in SANS between conventional gels (PTHF gel) and tetra-PEG gels is discussed. The main conclusion of the difference was the presence/absence of low q-scattering, respectively, for a conventional gel and tetra-PEG gel.

Though the combination of NHS-terminated and amine-terminated tetra-PEG macromers was very successful,[78] it had a drawback. Because the NHS-terminated tetra-PEG macromers gradually hydrolyzed spontaneously in water, the activity of the NHS end-group deteriorated with time.[82] For preparation of defect-free gels, a combination of maleimide-terminated and thiol-terminated tetra-PEG macromers is more suitable for preparation of precisely controlled tetra-PEG gels, because there is negligible byproduct in this coupling reaction.[83,84]

5.2 Physics driven by tetra-PEG gels

Because of their uniform network structure, tetra-PEG gels have been used for various purposes and applications.[85] Fig. 13 illustrates the physics developed because of the discovery of tetra-PEG gels. The uniform network structure of tetra-PEG gels (a) allowed investigations of the deformation mechanism,[86] a model network system for examination of rubber elasticity,[87,88] molecular sieves,[82] microscopic dynamics with probe diffusion,[75] and the kinetics of tetra-PEG gels.[89,90] The tunability (p-tuning) of the network structure (b) is used for fabrication of controlled-defect networks (p-tuned gels) and for percolation studies, where p ($0 < p \leq 1$) is the bond probability of the network.[88,91] Non-stoichiometric gelation of tetra-PEG gels (nonstoichiometry) (c) is used for studying critical gels.[92] Conetwork gels (d) obtained by copolymerization with environment-sensitive tetra-macromers have also opened a new direction for various applications, including thermosensitive gels,[93,94] solvent-sensitive gels,[95] and model polyelectrolyte gels.[96,97] Regarding (d), nonswellable gels that do not swell in the body have been fabricated. In medical applications, nonswellability is crucial to avoid damaging tissue. Such a nonswellable gel was made by fabricating a conetwork in which the components have opposite temperature dependence.[94] Fabrication of tetra-PEG gels in ionic liquids (ion gels) (e) opened a new door for realization of non-volatile gels.[98–100]

Here, percolation theory is a theory that deals with how target substances are connected within a system and how their characteristics are reflected in the properties and dynamics of the system.[101,102] There are two basic types of percolation: bond percolation and site percolation. Let us consider a lattice model, which can be a two dimensional or three dimensional model or something else. In the case of bond percolation, all sites are pre-occupied by monomers and the connectivity is statistically controlled by the bond probability, p_b. When any finite clusters interconnected *via* bonds reach the system size, a bond percolation is attained. In the case of site percolation, on the other hand, monomers are randomly placed in sites of the lattice. If there is a neighbor, they spontaneously bond to each other and form clusters. The fraction of occupancy is defined as the site probability, p_s. When any of the finite clusters reach both ends of the system, it is called percolation. Another type of model called site-bond percolation, proposed by Coniglio *et al.*,[103] is more suitable for description of polymer gels because the site corresponds to a monomer and the bond corresponds to a cross-linker.[71,104]

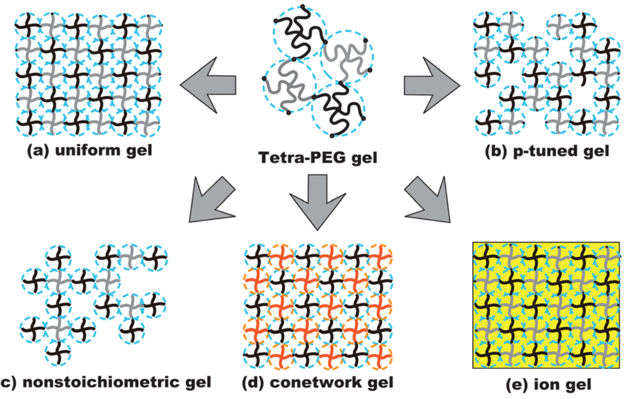


Fig. 13 Schematics of the derivatives of tetra-PEG gels: (a) uniform gels, (b) p-tuned gels, (c) nonstoichiometric gels, (d) conetworks, and (e) ion gels. Black and grey lines show a set of NHS-terminated tetra-PEG and amine-terminated tetra-PEG macromers, or a set of maleimide-terminated and thiol-terminated tetra-PEG macromers. Red lines denote environment-sensitive macromers, such as thermosensitive macromers. The yellow box shows an ionic liquid environment instead of an aqueous environment.

In the following, two examples, *i.e.*, re-exploration of rubber elasticity and of diffusion coefficients, are given.

5.2.1 Rubber elasticity. Nishi *et al.* examined rubber elasticity by using entanglement-free model networks.[106] They prepared well-defined model polymer networks with maleimine- and thiol-terminated tetra-PEGs, and measured the elastic modulus G for a broad range of polymer concentrations and connectivity probabilities, p.[106] They first confirmed that the percolation threshold is $p_c \approx 0.39$, which is analogous to the conductivity of a resistor network[107] and not to the classical model (0.33 for a tetra-arm Bethe lattice). They also observed two distinct features different from those believed for classical Gaussian chain behaviors: (1) the critical exponent t on the shear modulus G near the gelation threshold, $G \propto |p - p_c|^t$, where p and p_c are the fraction of bonds that connect neighbor sites and the percolation threshold, respectively, and (2) deviation from affine and phantom chain models. Regarding (1), the classical theories predict $t = 3$,[61] whereas de Gennes and Daoud predict $t = 1.9$[107] and 2.6,[108] respectively. Nishi *et al.* observed $t = 1.95 \pm 0.05$ for a wide range of initial gel concentrations, $40\ \mathrm{mg\ mL^{-1}} \leq C_0 \leq 120\ \mathrm{mg\ mL^{-1}}$ and $0.03 \leq p - p_c$. They confirmed the validity of the effective medium theory (EMA) of percolation on a central-force elastic network.[88]

Regarding (2), Fig. 14 shows (a) an experimental G–p plot and theoretical predictions for the affine model and phantom model ($C_0 = 120\ \mathrm{mg\ mL^{-1}}$), and (b) the p dependence of the reduced elastic modulus at various C_0 values. Note that the G/G_0–p curves fall onto a single master curve, where G_0 is that of $p = 1$ and the solid line corresponds to the theoretical prediction from the effective medium approximation (EMA). In the inset, g_0 is the elastic constant of a single chain and g_m is the normalized elastic constant of the uniform effective medium.[105,106]

5.2.2 Diffusion coefficients. Sakai *et al.* revisited some of the essential problems of the physics of polymer gels, such as solvent diffusion, the shear modulus and the friction factor, using near-ideal polymer network gels.[109] Their studies include the permeation of water through hydrogels with a controlled network structure,[83] comparison of the three diffusion coefficients (D_{sw}, *via* swelling experiments; D_{DLS}, *via* DLS; and D_{w}, *via* water permeation),[110] mixing and elastic contributions to the diffusion coefficient of polymer networks,[111] the shear modulus dependence of the diffusion coefficient of a polymer network,[112] and structure–property relationships of a model network containing solvent.[113] Here, the scaling theory on the

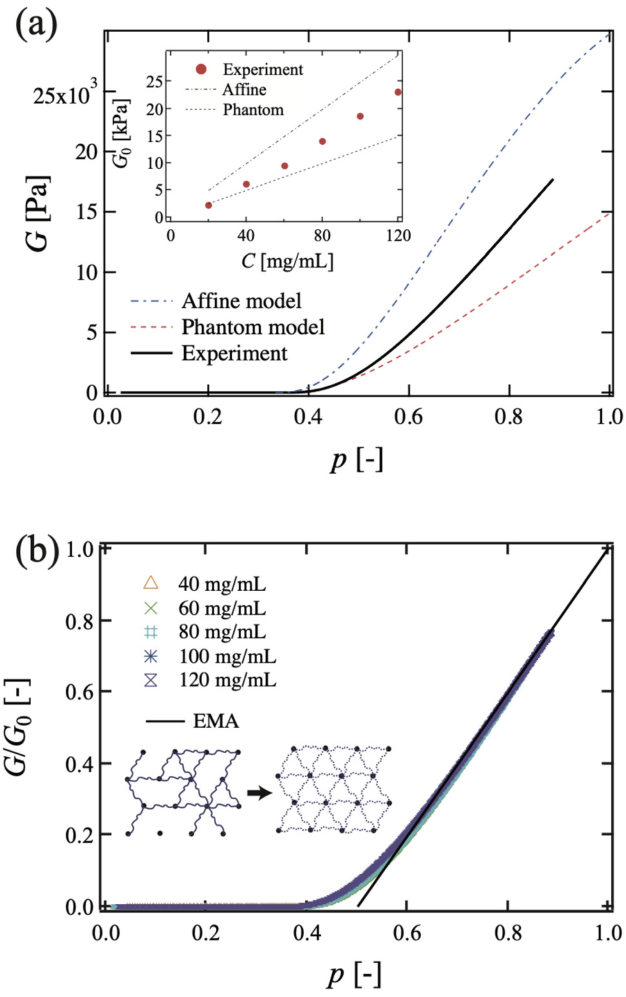


Fig. 14 (a) Experimental G–p plot and theoretical predictions for the affine model and phantom model (C_0 = 120 mg mL^{-1}). Inset: Concentration dependence of the elastic modulus at p = 1, as evaluated from the fitting result. The theoretical predictions of the affine and phantom network model are also shown. (b) The p dependence of the reduced elastic modulus at various C_0 values. The solid line corresponds to the theoretical prediction from the effective medium approximation (EMA). Inset: Schematic illustration of the EMA. The network on the left represents the original system in which neighboring sites are randomly connected with chains of elastic constant g_0. The network on the right represents the EMA with a nondisordered structure in which all neighboring sites are connected with chains of elastic constant g_m. (Reprinted from ref. 106 with permission. Copyright 2017 American Physical Society.)

friction factor and the blob size is experimentally derived,[83] and the validity of the THB and TF theories is discussed.[110–112] These works could only be achieved with monodisperse-strand model networks free of entanglements and defects.

5.3 Flexible and highly ordered three-dimensional networks: super-homogeneous gels

Although tetra-PEG gels are very homogeneous with a low level of defects and are regarded as "near-ideal polymer networks", there still remain noticeable speckles and forward scattering. Recently, Li *et al.* employed an innovative strategy and succeeded in the fabrication of "super-homogeneous gels."[114] This is based on the "bond percolation" model, which is one of the classical percolation models,[103] as discussed above. The bond percolation model assumes that the space is uniformly pre-packed with mutually exclusive units in the beginning, and the percolation occurs as a consequence of cross-linking between the nearby units, *i.e.*, a reaction-controlled process.[115] Because the units are mutually exclusive, the space is always uniformly filled by the units regardless of the extent of cross-linking and network formation, leading to a highly ordered, ideal network structure after the reaction completes.

The following is the protocol of the preparation of the bond-percolation gels: (i) it starts with monodisperse star polymers, *e.g.*, four-armed poly(ethylene glycol), as space filling units (Fig. 15A) because polymers with multiple arms show a strong excluded volume effect that prevents other polymers from coming into the pervaded volume.[116] Then, (ii) dissolving the star polymers in a good solvent at a concentration well above their chain overlapping concentration ensures that the star polymers uniformly and tightly fill the space (Fig. 15B) as the bond percolation model assumes. (iii) To prevent the segregation of polymer chains during cross-linking,[117] dehydrated acetonitrile is chosen as the solvent because it shows excellent affinity to the star polymers used in this study. Moreover, (iv) to remove dust and nanobubbles[118] from the solution as much as possible, the dissolved polymer solutions are filtered through ultrafine syringe filters. Although all the aforementioned issues have already been pointed out separately in past studies, they have never been resolved altogether in a single system.

The thus-obtained gel (Fig. 15C) was examined using SLS and SAXS over a wide q range and it was confirmed that the scattering function of the gel is almost identical to that of the pregel solution and is well represented by the OZ equation. This indicates that (1) gelation of the star polymers proceeded *via* bond percolation and (2) the spatial correlation between the polymer chains did not change with cross-linking. Furthermore, speckle patterns, which are an indication of spatial defects and the sol–gel transition, were not observed at all throughout the whole gelation process.

The success of the development of "super-homogeneous gels" has opened a new door in gel science for further refinement of the theories of rubber elasticity, polymer gels, polymer networks, and polymer solutions, but also for advanced applications in filtration,[119] sensing,[120] drug release,[121] electronics,[122] and so on. The realization of super-homogeneous gels would be a key theoretical and technological advance in polymer science and technology because of their defect-free and entanglement-free three-dimensional network structure.

6 Future directions

The history of the physics of polymer gels has been considered along with the footprints of Toyoichi Tanaka. One of the future directions of gel physics would be deeper and unified understanding of connectivity- or percolation-related phenomena,

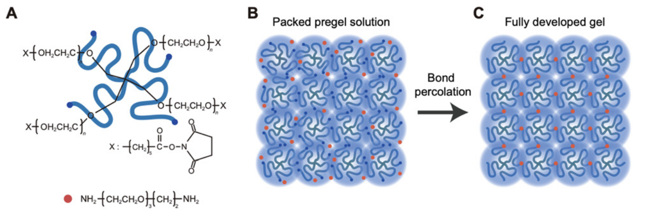


Fig. 15 Schematic of the gel preparation *via* bond percolation. (A) Star polymer: tetrafunctional poly(ethylene glycol) (PEG) with active ester end groups; bifunctional cross-linker: 1,14-diamino-3,6,9,12-tetraoxatetradecane (amino-PEG4-amine). (B) Stoichiometric mixture of the star polymer and the cross-linker in a good solvent. The system is uniformly prepacked with the star polymers. (C) Polymer gel formed by end-linking of the star polymers with the small cross-linkers *via* bond percolation. 2D schematics are shown instead of the real 3D polymer network for the sake of legibility. (Reprinted from a part of Fig. 1 of ref. 114 with permission. Copyright 2019 American Association for the Advancement of Science.)

i.e., sol–gel transitions, vitrification, and jamming transitions. The physics of polymer gels, polymer glasses, and colloids has been developed rather independently, but could be generalized *via* the key word of "connectivity" or "percolation".

Fig. 16 shows the relationship among polymer gels, polymer glasses, and polymer colloids. Gels are made by polymerization in the presence of cross-linkers. Polymer colloids are made from monomers in solvent in the presence of a surfactant. Glasses are formed by bulk polymerization of monomers. Here, the significant phenomena in physics are sol–gel transitions, vitrification, and jamming transitions. As shown in the figure, these transitions also exist between gels and colloids, between gels and glasses, and between colloids and glasses by tuning the "density" (ρ = monomer concentration, cross-linker concentration, surfactant concentration, *etc.*). Here, translational diffusion, cooperative diffusion, and slow dynamics have been hot topics in soft-matter physics. Scattering and spectroscopic methods, including DLS and SANS, have been used for unveiling the physics connecting these different materials, namely, vitrification *vs.* gelation[123] and jamming transitions,[124] which will be further advanced in the future by using modern experimental methods.

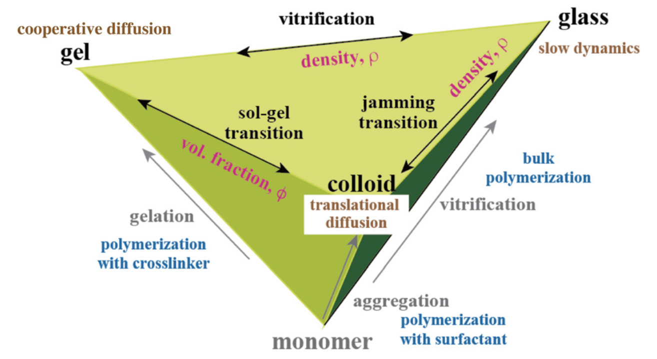


Fig. 16 Gel–glass–colloid diagram. Polymer gels, polymer glasses, and polymer colloids have a common origin, monomers, but are formed in different environments/conditions. There are at least interconversions *via* connectivity transitions, such as sol–gel transitions (chemical and/or physical bond; polymer volume fraction ϕ), jamming transitions (space filling; colloid density ρ), and vitrification (mobility freezing; gel density ρ).

Another and more alluring direction of gel physics is the understanding of life and biological functions, in which Tanaka himself was deeply involved in his last decade. As is well known, life is defined by its capacities for homeostasis, organization, metabolism, growth, adaptation, response to stimuli, and reproduction. We have been learning and imitating these biological functions. Responsive gels are typical examples and have been developed since the 1990s.[34,35] Today, synthetic gels with sophisticated biological functions are designed and realized, such as self-healing gels, self-growing gels,[125,126] *etc.* This direction will be a great step forward.

7 Conclusions

The history of the physics of polymer gels over about half a century, starting with the work of Toyoichi Tanaka, has been reviewed. In particular, (1) the Tanaka–Hocker–Benedek theory, and the discoveries of (2) the volume phase transition of polymer gels and (3) the temperature-induced volume phase transition have influenced not only polymer science but also other fields.

The understanding of gel inhomogeneities led not only to the developments of various gel characterization methods, such as neutron scattering, X-ray scattering, and pulsed NMR, but also to providing novel ideals to circumvent various problems that conventional gels have and to the search for defect-free homogeneous ideal polymer gels.

The fabrication of ideal polymer networks has great physical significance that can be compared with the success of the preparation of monodisperse polymers by Szwarc in 1956.[127] He developed an anionic living polymerization method for the preparation of narrow-molecular-weight dispersed polystyrene. After the acquisition of this "standard polymer", the theories of polymer solutions[128] and rubber elasticity,[129] polymer rheology,[130] and the scaling theory of polymer physics[61] have made great advances. Now, tetra-PEG gels are a model polymer network system for the refinement of rubber elasticity, percolation theory,[101,102] and so on.

Lastly, this review closes with repeating a part of the preface of a book Tanaka edited:[122] "Polymers are considered among the most important materials in science and technology for the 21th century. The uses of polymers in our everyday life are being extended and diversified day by day. The chemical, medical, and agricultural industries as well as many others are heavily dependent on a wide variety of polymers. Moreover, polymers are the materials that nature chose as the vehicle for life that appeared on this earth." Here, Tanaka would have substituted the term "polymers" by "polymer gels".

Data availability

Since this is a review paper, in principle, no new data are provided in this work and the data can be obtained in the references. If not, the data that support the findings of this study are available from the corresponding author, MS, upon reasonable request.

Conflicts of interest

There are no conflicts to declare.

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