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Preface

Polymer gels, which have both solid- and liquid-like properties, are an astonishing and fascinating material. At a first glance, they are just composed of a cross-linked polymer network and interstitial fluid. The ability of cross-linked water-soluble polymers to absorb large amounts of water and to form hydrogels makes them ideal vehicles for the storage or transport of active ingredients. Polyelectrolyte gels have been developed as superabsorbent materials in diapers and for moisture control. These gels can contain over 99% water. The water uptake, the swelling process, is associated with a respective volume change. Hydrogels became part of our workaday life. Applications of hydrogels have become extraordinarily widespread, notably in food processing, cosmetics, pharmaceuticals, bio-technology, agriculture, and paint manufacturing.

Apart from the swelling, two other properties make hydrogels attractive.

First, a strong volume change can be excited by a large spectrum of different physical and chemical factors such as temperature, electrical voltage, pH, concentration of organic compounds in water, and salt concentrations. The possibility of a first-order volume phase transition in gels was suggested by K. Dušek and D. Patterson in 1968 based on an analysis of Flory–Rehner theory. It took ten years for the phenomenon to be experimentally observed after prediction. It was found by T. Tanaka that, when a critical amount of an organic solvent was added to a water-swollen poly(acrylamide) gel, the gel collapses. Many gels of synthetic and natural polymers have been studied. Subsequent experiments showed that a volume phase transition (swelling/collapse) could also be brought about by changes in other environmental parameters such as pH, ionic strength, and temperature.

Second, volume change due to these physical or chemical stimuli is reversible. Hence, hydrogels are chemomechanical transducers converting chemical energy into mechanical energy and vice versa. This offers a huge potential for new sensor and actuator principles especially for applications in all fields where aqueous solutions play a decisive role, e.g., in process engineering, fluidics, chemistry, cell biology, and drug delivery, and makes them real "smart" materials. Artificial muscles are another field where ionic hydrogels are getting more and more attention.

Most of the authors of this book are scientists from the Technische Universität Dresden, having been involved in the "hydrogel business" for many years. One of the roots for that was the Collaborative Research Center “Reactive Polymers” (spokesman: Prof. Hans-Jürgen Adler) established in 1996 at the TU Dresden and funded by the German Research Foundation (DFG Deutsche Forschungsgemeinschaft). One of the foci of this centre was to investigate the chemistry and the physics of hydrogels, their synthesis, and their integration into engineering solutions. The close collaboration between chemists, physicists, and engineers was the prerequisite to get a profound understanding of the complex interactions within smart hydrogels and their prospects for new sensor and actuator systems.

Undoubtedly, a single institution is not capable of dealing with all aspects of such a complex matter. This is the reason why we were strongly interested in enlisting colleagues from the Universities of Stuttgart and Freiburg as well as from the Max Bergmann Centre, Dresden, as experts for several aspects with important relevance to hydrogel sensors and actuators. We are deeply indebted to them.

The book is organized in the following manner. After a short introduction of the general properties of hydrogels, Chap. 2 discusses the fabrication of hydrogels. Afterward, Chap. 3 introduces the thermodynamic processes down to the molecular level taking place in hydrogels during swelling and shrinkage. Since Chaps. 2 and 3 describe the complex chemical, physical, and physicochemical properties of hydrogels, their number of pages is larger than that of the following chapters. We did not take them to pieces to show the interactions and relationships in its complexity, but we structured the text in subchapters such that each of them has its own reference list.

Based on the understanding of the chemical and physical effects, the chemo-electro-mechanical coupling in hydrogels will be presented in Chap. 4. To predict the functioning of hydogel-based devices, models are needed to describe the complexity of occurring interactions and to enable the simulation of technical devices. The following three chapters (Chaps. 5–7) focus on the application of hydrogels in chemical and biosensors and for actuators. Finally, Chap. 8 shows a particular application of hydrogels in cell biology as cell culture carriers.

The editors of this book hope that the contents depict the most recent progress in hydrogel research for sensor and actuator devices. As it can be seen, it still needs a lot of efforts to bridge the gap between state-of-the-art research and existing demands for a future market introduction. However, there are plenty of ideas to overcome the still remaining problems. Let the book be an inspiration to all the colleagues involved in hydrogel research and development!

We thank all our coauthors who have contributed their comprehensive knowledge with their particular competence to this book. We also thank those companies and institutions that allowed us to use figures and material and which are named in the captures of the individual figures. Furthermore, we thank Springer-Verlag and in particular Thomas Lehnert and Ulrike Butz for the cordial cooperation and also for the patience when faced with repetitive delays due to the authors’ workload. We are deeply grateful to the Springer staff for their support during the entire process, from the first idea all the way through to the final book.

Dresden, January 2009

Gerald Gerlach
Karl-Friedrich Arndt

Contents

General Properties of Hydrogels

O. Okay

Abstract In the application areas of polymer hydrogels, precise information on their molecular constitution as well as their elastic properties is required. Several interesting molecular features control the elastic properties of the hydrogels. In this chapter, we describe general properties of hydrogels formed by free-radical crosslinking copolymerization of vinyl/divinyl monomers in aqueous solutions. Special attention is paid to the relationships between the formation conditions of hydrogels and their properties such as swelling behaviour, elastic modulus, and spatial inhomogeneity. New developments achieved in the design of hydrogels with a good mechanical performance and a fast response rate is also presented.

Keywords Hydrogels • Elasticity • Swelling • Inhomogeneity

Contents

Abbreviations

AAm	Acrylamide
AMPS	Na sodium salt of 2-acrylamido-2-methylpropane sulfonic acid
DMSO	Dimethylsulfoxide

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FH	Flory–Huggins
MBAAm	*N*,*N*-methylene bisacrylamide
PAAc	Poly(acrylic acid)
PAAm	Poly(acrylamide)
PDMAAm	Poly(*N*,*N*-dimethylacrylamide)
PEG-300	Poly(ethylene glycol) of molecular weight 300 $\mathrm{g\,mol^{-1}}$
PNIPAAm	Poly(*N*-isopropyl acrylamide)
TBA/AAm	Poly(*N*-*t*-butylacrylamide-co-AAm)

Symbols

$\mathrm{C_o}$	Initial monomer concentration (g monomer / 100 mL solution)
f	Effective charge density of the network
G_r	Reduced elastic modulus
G_o	Modulus of elasticity after gel preparation
N_s	Number of segments between two successive cross-links
Q_v	Volume swelling ratio (swollen gel volume / dry gel volume)
$R_\mathrm{ex,q}$	Excess scattering intensity at the scattering vector q
V	Gel volume at a given degree of swelling
V_eq	Equilibrium swollen normalized gel volume
V_o	Gel volume in after-preparation state
V_r	Normalized gel volume
V_sol	Equilibrium swollen gel volume in solution
V_w	Equilibrium swollen gel volume in water
$\mathrm{x_i}$	Ionic monomer mole fraction in comonomer feed
α	Linear deformation ratio
ΔG_{el}	Gibbs free energy of elastic deformation
ΔG_{ion}	Ionic contribution to Gibbs free energy
ε_{xl}	Cross-linking efficiency of cross-linker
φ_2	Volume fraction of cross-linked polymer in gel
φ_2^0	Volume fraction of cross-linked polymer after gel preparation
ν_c	Effective cross-link density

1 Introduction

Hydrophilic gels called hydrogels are cross-linked materials absorbing large quantities of water without dissolving. Softness, smartness, and the capacity to store water make hydrogels unique materials (Tanaka 1981; Shibayama and Tanaka 1993). The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymer backbone while their resistance to dissolution arises from cross-links between network chains. Water inside the hydrogel allows free diffusion of some solute molecules, while the polymer serves as a matrix to hold water together. Another aspect of hydrogels is that the gel is a single polymer molecule, that is, the network chains in the gel are connected to each other to form one big molecule on macroscopic scale. It is natural to expect that the conformational transitions of the elastically active network chains become visible on the macroscopic scale of hydrogel samples. The gel is a state that is neither completely liquid nor completely solid. These half liquid-like and half solid-like properties cause many interesting relaxation behaviours that are not found in either a pure solid or a pure liquid. From the point of view of their mechanical properties, the hydrogels are characterized by an elastic modulus which exhibits a pronounced plateau extending to times at least of the order of seconds, and by a viscous modulus which is considerably smaller than the elastic modulus in the plateau region (Almdal et al. 1993).

Hydrogels may exhibit drastic volume changes in response to specific external stimuli, such as the temperature, solvent quality, pH, electric field, etc. (Dusek and Patterson 1968; Tanaka 1978). Depending on the design of the hydrogel matrices, this volume change may occur continuously over a range of stimulus level, or, discontinuously at a critical stimulus level. The volume transition behaviours of hydrogels received considerable interest in the last three decades and large parts of the work have been collected in different reviews (Shibayama and Tanaka 1993; Khokhlov et al. 1993).

Polymeric hydrogel networks may be formed by various techniques, however the most common synthetic route is the free-radical cross-linking copolymerization of a hydrophilic non-ionic monomer such as acrylamide (AAm) with a small amount of a cross-linker, e.g., *N*,*N*'-methylenebis(acrylamide) (MBAAm). In order to increase their swelling capacity, an ionic comonomer is also included into the reaction mixture. Since the monomers for hydrogel preparation are usually solid at the usual polymerization temperature, it is necessary to carry out the polymerization reactions in an aqueous solution. Hydrogel structure and, thus, the hydrogel properties are closely related to the conditions under which the hydrogels are formed, i.e., the cross-linker concentration, the initial degree of dilution of the monomers and the chemistry of the units building the network structure. The understanding of the formation mechanism of hydrogels under various experimental conditions is of great interest to predict their physical properties.

2 Swelling and Elasticity of Hydrogels

The equilibrium swelling degree and the elastic modulus of hydrogels depend on the cross-link and charge densities of the polymer network as well as on the cross-linked polymer concentration after the gel preparation. Although the theories predict the swelling properties and the elastic behavior of hydrogels formed under various conditions, the agreement between theory (see Chap. 3 Sect. 1.2) and experiments is only qualitative. Figure 1 illustrates the characteristic features of

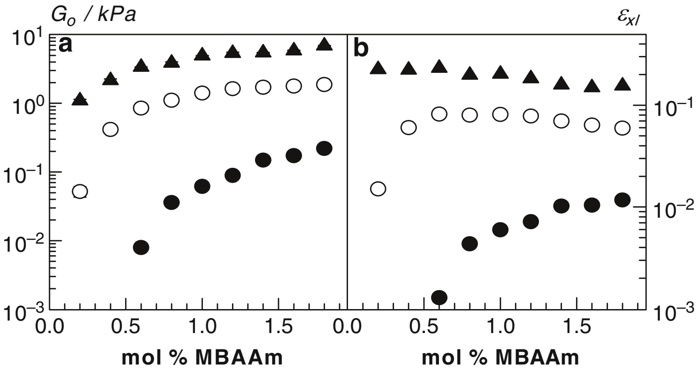

Fig. 1 The elastic modulus G_o of PAAm hydrogels after preparation (**a**) and the cross linking efficiency ε_{xl} (**b**) shown as a function of MBAAm concentration. Initial monomer concentration $C_o = 3$ (*filled circle*), 5 (*open circle*), and 7 w/v % (*filled triangle*). Reprinted from Orakdogen and Okay (2006a) with kind permission of Springer Science + Business Media

poly(acrylamide) (PAAm) hydrogels prepared from AAm and MBAAm in aqueous solutions (Kizilay and Okay 2003a; Orakdogen and Okay 2006a). In Fig. 1a, the modulus of elasticity after the gel preparation, G_o, is plotted against the cross-linker (MBAAm) content for three series of gels prepared at various initial monomer concentration C_o. Hydrogels exhibit elastic moduli in the range of 0.01 to 10 kPa, which are much smaller than the calculated values from their cross-linker contents. The initial period of the G_o versus MBAAm % plots can be used to estimate the lower limit of the cross-linker concentration required for the onset of gelation. The best-fit curves through the G_o versus % MBAAm data intersect with the positive abscissa at 0.03, 0.19, and 0.55 mol % MBAAm for $C_o = 7$, 5, and 3 %, respectively (Orakdogen and Okay 2006a). Thus, the larger the dilution degree of the reaction system, the higher is the threshold concentration of MBAAm for the formation of an infinite network. Figure 1b shows cross-linker concentration dependence of the cross-linking efficiency ε_{xl} of MBAAm, that is the fraction of MBAAm forming effective cross-links. ε_{xl} is less than 20% and, it further decreases below 1% as the initial monomer concentration is decreased. This is a consequence of the increase of probability of cyclization and multiple cross-linking reactions as the initial monomer concentration decreases (Funke et al. 1998).

The polymer network concentration at the state of gel preparation (index o), represented by the cross-linked polymer volume fraction φ_2^0, also alters significantly the hydrogel structure and, in turn, alters the hydrogel properties. The effect of φ_2^0 on the hydrogel properties is illustrated in Fig. 2 for polyacrylic acid (PAAc) hydrogels prepared at various φ_2^0 (Yazici and Okay 2005). In Fig. 2a, the modulus of elasticity G_o and the effective cross-link density ν_c of PAAc hydrogels are plotted against φ_2^0. Figure 2b shows φ_2^0 dependence of the swelling ratio of PAAc gels in terms of the volume swelling ratio Q_v (volume of swollen gel in water / volume of dry gel). G_o increases from 1.4 kPa to 50 kPa as φ_2^0 is increased. The inset to Fig. 2a shows that the modulus data can be described by a power law

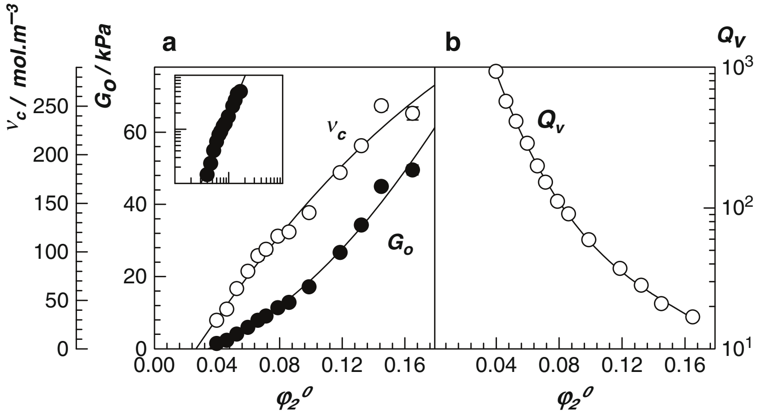

Fig. 2 The modulus of elasticity G_o, the effective crosslink density ν_c (**a**) and the volume swelling ratio Q_v of PAAc hydrogels in water (**b**) as function of the polymer network concentration φ_2^0; 1.2 mol % MBAAm. The inset to Fig. 2a shows a double logarithmic G_o vs. φ_2^0 plot. Reprinted from Yazici and Okay (2005) with kind permission from Elsevier

$G_0 \propto \left(\varphi_2^0\right)^x$ where $x = 2.1 \pm 0.1$. The exponent is much larger than the linear dependence ($x = 1$) predicted by the theory of rubber elasticity (Flory 1953; Treloar 1975), and indicates existence of non-idealities during the gel formation process. Increasing number of wasted MBAAm molecules in cycles on raising the dilution of the reaction solution explains this discrepancy (Naghash and Okay 1996). Indeed, ν_c is an increasing function of φ_2^0 (Fig. 2a), that is, the higher the initial monomer concentration, the larger the effective cross-link density of the hydrogels and the smaller their swelling capacity (Fig. 2b).

Increasing number of ionic groups in hydrogels is known to increase their swelling capacities. This is mainly due to the simultaneous increase of the number of counterions inside the gel, which produces an additional osmotic pressure that swells the gel (Flory 1953). The excess swelling over the swelling of the corresponding non-ionic hydrogels can be suppressed with increasing salt concentration in the external solution, which decreases the concentration difference of the counterions between the inside and outside the gel phase. Figure 3 illustrates the typical swelling behaviour of ionic PAAm hydrogels of various charge densities in water and in aqueous NaCl solutions (Durmaz and Okay 2000). The ionic comonomer used in the hydrogel preparation is sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS Na). AMPS Na units dissociate completely over the entire pH range so that AMPS Na containing hydrogels exhibit pH-independent swelling. Increase of the AMPS Na content from 0 to 80 mol % results in a 27-fold increase in the hydrogel volume in water. In 1.0 M NaCl solution, the swelling ratio is almost independent on the ionic group content due to screening of charge interactions within the hydrogel.

Since ionic hydrogels are highly swollen in water, their swelling equilibrium is mainly determined by the mixing entropy of the counterions, which is balanced by the gel´s rubberlike elasticity. According to the theory of rubber elasticity of

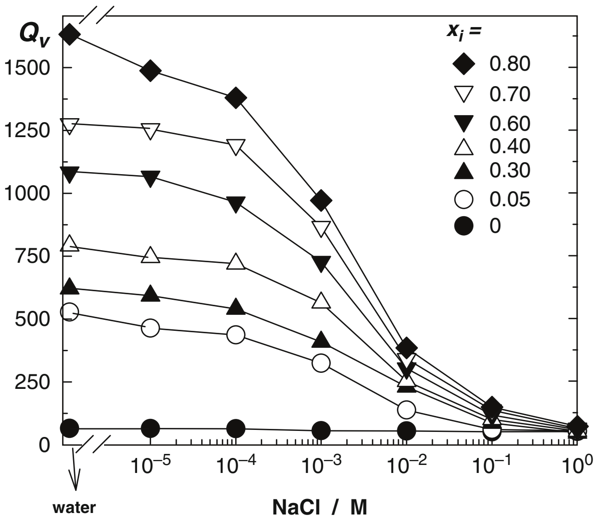

Fig. 3 Equilibrium volume swelling ratio Q_v of ionic PAAm hydrogels shown as function of the NaCl concentration in the external solution; 1.2 mol % MBAAm. AMPS Na mole fraction x_i in the comonomer mixtures is indicated. Reprinted from Durmaz and Okay (2000) with kind permission from Elsevier

Gaussian chains (Flory 1953), the Gibbs free energy of elastic deformation ΔG_{el} scales with the deformation ratio as

$$\Delta G_{el} \approx N_s^{-1} \alpha^2, \tag{1}$$

where N_s is the number of segments between two successive cross-links, and α the linear deformation ratio. α is related to the normalized gel volume V_r by the equation $\alpha = (V/V_o)^{1/3} = V_r^{1/3}$, where V is the gel volume at a given degree of swelling and V_o is the gel volume in the reference state, i.e., at the state after preparation. On the other hand, the existence of fixed ions on the network chains results in an unequal distribution of mobile counterions between the inside and outside of the gel. The ionic contribution to the Gibbs free energy ΔG_{ion} may be written as

$$\Delta G_{ion} \approx f \ln\left(f \varphi_2^0 / \alpha^3\right), \tag{2}$$

where f is the effective charge density of the network (Flory 1953). Balancing the two opposite free energy contributions represented by ΔG_{el} and ΔG_{ion} by minimizing their sum with respect to α, one obtains[1]

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[1] To minimize the energy function, one needs to take the derivatives of the energy contributions with respect to α, and set the sum of the derivatives to zero. Thus, since $\partial \Delta G_{el}/\partial \alpha \approx N_s^{-1} \alpha$ and $\partial \Delta G_{ion}/\partial \alpha \approx f/\alpha$, one obtains $\alpha \approx (f N_s)^{1/2}$, i.e., (3) in the text.

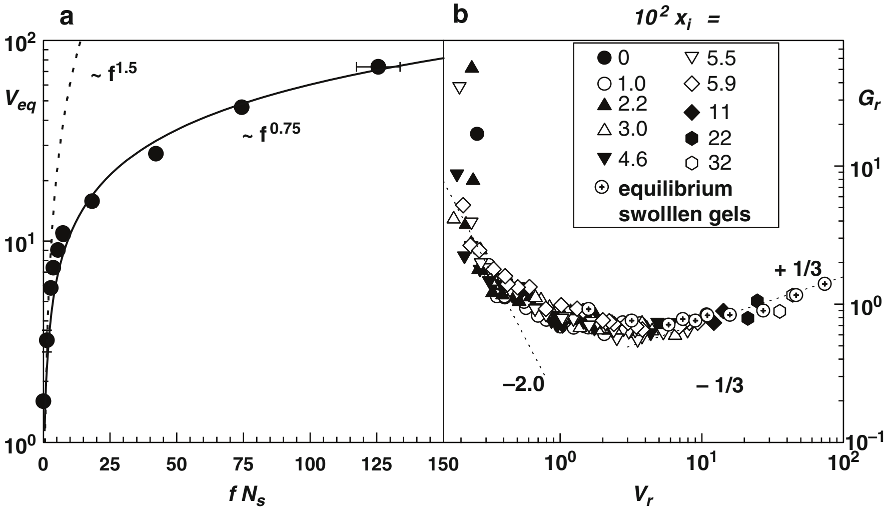

Fig. 4 The equilibrium swollen normalized gel volume V_{eq} of ionic PNIPAAm hydrogels as function of the number $f N_s$ of charges per network chain (see (3)) (**a**) Reduced modulus G_r of ionic PNIPAAm hydrogels as function of the normalized gel volume V_r (**b**) The mole fractions x_i of AMPS Na are indicated in the figure. Reprinted from Gundogan et al. (2002) with permission of American Chemical Society

$$V_{eq} \approx (f N_s)^{3/2}, \tag{3}$$

which indicates a scaling parameter of 3/2 between the equilibrium swollen normalized gel volume V_{eq} and the number of charges per network chain $f\ N_s$.

Figure 4a shows the double-logarithmic plot of V_{eq} against $f\ N_s$. Experimental data are for poly(*N*-isopropyl acrylamide) (PNIPAAm) hydrogels prepared in the presence of the ionic comonomer AMPS Na (Gundogan et al. 2002). The dotted curve in the Figure represents the prediction of (3), i.e., Flory–Huggins (FH) theory with a scaling parameter of 3/2. The solid curve is the best fitting curve to the experimental swelling data, which gives a scaling relation $V_{eq} \approx (f N_s)^{3/4}$. The scaling parameter 3/4 is much smaller than the predicted value of 3/2 of the FH theory. An exponent between 0.6 and 0.8 has been reported for both weak and strong polyelectrolyte hydrogels equilibrium-swollen in water (Durmaz and Okay 2000; Silberberg-Bouhnik et al. 1995; Bromberg et al. 1997; Melekaslan and Okay 2000).

The discrepancy between theory and experiment is related to the non-Gaussian behaviour of fully swollen hydrogels in water. The theory (3) assumes that the polymer network is a collection of Gaussian chains, which can be extended to infinity. However, the network chains in the equilibrium swollen ionic hydrogels as given in Fig. 4a are three to nine times as elongated as in the dry state. At such high swelling ratios, deviation from the Gaussian statistics may appear due to the finite extensibility of the network chains. A further evidence for the non-Gaussian behaviour of the network chains in the swollen hydrogels comes from the elasticity data. In Fig. 4b, the dependence of the reduced modulus G_r of ionic PNIPAAm hydrogels is shown as a function of the normalized gel volume V_r (Gundogan et al. 2002). The reduced modulus G_r is defined as the ratio of the elastic modulus of the gel at a given degree of swelling $Q_v = 1/\varphi_2$ to that one of the same gel after its preparation. G_r is given for a network of Gaussian chains by (Flory 1953)

$$G_r = G(\varphi_2)/G(\varphi_2^o) = V_r^{-1/3}. \tag{4}$$

However, Fig. 4b shows that the dependence of the reduced modulus on the gel volume cannot be described by a single scaling exponent. For the gel volumes V_r of less than 0.4, the reduced modulus G_r decreases sharply with increasing volume V_r. The rapid decrease of G_r with increasing gel volume V_r in the first regime is usually interpreted as the transition of the polymer from the glassy to the rubbery state by addition of solvent (Gundogan et al. 2002). In the range of the gel volume V_r between 0.4 and 3.5, the slope of G_r versus V_r plot is -0.32, close to the theoretical value of $-1/3$. Thus, PNIPAAm hydrogels in this regime behave as Gaussian. For gel volumes larger than 3.5, the reduced modulus G_r starts to increase with increasing gel volume with a slope of 0.22 which is an indication of the limited extensibility of the network chains and is connected with the high stretching of the network chains.

Swelling behaviour of hydrophobically modified hydrogels has also received considerable attention due both to fundamental and to technological interests (Hirotsu 1993). Such hydrogels generally exhibit a temperature sensitivity, which is associated with the temperature dependence of hydrogen bonding and hydrophobic interactions (Hirotsu 1993; Arndt et al. 2001). A phenomenon called reentrant swelling transition was also observed in hydrophobically modified hydrogels immersed in aqueous solutions of organic solvents or linear polymers (Katayama et al. 1984; Melekaslan and Okay 2001; Okay and Gundogan 2002). In such a transition, the gel first collapses and then reswells if a particular external parameter such as the organic solvent or linear polymer concentration is continuously varied. As a consequence, the organic solvent (or linear polymer) first flows from the gel to the solution phase but then reenters the gel phase at higher concentrations. Examples of such transitions are illustrated in Fig. 5 for PNIPAAm, poly(*N*,*N*-dimethylacrylamide) (PDMAAm), and poly(*N*-*t*-butyl-acrylamide-co-AAm) (TBA/AAm) hydrogels immersed in aqueous solutions of poly(ethylene glycol) of molecular weight 300 $\mathrm{g\,mol^{-1}}$ (PEG-300), acetone, and dimethylsulfoxide (DMSO), respectively (Melekaslan and Okay 2001; Orakdogen and Okay 2006b; Ozmen and Okay 2003). The competing attractive forces between the gel components are responsible for the reentrant transition behavior of hydrophobically modified hydrogels.

3 Inhomogeneity of Hydrogels

Another non-ideal feature of hydrogels is the so-called spatial gel inhomogeneity (Shibayama 1998; Bastide and Candau 1996). In contrast to ideal gels with a homogeneous distribution of cross-links, hydrogels always exhibit an inhomogeneous

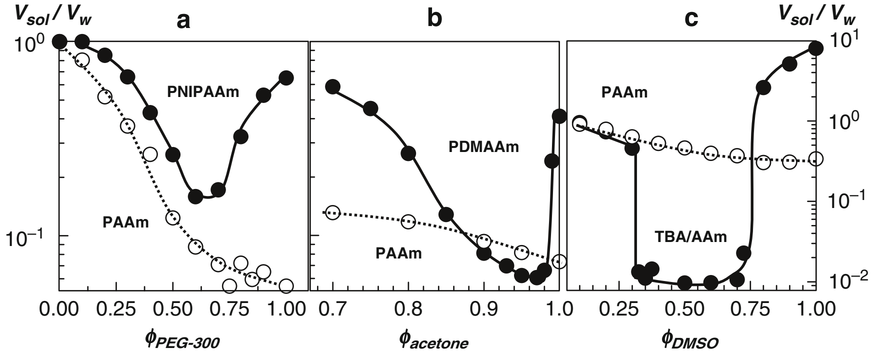

Fig. 5 Variation of the volume ratio V_{sol}/V_w (equilibrium swollen gel volume in solution / equilibrium swollen gel volume in water) of PNIPAAm, PDMAAm, and TBA/AAm (60/40 by mole) hydrogels (*filled symbols*) and PAAm hydrogels (*open symbols*) with the volume fraction Φ of PEG-300, acetone, and DMSO in the outer aqueous solution. (**a**) reproduced from Melekaslan and Okay (2001) with permission from Wiley-VCH Verlag GmbH & Co. KGaA; (**b, c**) reproduced from Orakdogen and Okay (2006b) and Ozmen and Okay (2003) with permissions from Elsevier

cross-link density distribution, known as the spatial gel inhomogeneity. The spatial inhomogeneity is undesirable because it dramatically reduces the optical clarity and strength of hydrogels. Since the gel inhomogeneity is closely connected to the spatial concentration fluctuations, scattering methods such as light scattering, small angle X-ray scattering, and small angle neutron scattering have been employed to investigate the spatial inhomogeneities. The gel inhomogeneity can be manifested by comparing the scattering intensities from the gel and from a semi-dilute solution of the same polymer at the same concentration (Lindemann et al. 1997). The scattering intensity from gels is always larger than that from the polymer solution. The excess scattering over the scattering from polymer solution is related to the degree of the inhomogeneities in gels.

In general, the spatial inhomogeneity increases with the gel cross-link density due to the simultaneous increase of the extent of network imperfections producing regions more or less rich in cross-links. On the other hand, the inhomogeneity decreases with the ionization degree of gels due to the effects of the mobile counter ions, electrostatic repulsion and the Donnan potential (Kizilay and Okay 2003b). The degree of swelling of gels subjected to scattering measurements also affects the scattering intensities (Kizilay and Okay 2004; Gundogan et al. 2004; Orakdogen et al. 2005). The scattering intensity at low scattering vectors is enhanced as the swelling degree is increased. This behaviour was interpreted as the enhancement of the difference of polymer concentration between the more and the less cross-linked regions. The initial monomer concentration used in the gel preparation significantly affects the scattering intensities (Kizilay and Okay 2003a, 2004; Gundogan et al. 2004). An inflection point was observed in the excess scattering versus monomer concentration plot, at which the inhomogeneity attained a maximum value.

Fig. 6 Excess scattering intensities from PAAm hydrogels $R_{ex,q}$ measured at the scattering vector $q = 1 \times 10^{-2}\,\mathrm{nm}^{-1}$ shown as function of φ_2^0. The filled and open symbols represent results of measurements after gel preparation and after equilibrium swelling in water, respectively; 1.5 mol % MBAAm. Reprinted from Kizilay and Okay (2004) with permission from Elsevier

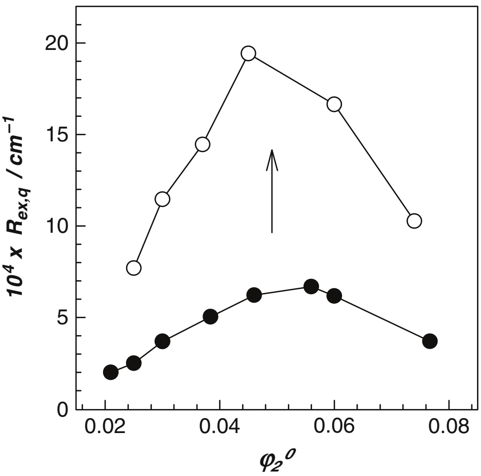

Figure 6 shows excess scattering intensity $R_{ex,q}$ plotted as a function of φ_2^0 for PAAm hydrogels with 1.5 mol % MBAAm cross-linker (Kizilay and Okay 2004). $R_{ex,q}$ significantly increases as the gel swells beyond its swelling degree after preparation. Moreover, PAAm gels at both states exhibit a maximum scattering intensity at a critical polymer network concentration. As the monomer concentration is increased, the effective density of cross-links also increases (Fig. 1), so that the spatial inhomogeneity becomes larger. Opposing this, increasing monomer concentration, i.e., decreasing the degree of swelling of the gels after preparation reduces progressively the concentration difference between densely and loosely cross-linked regions of gel, so that the apparent inhomogeneity decreases. The interplay of these two opposite effects determines the inhomogeneity in PAAm gels and results in the appearance of a maximum gel inhomogeneity at a critical monomer concentration.

4 Hydrogels with Improved Properties

The design of hydrogels with a good mechanical performance is of crucial importance in many existing and potential application areas of soft materials. Several attempts, such as topological gels and double network gels, have been made in recent years to design hydrogels with even better mechanical performance (Tanaka et al. 2005). The nanoscale dispersion of layered silicates or clays in polymer networks is one of the techniques offering significant enhancements in the material properties of hydrogels. Haraguchi et al. prepared such nanocomposite hydrogels starting from AAm-based monomers together with Laponite as a physical cross-linker, replacing the traditional chemical cross-linkers (Haraguchi and Takehisa

2002). Laponite, a synthetic hectorite clay, when suspended in water, forms disc-like particles with a thickness of 1 nm, a diameter of about 25 nm, and a negative surface charge density stabilizing dispersions in water. Formation of a cross-linked polymer network using a small amount of Laponite indicates that these nanoparticles act as a multifunctional cross-linker with a large effective functionality (Okay and Oppermann 2007).

A fast response of hydrogels to the external stimuli is also a requirement in many application areas of these materials. However, the kinetics of hydrogel volume change involves absorbing or desorbing solvent by the polymer network, which is a diffusive process. This process is slow and even slower near the critical point of volume phase transition (Shibayama and Tanaka 1993). Increasing the response rate of hydrogels has been one of the challenging problems in the last 25 years (Arndt Schmidt et al. 2004). In order to increase their response rate, several techniques were proposed (see also Chap. 3 Sect. 3.2):

- Submicrometer-sized gel particles: Since the rate of response is inversely proportional to the square of the size of the gel (Shibayama and Tanaka 1993), small hydrogel particles respond to the external stimuli more quickly than bulk gels (Oh et al. 1998).
- Gels having dangling chains: Attachment of linear polymer chains on the gel particles is another approach to increase the response rate of hydrogels (Yoshida et al. 1995). Dangling chains in a gel easily collapse or expand upon an external stimulus because one side of the dangling chain is free.
- Macroporous gels: Another technique to obtain fast-responsive hydrogels is to create voids (pores) inside the hydrogel matrix, so that the response rate becomes a function of the microstructure rather than the size or the shape of the gel samples (Okay 2000). For a polymer network having an interconnected pore structure, absorption or desorption of water occurs through the pores by convection, which is much faster than the diffusion process that dominates the nonporous hydrogels.

The basic technique to produce macroporous hydrogels involves the free-radical cross-linking copolymerization of the monomer-cross-linker mixture in the presence of an inert substance (the diluents), which is soluble in the monomer mixture (Okay 2000). In order to obtain macroporous structures, a phase separation must occur during the course of the network formation process so that the two-phase structure formed is fixed by the formation of additional cross-links. After polymerization the diluent was removed from the network, leaving a porous structure within the highly cross-linked polymer network. Thus, the inert diluent acts as a pore-forming agent and plays an important role in the design of the pore structure of cross-linked materials. Another technique to create a macroporous network structure is the use of inert templates in the preparation of hydrogels. By this technique, the polymer formation reactions are carried out in the presence of templates; a macroporous structure in the final hydrogel matrix appears after extraction of template materials. For example, by the cryogelation technique, the polymer formation reactions are carried out below the bulk freezing temperature of the

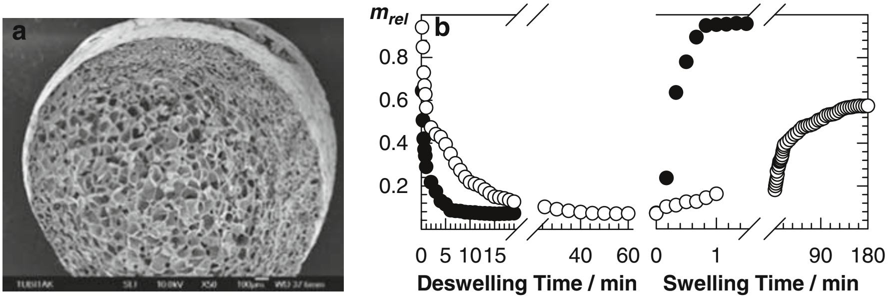

Fig. 7 (**a**) SEM of PAAm network prepared by cryogelation at −18 C. $C_o = 3$ w/v %; 1.2 mol % MBAAm; magnification 50; scaling bar 100 μm. Reprinted from (Ozmen et al.2007) with permission from Taylor & Francis Group. (**b**) Swelling and deswelling kinetics of PAAm hydrogel in water and in acetone, respectively, shown as variation of the relative weight swelling ratio m_{rel} with time of swelling or deswelling. $C_o = 3$ w/v %; 1.2 mol % MBAAm; polymerization temperature − 18 °C (*filled circle*) and + 21 °C (*open circle*). Reprinted from Dinu et al. (2007) with permission from Elsevier

reaction system (Lozinsky 2002). The essential feature of such reaction systems is that the monomers and the initiator are concentrated in the unfrozen microzones of the apparently frozen system. The polymerization and cross-linking reactions proceed in the unfrozen microzones of the reaction system. A macroporous structure in the final material appears due to the existence of solvent crystals acting as a template for the formation of the pores. The advantage of these so-called "cryogels" compared to the macroporous hydrogels obtained by phase separation is their high mechanical stability (Dinu et al. 2007). They are very tough and can withstand high levels of deformations, such as elongation and torsion; they can also be squeezed under mechanical force to drain out their solvent content. A typical SEM image of such materials in their dried state is shown in Fig. 7a illustrating their honeycomb morphology. These materials respond against the external stimuli such as the solvent composition change immediately (Fig. 7b).

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Synthesis of Hydrogels

Dirk Kuckling, Karl-Friedrich Arndt, and Sven Richter

Abstract In order to tailor hydrogels for the application as actuator-sensor microsystems based on the responsive behaviour of smart gels, a general strategy has to be developed. Since the phase transition phenomenon of hydrogels is theoretically well understood advanced materials based on the predictions can be prepared. The requirements for applying hydrogels can be summarized as follows:

- Development of novel sensitive polymers: Polymer networks with a large volume transition in combination with a sufficient high elastic modulus and short response times have to be prepared.
- Definition of the stimulus: Responsive behaviour of the gels towards relevant stimuli (e.g. temperature, pH value, solvent composition, low molecular weight solutes etc.) has to be realized. The hydrogels have to show a strong, non-linear response towards these stimuli. The defined adjustment of the stimuli must be possible.
- Speed of response: The response time of the smart hydrogels have to be decreased by some orders of magnitude compared with conventional gels. Fast responsive hydrogels are necessary to obtain sufficient fast cycle times.

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- Specific stimulation: The subsequent adjustment of the transition by modification (e.g. changing the pH value) of the applied polymers must be possible. The external stimulation (e.g. by photo-switching) is desirable. Advanced materials will show multi-sensitive behaviour.

Since the volume phase transition of hydrogels is a diffusion-limited process the size of the synthesized hydrogels is an important factor. Consistent downscaling of the gel size will result in fast smart gels with sufficient response times. In order to apply smart gels in micro-systems, new preparation techniques for hydrogels have to be developed. For the up-coming nano-technology, nano-sized gels as actuating material would be of great interest.

An often applied method for the synthesis of hydrogels, especially for applications in medicine and pharmaceutics, is based on radiochemistry. The hydrogel can be formed by irradiation of monomers, polymers dissolved in water, or polymers in dry state. Electrons of different energies or γ-rays are used as high-energy radiation. The possibilities of the radiation-chemical synthesis of smart hydrogels are discussed on different examples. The technique is applied to bulk polymers, to micro- and nanogel particles, and to patterned layers on different materials. The basics and fundamentals of irradiation techniques as well as the equipment are described.

In addition to synthesis of hydrogels, the theory of thermoreversible gelation and the gel point itself, the determination of the gel point on gelatin by using dynamic light scattering (DLS), oscillatory shear rheology as well as nuclear magnetic resonance (NMR) diffusion experiments will be described. Special attention has been devoted to the comparison of the results each methods have been provided when monitoring the gelatin gelation process. Furthermore, an important point is the estimation of the critical dynamical exponents in DLS and rheology at the gel point and their comparison with the theoretical prediction, which was given by Doi and Onuki.

Keywords Patterning • Stimuli-responsive • Cross-linking • Radiation • Gel point

Contents

Abbreviations

2VP	2-vinyl pyridine
AAmPA	3-acrylamido propionic acid
ATR-FTIR	Attenuated total reflection Fourier transform infra red
DI	De-ionized
DLS	Dynamic light scattering
DMAAAm	2-(dimethylamino)-*N*-ethyl acrylamide
DMAAm	*N*,*N*-dimethylacrylamide
DMIAAm	2-(dimethyl maleimido)-*N*-ethyl-acrylamide
DSC	Differential scanning calorimetry
EBL	Electron beam lithography
FESEM	Field emission scanning electron microscopy
HCl	Hydrochloric acid
HPC	Hydroxypropylcellulose
LBG	Locust bean gum
LCST	Lower critical solution temperature
MBAAm	*N*,*N*-methylene bisacrylamide
MWD	Molecular weight distribution
NIPAAm	*N*-isopropyl acrylamide
NMR	Nuclear magnetic resonance
OWS	Optical waveguide spectroscopy
P2VP	Poly(2-vinyl pyridine)
P4VP	Poly(4-vinyl pyridine)
PAAc	Poly(acrylic acid)
PEO	Poly(ethylene oxide)
PFG-NMR	Pulsed field gradient nuclear magnetic resonance
PNIPAAm	Poly(N-isopropyl acrylamide)
PPO	Poly(propylene oxide)
PVA	Poly(vinyl alcohol)
PVCL	Poly(vinyl caprolactam)
PVDF	Poly(vinyliden fluorid)
PVME	Poly(vinyl methyl ether)

PVP	Poly(vinyl pyrrolidone)
SEM	Scanning electron microscopy
SPR	Surface plasmon resonance
TCF	Time correlation function
UV	Ultraviolett
XG	Xanthan gum

Symbols

A	Area
c_P	Concentration of polymer solution
d	Diameter in equilibrium state
d_0	Diameter at preparation
d_f	Fractal dimension of the critical gel
D	Diffusion coefficient
D	Irradiation dose
D_{av}	Average dose
D_g	Gelation dose
D_p	Fractal exponent
D_V	Virtual dose
g	Gel fraction
$g_1(q,t)$	Electric field correlation function
$g_2(q,t)$	Time-intensity correlation function
$G(t)$	Shear stress relaxation modulus
$G'(\omega)$	Shear storage modulus
$G''(\omega)$	Shear loss modulus
$I(t)$	Scattering intensity at time t
l	Layer thickness
l_0	Layer thickness in dry state
M_n	Number-averaged molecular weight
M_w	Weight-averaged molecular weight
n	Critical exponent in shear rheology
n	Refractive index
p_0	Average number of main chain scissions per monomer unit and per unit dose
q	Scattering vector
q_0	Proportion of monomer units cross-linked per unit dose
Q	Degree of swelling
Q_m	Weight degree of swelling
s	Sol fraction
S	Gel stiffness