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ORIGINAL CONTRIBUTION

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Intelligent polymer gels controlled by magnetic fields

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Abstract In this paper we summarise the effects induced by electric and magnetic fields on the mobility and shape of polymer gels containing a complex fluid as a swelling agent. Magnetic-field-sensitive gel beads and monolith gels have been prepared by introducing magnetic particles of colloidal size into chemically cross-linked poly(*N*-isopropylacrylamide) and poly(vinyl alcohol) hydrogels. The influence of uniform and nonuniform fields has been studied. In uniform magnetic fields the gel beads form straight chainlike structures, whereas in nonhomogeneous fields the beads aggregates due to the magnetophoretic force directed to the highest field intensity. The ability of magnetic-field-sensitive gels to undergo quick, controllable changes in shape can be used to mimic muscular contraction.

Key words Intelligent material · Responsive gels · Magnetic-field-sensitive polymer gel · Artificial muscle

Intelligent materials

Progress in material science stimulates the economy and greatly influences the living standards of a society. Intelligent materials are based on a new concept where the information science is introduced to the material. Today it is a challanging task to manufacture new multifunctional materials which posses intelligence at the material level. We refer to material intelligence in terms of three main functions: sensing changes in environmental conditions, processing the sensed information and finally making judgement (actuating) by moving away from or to the stimulus [1]. The innovative functions of these new materials are in many respects similar to those of living organisms. Biological systems continuously adapt to a dynamically evolving environment, while developing innate properties of homeostasis. The intelligent materials should also display these characteristics while maintaining harmony with the environment.

The current generation of intelligent materials can be divided into two main parts.

1. Hard and dry materials, such as metals, ceramics and plastics. Intenstive research is currently being devoted to compound semiconductors, dielectric ceramics, thin ferroelectric films and photovoltaic energy converters.
2. Soft and wet materials, such as electrorheological fluids, magnetic fluids and polymer gels.

In technical applications we generally exploit the actuation characteristics of these materials.

In the last few years we have observed a migration of interest and activity from the traditional hard materials towards soft materials, such as biomaterials, self-assembly materials, complex fluids and polymer gels. We are aware that soft materials will probably never replace hard ones, but their study has led to significant advances in areas such as artificial tissues, controlled drug delivery, molecular recognition, chemical valves, artificial muscles and chemomechanical energy conversion.

For any technical application it is of great importantance to have a quick and reliable control system. Electric or magnetic fields are the most practical stimuli from the point of view of signal control. In this paper we first briefly summarise the possible application of electric and magnetic fields as new driving mechanisms for

polymer gels, and this is followed by a summary of magnetically controlled polymer gels.

Responsive gels

Polymer gels are unique materials in the sense that no other class of materials can be made to respond to so many different stimuli as polymer gels. The stimuli that have been demonstrated to induce abrupt changes in physical properties are diverse and include temperature, pH, solvent or ionic composition, electric field, light intensity as well as the introduction of specific ions [2–5]. In the last few years, these gels have become of major interest as novel intelligent materials. Many kinds of such gels have been developed and studied with regard to their application to several biomedical and industrial fields, for example, controlled drug delivery systems, musclelike soft linear actuators, biomimetic energy-transducing devices and separation techniques.

Poly(*N*-isopropylacrylamide) hydrogel, abbreviated as NIPA gel, is one of the most frequently studied temperature-responsive hydrogels. This gel has negative thermosensitivity, i.e. it shrinks with increasing temperature. A noncontinuous collapse transition takes place around 34 °C. There are several other gels which show reversible noncontinuous swelling and shrinking transitions at different temperatures [5, 6].

Attempts at developing stimuli-responsive gels are often complicated by the fact that structural changes, such as volume changes, are kinetically restricted by relatively slow swelling or deswelling process [3]. This disadvantage often hinders the efforts to design optimum gels for different purposes. Other applications require noncontact modes of deformation and movability. In order to accelerate the response rate and to achieve noncontact agitation a new driving mechanism had to be found. Electric and magnetic fields seemed to be promising stimuli.

Polymer gels in electric and magnetic fields

All materials experience forces or torques when subjected to electric or magnetic fields. These interactions are strong for certain solid materials, but are rather weak for fluid systems. In order to enhance the influence of external fields on solution and/or gel properties, it is necessary to combine solidlike and fluidlike behaviour. New colloidal solutions, termed complex fluids, have been introduced. Electrorheological fluids, magnetorheological fluids and ferrofluids contain dispersed small particles in the size range from nanometres to micrometres [7]. These fluids respond to an applied fields by rapidly changing their apparent viscosity and yield stress. Since polymer gels contain a substantial amount of liquid as a swelling agent, it is possible to make field-sensitive gels by using a polymer network swollen by a complex fluid. The colloidal particles incorporated, characterized by strong adsorptive interactions between solid particles and polymer chains, couple the shape and physical properties of the gel to the external field. These field-sensitive gels can be exploited to construct new types of soft actuators, sensors, micromachines, biomimetic energy-transducing devices and controlled delivery systems.

If a field-sensitive gel is exposed to an external field, two distinct types of interactions can be identified: field–particle interaction and particle–particle interaction [7, 8]. If the field is nonuniform, the field–particle interactions are dominant. The particles experience a dielectrophoretic (DEP) or a magnetophoretic (MAP) force. As a result the particles are attracted to regions of stronger field intensities. Because of the cross-linking bridges in the network, changes in molecular conformation due to either DEP or MAP forces can accumulate and lead to macroscopic shape changes and/or motion. The main features of the DEP and MAP forces are summarised in Table 1.

In uniform fields the situation is completely different. Due to the lack of a field gradient, there are no attractive or repulsive field–particle interactions. The particle–particle interactions become dominant. The imposed field induces electric or magnetic dipoles. As a result, mutual particle interactions occur if the particles are so closely spaced that the local field can influence their neighbours. This mutual interaction can be very strong, leading to a significant change in the structure of particle ensembles. The particles attract each other when aligned end to end, and repel each other in the side-by-side situation. Due to the attractive forces pearl-chain structure develops. The field-induced chain formation has major implications for a number of technologies [20].

Table 1 Particle–field interactions in nonuniform fields. *R* means the radius of solid particles, ε and μ stands for the permittivity and permeability, respectively. The *index* 2 refers to the colloidal particle and the *index* 1 denotes the swelling agent

Electric field Dielectrophoretic (DEP) force	Magnetic field Magnetophoretic (MAP) force
$f_{DEP} = 2\pi\varepsilon_1 R^3 K \nabla E_0^2$	$f_{MAP} = 2\pi\mu_1 R^3 K \nabla H_0^2$
Permittivities	Permeabilities
$K = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}$	$K = \frac{\mu_2 - \mu_1}{\mu_2 + 2\mu_1}$
Field gradient	Field gradient
∇E_0	∇H_0
Low energy consumption	Significant energy consumption
may be dangerous	safe

Magnetic-field-sensitive NIPA gels

We have prepared a novel polymer gel (MNIPA), characterised by temperature and magnetic field sensitivity. In the abbreviation of MNIPA, M Means NIPA with magnetic particles incorporated. By incorporation of magnetite nanoparticles into NIPA hydrogels we are able to target magnetic gel beads to a certain place and to separate the gel beads by a nonuniform magnetic field. Our main intention was to study both temperature and magnetic field sensitivity of MNIPA gels. Gel beads with an average diameter of 2,0 mm and a narrow size distribution were prepared and investigated [21].

Several MNIPA gel beads distributed randomly in a Petri dish are shown in Fig. 1a. Without an external magnetic field, the beads do not attract each other and as a result they do not form aggregates. This visual observation tells us that the gel beads have no permanent magnetisation. This result is also supported by magnetisation measurements.

Magnetisable particles, such as MNIPA gel beads, experience a force in nonuniform magnetic fields. This phenomenon, called magnetophoresis, is the result of a MAP force directed along the gradient of the magnetic field (Table 1): this effect is shown in Fig. 1b. The nonuniform magnetic field is induced by a permanent magnet (not seen in the figure) placed under the Petri dish. The beads are attracted to point where the magnetic field has its maximum intensity and are repelled from the point where the magnetic field is a minimum. As a consequence all the beads gather where the field intensity has the highest value. This position corresponds to the surface of the permanent magnet, which cannot be seen in the figure. It can also be seen from the figure that the time required to collect all the beads is rather short: this process took place within 24 s. When the field is turned off, the induced magnetic moment of the beads vanishes and the aggregation can be destroyed by slight mechanical agitation.

The situation is somewhat different if we put the magnetic gel beads in a homogeneous magnetic field. In this case no force is exerted on the gel beads, but the magnetic field polarises the beads and induces a magnetic moment in them. The induced magnetic moments are aligned parallel to the imposed field. The attractive interactions between the induced magnetic dipoles lead to chain formation (Fig. 1c). The interacting particles are aligned parallel with respect to the applied field.

We have studied the temperature dependence of the magnetic gel beads. The temperature sensitivity is an important property for several applications, for example, controlled drug release, soft actuator. It was found that as for the nonmagnetic NIPA gels, an abrupt volume change in response to the temperature change observed. This is demonstrated in Figs. 2 and 3.

Figure 2 shows that due to an increase in temperature, the volume of the gel bead decreases significantly. The degree of swelling has changed form 1 to 0.15.

In order to study the effect of incorporated magnetite nanoparticles on the temperature sensitivity of the gels, we determined the temperature dependence of the bead size. These results are shown in Fig. 3. It is seen that the temperature dependence of the volume (or size) charges of MNIPA gels is very similar to that of unloaded NIPA gels. This finding means that incorporation of magnetite nanoparticles into NIPA gels does not affect the temperature sensitivity significantly.

Muscular contraction mimicked by magnetic gels

Since muscle tissue consists of 80% multicomponent aqueous solution and 20% proteins that comprise the

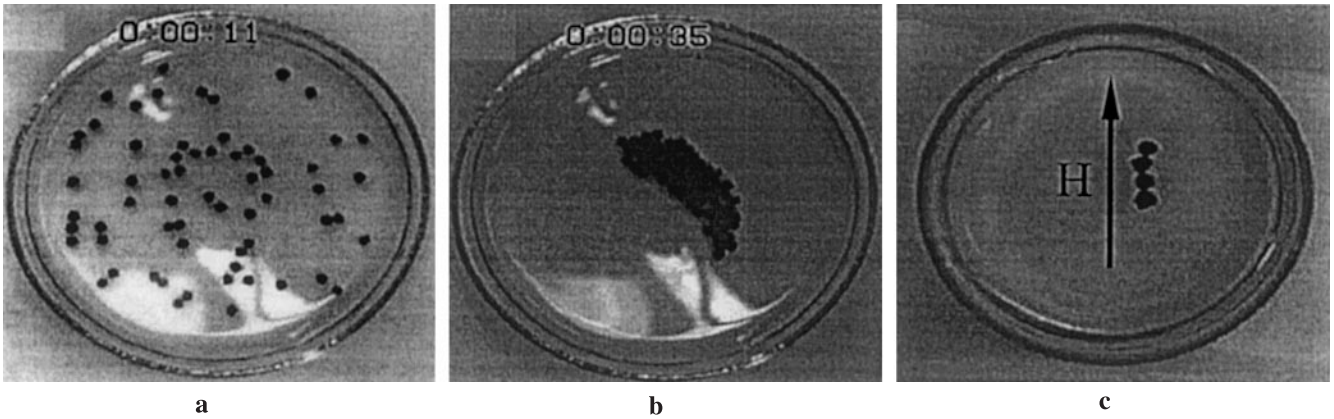

Fig. 1a–c Influence of uniform and nonuniform magnetic fields on ■ (*MNIPA*) gel beads. **a** No magnetic field is applied, **b** nonuniform magnetic field is created by a permanent magnet, **c** homogeneous magnetic field. The *arrow* indicates the direction of the field

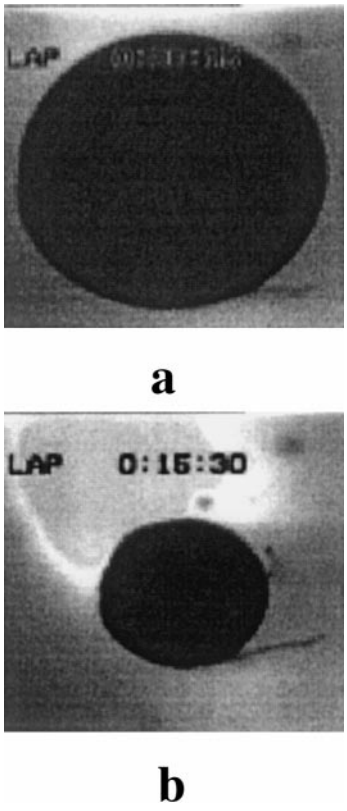

Fig. 2a, b Collapse transition of a MNIPA gel bead. **a** Temperature below the lower critical solubility temperature (*LCST*), $T = 25$ °C and $d = 1.87$ mm; **b** temperature above the LCST, $T = 40$ °C and $d = 1.00$ mm

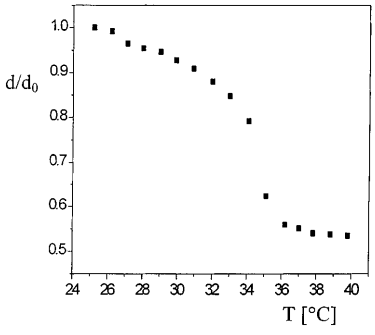

Fig. 3 The dependence of the size of a MNIPA gel bead on the temperature. d is the diameter of the gel bead and d_0 represents this value at 25 °C

elastic material, it is not surprising that efforts to develop artificial muscle have been devoted to polymer gels [9].

From an engineering point of view, muscles are soft and wet mechanical transducers, capable of performing their functions by quick and reversible shortening in a process called unidirectional contraction. Forces internal to the muscle are derived from a special mechanism which is designed to transform chemically bound energy into mechanical work or locomotion. During muscular contraction one end of the muscle remains fixed, while the other end moves towards the origin. Since the volume of the muscle remains essentially unaltered, it also experiences an increase in diameter.

In the analyses of the mechanical behaviour of an isolated muscle it is customary to introduce two types of strain [10]. Under load conditions the muscle is first stretched passively before being stimulated to contract. This process is then followed by active contraction due to shortening of fibres. Therefore under load conditions muscular thickening may be considered as a net effect of both passive and active strains taking place simultaneously.

When contraction takes place against a resistance, a force is generated and mechanical work is done. When contraction occurs against the maximum resistance, the maximum muscular force develops, but no measurable change in muscle length, as well as in mechanical work, can be observed. This isometric contraction represents the largest force that a muscle can actively generate. Under no load conditions the stimulation of muscle will cause it to contract to its smallest length without development of any active tension.

The passive–active nature of muscular contraction cannot be realised by a traditional elastic material, the deformation of which depends only on the surface traction. In a material designed for artificial muscle application there must be a physical or chemical process that can generate mechanical stress inside the material independently of the acting surface traction. This controllable ''body force'' is able to determine the rate and measure of contraction even if the material is preloaded and it is needed to make the material capable of mimicking the passive and active mechanisms of muscles.

An artificial muscle must reproduce at least two main characteristics of real muscle fibres, namely the high and fast contractility. It is also important to have a reliable control system.

The ability of magnetic-field-sensitive gels to undergo a quick controllable change of shape can be used to mimic muscular contraction. The peculiar magnetoelastic properties of these gels may be used to create a wide range of motion and to control the shape change and movement, that are smooth and gentle, similar to what is observed in muscles [11–17].

In order to be able to mimic muscular contraction we studied the unidirectional shortening of magnetic gel samples excited by a nonhomogeneous magnetic field. A cylindrical gel sample of poly(vinyl alcohol) (PVA) containing magnetite nanoparticles was suspended vertically in water between the plane-parallel poles of an electromagnet. The position of the top surface of the gel was fixed and the highest field strength was located at

this point. The steady current intensity in the solenoid-based electromagnet was varied in order to produce different magnetic field distributions. The maximum magnetic field strength (magnetic flux density) of 300 mT developed at the upper part of the gel and disappeared within 120 mm along the axis of the cylindrical gel sample. It is worth mentioning that 300 mT is a field strength which is less than the field strength measured at the surface of common permanent magnets. Due to the field gradient directed from bottom to top along the gel axis, contraction occurs. Figure 4 shows that under load conditions stimulation of a magnetic gel will cause it to contract.

Since the highest magnetic field strength can be controlled by the intensity of the steady current flowing through the electromagnet, it is possible to realise different degrees of contraction as shown in Fig. 4. The maximum field strength can be seen to increase from left to right in Fig. 4. One can establish the fact that significant contraction can be induced by moderate magnetic field gradients. In this case the strongest field intensity is 300 mT, and this disappears within 120 mm along the gel axis.

The contractile activity of magnetic gels can be used to lift a load that is to produce work. A nonmagnetic load (lead) of variable mass was connected to the lower end of the gel. A charge-coupled-device camera providing the displacement of the lower part of the gel with an accuracy of 0.01 mm monitored the contraction of the gel.

In the presence of a load the gel first elongates (passive strain). When a magnetic field is created, as a consequence, a contraction (active strain) takes place. If the mass of the load is not too high, the net effect is a significant contraction. It can be seen that the magnetic stimulus results in a large decrease in the length of the gel. When the field is turned off, the gel stretches again.

We have determined the work done by the ferrogel as a function of the load. These results can be seen in Fig.5. It is worth mentioning that we used a cylindrical gel, which had an overall volume of 12 cm^3. The gel contained 0.72 g polymer (PVA) and 0.96 g magnetite nanoparticles.

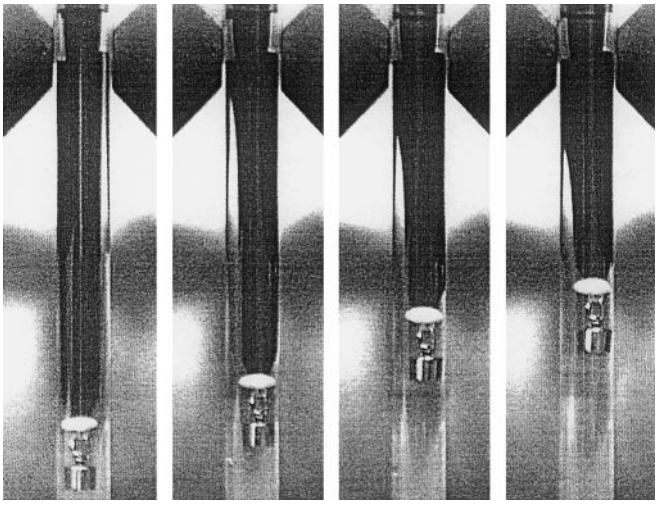

Fig. 4 Active deformation of a magnetic-field-sensitive gel under a load

Control of pseudomuscular contraction

Besides theoretical interest, for future applications it is necessary to understand the basic relationships between the work done, the properties of gels as well as the magnetic field distribution. We consider here a vertically suspended cylindrical magnetic gel by means of which a nonmagnetic load can be lifted up. First the gel is preloaded with a mass, M. As a consequence a passive strain, λ_M, develops. The magnitude of this extension can be calculated on the basis of rubber elasticity theory [18]:

$$\lambda_M^3 - \alpha\lambda_M^2 - 1 = 0 \ . \tag{1}$$

In this equation it is assumed that Gaussian behaviour could be used as an approximation. The dimensionless quantity α includes the ratio of nominal stress, σ_n and the modulus, G:

$$\alpha = \frac{\sigma_n}{G} = \frac{Mg}{a_0 G} \ . \tag{2}$$

Here g represents the gravitational constant and a_0 denotes the undeformed cross-sectional area of the gel at rest. When an external magnetic field is applied the strain will be changed to $\lambda_{M,H}$, which is the overall strain. Considering the homogeneous deformation and the linear relationship between magnetisation and magnetic field strength, on the basis of the additivity of mechanical and magnetic stress it is possible to derive Eq. (3) [17].

$$\lambda_{M,H}^3 - \alpha\lambda_{M,H}^2 - \beta\left(H_h^2 - H_m^2\right)\lambda_{M,H} - 1 = 0 \ , \tag{3}$$

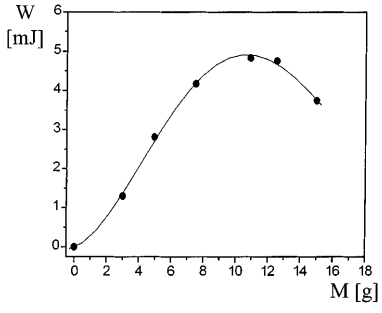

Fig. 5 Mechanical work released by a ferrogel as a function of the load

where H_h and H_m denote the magnetic field strength at the bottom and the top of a ferrogel cylinder, respectively. β can be considered as the stimulation coefficient defined as

$$\beta = \frac{\mu_0 \chi}{2G} \quad . \tag{4}$$

where μ_0 means the permeability of the vacuum and χ denotes the susceptibility of the gel.

The mechanical work produced by the active strain can be expressed as follows

$$W = Mg\Delta h = Mgh_0(1 - \lambda_{M,H}) \quad , \tag{5}$$

where h_0 denotes the undeformed length of the magnetic gel and Δh represents the displacement of the load.

As an example, we have calculated the mechanical work as a function of the load [17]; the results are shown in Fig. 6. It is obvious that the mechanical work strongly depends on the applied load. One can see that for small loads the work increases with the load. $M = 18$ g represents the highest mechanical work. Above a certain value it is seen that if the load is comparatively heavy, the work decreases with increasing mass. Similar results have been found for mechanical work produced by swelling [19]. Any other experimental situation can be studied with the aid of Eqs. (3)–(5).

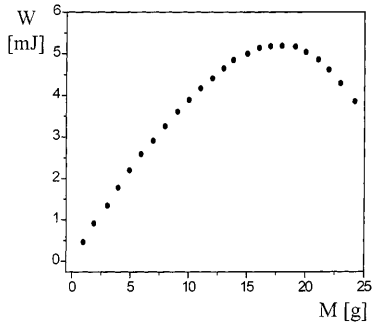

Fig. 6 The mechanical work as a function of the load calculated on the basis of Eqs. (3)–(5)

Conclusion

Magnetic-field-sensitive polymer gels have been prepared by introducing magnetic particles of colloidal size into chemically cross-linked NIPA and PVA hydrogels. These gels represent a new class of stimuli-responsive gels. The influences of uniform and nonuniform fields as well as the temperature have been studied. In uniform fields the magnetic gel beads form straight chainlike structures, whereas in nonhomogeneous fields the beads form aggregates due to the MAP force directed to the highest field intensity. It is possible to target the temperature- and magnetic-field-sensitive gels to certain positions by using MAP interactions.

An understanding of magnetoelastic coupling in gels will hasten the gel engineering of switches, sensors, micromachines, biomimetic energy-transducing devices and controlled delivery systems. Significant contraction can be realised by magnetic gels. Their unique magnetoelastic properties make it possible for them to mimic muscular contraction. If the magnetic field is created inside the gel by incorporating small powerful electromagnets and the field is co-ordinated and controlled by a computer, then the magnetic-field-sensitive gel may be used as an artificial muscle.

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