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INVITED REVIEW

Thermoresponsive magnetic colloids

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Abstract The combination of magnetic nanoparticles with thermoresponsive polymer systems leads to the formation of hybrid particle dispersions or composites with a variety of interesting properties and perspectives, including instant dispensability, thermoreversible formation of magnetic fluids, and novel magnetoresponsive properties. Special interest is gained by the magnetic heatability of magnetic particles that allows the activation of thermal effects by the application of a high-frequency electromagnetic field. This review summarizes the recent developments in this young field of research with application potential for magnetic separation, drug release systems, and for sensor and actuator purposes.

Keywords Magnetic fluids · Stimuli-sensitive materials · Core-shell particles · Superparamagnetic · Nanocomposites

Abbreviations

AAEM	acetoacetoxyethyl methacrylate
DMSO	dimethylsulfoxide
ELISA	enzyme-linked immuno sorbent essay
GPC	gel permeation chromatography
IPN	interpenetrating polymer network
LbL	layer-by-layer
LCST	lower critical solution temperature
MAA	methacrylic acid
MBA	*N*,*N*-methylene-bis-acrylamide
MPS	methacryloxypropyltrimethoxysilane
MRI	magnetic resonance imaging
NiPAAm	*N*-isopropyl acrylamide
NP	nanoparticle
PCL	poly(ε-caprolactone)
PEG	poly(ethylene glycol)
PMEMA	poly(2-methoxethyl methacrylate)
SDP	single domain particle
SHP	specific heating power
TEM	transmission electron microscopy
UCST	upper critical solution temperature
VCL	vinyl caprolactam
W/O	water-in-oil
XRD	X-ray diffractometry

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Introduction

The unique size-dependent properties of magnetic nanoparticles lead to a growing interest in nanostructured magnetic materials, composites, and dispersions, with interesting perspectives in current technology and future applications [1]. Colloidal magnetic dispersions, known as magnetic fluids or ferrofluids, [2, 3] usually contain magnetic particles in the range of 10 to 20 nm, and differ in there properties from the magnetorheological fluids that are based on micrometer-sized granules. Colloidal stable magnetic fluids have firstly been synthesized in the early 1960s and since then attracted much interest as their physical properties and flow behavior can be controlled by external magnetic fields, with application potential in as well technical and biomedical applications [4–10].

In current research, much respect is paid to the combination of such particles with polymers to benefit from their materials properties or the presence of functional groups along the polymer chain. A polymeric shell can serve

as compatibilizer with the environment, e.g., in polymer-stabilized magnetic dispersions, and can be supplied with biologically or catalytically active functional sites [11–13]. On the other hand, the magnetic properties of the nanoparticles allow the manipulation of the colloidal or composite systems.

The magnetic heatability of the particles is an additional feature; the ability of ferrofluids to convert magnetic energy into heat by relaxational and hysteresis effects [14] is known for a long time and has recently gained much attention for antitumor therapy [4].

In combination with thermosensitive polymeric systems, this property can be used to induce thermal effects in these systems by the application of a suitable magnetic field. This review gives a short introduction on the basic physical principles of thermoresponsive polymer systems and of magnetic nanoparticles and highlights recent developments in the synthesis and investigation of thermoresponsive magnetic colloids.

Basic principles

Stimuli-sensitive materials are designed to respond to an external stimulus by producing a desired effect [15]. The stimuli may include temperature, light, hydrostatic pressure, mechanical stress, chemical and biological substances, pH, ionic strength, electric and magnetic fields, or the like. Responds consist typically in a discontinuous change of physical properties like optical or mechanical behavior, surface properties, or a change in volume or shape.

Thermoresponsive magnetic colloids are characterized by a coupled magnetoresponsive and thermoresponsive behavior by the combination of magnetic nanoparticles with a suitable polymeric system and, if present, carrier fluid.

Thermoresponsive polymers

Macromolecules offer many ways of creating stimuli-sensitive behavior. Synthetic methods for the creation of polymeric molecules, structures, and architectures that can be assembled in a variety of ways to perform useful functions are available. The polymers can be present in these systems in different forms, that is, free chains in solution, chains grafted on a surface, covalently crosslinked networks and gels, phase-separated materials, and reversible or physical networks and gels.

Many different polymeric materials and systems are known that show thermoresponsive behavior, including hydrogels with a temperature-depending swelling behavior, [16–19] membranes of thermosensitive permeability [20, 21], and materials possessing a change of shape [22–24] or color [25] upon reaching a certain temperature.

In the context of magnetic colloids, thermoresponsive behavior is found that are based either on a critical solution behavior or a shape memory effect of a polymeric component present in the system.

Gels with critical solution behavior

Gels that react on a change of temperature with a sol–gel-transition or a volume change are often based on a critical solution behavior of the polymeric structure within the surrounding medium [26]. At a critical solution temperature, the solvation of polymer segments in a certain solvent is suddenly changed strongly due to the inversion of the free energy of mixing in the polymer/solvent system at that temperature. This may be due to entropic or enthalpic effects, and there are numerous systems with an upper or a lower critical solution temperature (UCST or LCST) known as well in aqueous as in organic systems.

The critical solution temperature is often closely related to the theta (Θ) temperature of a polymer/solvent system, a characteristic temperature where the polymer-solvent interaction forces are just compensating those between the polymer segments. This results in a coil-to-globule transition of the polymer chains at that temperature and a phase separation at higher concentrations [26]. A well-investigated system of this kind is polystyrene in cyclohexane that exhibits an UCST phase separation that can be related to the theta transition of this system at 34 °C.

In water-based gels (hydrogels) with a thermoresponsive gelation or volume transition, an LCST-behavior can often be observed. This can be attributed to the failure of hydrogen bonds between water molecules and the polymeric chains at higher temperatures, causing a phase separation. A well-investigated polymer with LCST in water is poly (*N*-isopropyl acrylamide) (PNiPAAm). The volume transition of covalently crosslinked hydrogels that is observed upon heating above 32 °C [27] has been predicted as early as 1968 by Dusek and Patterson [28]. Kinetic investigations of the swelling process show a proportional relationship to the square length of a characteristic, linear gel dimension [29]. To shorten the response time after the application of the stimulus, microgels [30] have been developed that allow the investigation of the temperature-induced volume change by light scattering methods [31] and rheology [32].

Water-based thermoresponsive microgels show a high application potential for controlled drug release, bioseparation and in sensor- and microactuator systems [33–36]. The temperature effect is used to control the colloidal stability of the microgels, the thermoreversible adsorption of proteins, and of the diffusion rate for low molecular substances. By the introduction of functional groups or

metallic nanoparticles, the microgels can be used as thermoresponsive catalytic systems [37].

Shape memory polymers

Shape memory polymers are capable to perform complex shape transitions and to recover strains up to several hundred percent in response to an external stimulus after the application of a programming process [38, 39]. Generally, the shape memory effect directly results from the purposive design of physical properties and structure of the polymer systems and is observed in various materials with different chemical composition. Requirements include a permanently crosslinked network that determines the permanent shape of a given device. The transient introduction of physical crosslinks can fixate a second, temporary shape. Upon release of the physical crosslinks by the application of an appropriate stimulus, the permanent shape is restored.

One of the most common stimuli for shape memory polymer systems is temperature. Physical crosslinks can be introduced by cooling below a glass- or melting transition temperature T_{trans} in the material, which can be reversed again by heating above T_{trans} [40–43] The process of programming and restoring of a shape memory polymer device is shown in Fig. 1.

At first, the polymer is processed by conventional methods to its permanent shape and crosslinked either covalently or physically. Then, the sample is deformed (generally at $T>T_{trans}$) and fixed in the desired temporary shape by decreasing the temperature, leading to the formation of a glassy phase or crystallites acting as physical crosslinks. This fixation is of reversible (temporary) nature as it may be broken by simply heating the material across the transition temperature and thus restoring the original, permanent shape that is typically characterized by a entropically favored state of the polymeric chains between given network points. The process can be repeated, but every time, a new programming process is necessary. High degrees of fixing and restoring of more than 98% respectively 99% can be achieved [44, 45].

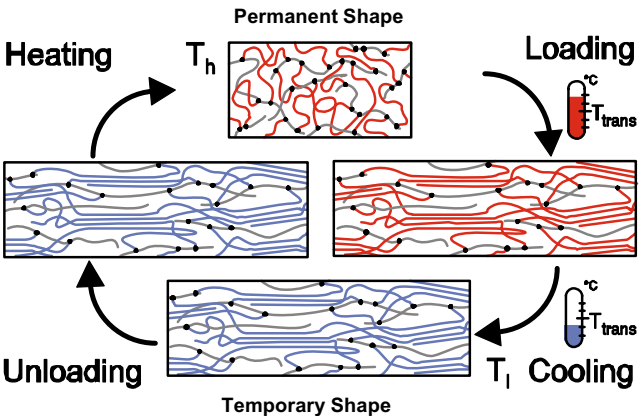

Fig. 1 Thermally induced one-way shape memory effect in polymers. During the programming process, the permanent shape is transformed to the temporary shape. By heating the device to a temperature above T_{trans}, the permanent shape is restored. Reprinted with permission from [44]. Copyright (2001) National Academy of Science of the USA

Since the 1960s, crosslinked polyethylene foils are used as heat-shrinkable wrapping that are based on the same principle [46, 47]. Polyurethane with shape memory properties are used as part of the auto-choke system. High potential is expected for the named materials for applications in the biomedical field, e.g., in minimal-invasive surgery, [48, 49] intravascular stents, or as smart suture fibers.

Nanomagnetism/magnetic colloids

Magnetic colloids are stable dispersions of nanometer-sized magnetic particles in a suitable carrier solvent. There are colloids based on ferromagnetic material like cobalt, iron, or nickel, but mostly ferrimagnetic iron oxides (maghemite γ-Fe_2O_3 and magnetite Fe_3O_4) or the mixed ferrites $Me^{II}Fe^{III}{}_2O_4$ of, e.g., Co^{II} and Zn^{II} are found due to their higher stability against oxidation and hydrolysis and better biocompatibility. As carriers, often water is used, but there are also dispersions based on oils and carbohydrates like toluene and heptane (Fig. 2).

Preparation of magnetic nanoparticles

The formation of nanoscaled particles of metals and metal oxides can principally occur by a bottom–up or a top–down approach. The second involves destruction of solid or micrometer-scaled objects by methods such as ball mills, laser or plasma treatment.

For the preparation of magnetic colloids, the bottom–up approach is by far more spread. It is based on the controlled condensation of low molecular precursors such as metal salts or (organo-) metallic complexes either in the gas phase or in solution. There are methods based on controlled nucleation and growth of the evolving nanoparticles. Alternatively, the growth of the primal particles can be controlled by a confined outer geometry, e.g., in micro- or miniemulsions or in a gel-, respectively glass matrix.

The preparation of magnetite Fe_3O_4 by a precipitation method is one of the most common principles for the preparation of magnetic nanoparticles and involves the alkaline precipitation of ferric and ferrous salts [50–52].

$$Fe^{2+}\,(aq) + 2\,Fe^{3+}\,(aq) + 8\,OH^- \xrightarrow[NH_3]{H_2O} Fe_3O_4\,(s) + 4\,H_2O$$

Fig. 2 Reaction scheme for the synthesis of Fe_3O_4

The method has often been adapted and varied and was extended to various mixed ferrites and maghemite.

Metal nanoparticles can be prepared either by the decomposition of neutral metal complexes such as $Co_2(CO)_8$ [53–55] or by reduction in metal salts [56, 57]. The synthesis is most often performed in organic solvents, as the precursors and products are in general hydrolytically unstable. Advantages are a narrow size distribution, and in some cases control over the particle size by the proper choice of reaction conditions.

Stabilization of magnetic colloids

Like other dispersions, magnetic colloids are subjected to a number of destabilizing forces that can lead to phase separation due to agglomeration and sedimentation.

As in conventional colloids, one of the main causes of phase separation is the van der Waals interaction between the high-surface particles that results in the formation of agglomerated material [58]. In contrast to this, the sedimentation of single particles by gravitational force is prevented by thermal motion in the focused size range (up to 20 nm). However, by the formation of small agglomerates due to van der Waals interaction (or magnetic interaction, see below), thermal motion is greatly reduced, and sedimentation may play an important role for the destabilization of a magnetic colloid.

As an additional challenge, the magnetic dipolar particles possess also magnetic interactions in relation to their relative distance that may be further enhanced by alignment of the dipoles in outer magnetic field gradients [2]. Consequently, the colloids have to be stabilized against agglomeration by creating a protecting shell for each particle that prevents the particles to come in too close contact with each other. This is possible using classical concepts from colloid chemistry, including electrostatic stabilization and steric stabilization. The latter either involves conventional surfactants or the creation of a polymeric shell. The polymers can be physisorbed or covalently attached to the particle surface, or may be crosslinked to encapsulate the magnetic core. The transition from conventional stabilization concepts to the creation of defined hybrid materials is diffuse. Regarding the synthesis of such systems, the particles are either prepared in the presence of the polymeric stabilizers, or they are encapsulated into in situ formed polymer shells or latexes after synthesis [59–62].

Physical properties of magnetic colloids

In addition to the complex properties of other colloidal dispersions, the unique behavior of magnetic colloids is dominated by their response to outer magnetic fields, including pattern formation and magnetic heating. The observations may be explained by the physical properties of the magnetic nanoparticles that are sketched below.

Equilibrium magnetization/superparamagnetism Macroscopic magnetic materials tend to the formation of magnetic domains, characterized by the parallel alignment of the involved magnetic moments on the atomic scale within the domain, and relative arrangement of the domains in such a way, that the net outer magnetization in the absence of outer fields is minimized. In the nanometer range, however, the formation of magnetic domains is energetically not favored, and the particles can be described as single-domain particles (SDP). The critical diameter for domain formation can be approximated at 150 nm for Fe_3O_4 and at 70 and 14 nm for Co and Fe, respectively [63].

Well-dispersed in a carrier fluid, the single particles act as magnetic dipoles that are able to reorientate by two mechanisms: either by rotation of the whole particle within the carrier (Brownian type) or by collective reorientation of the atomic magnetic moments within the crystal lattice of the particles (Néel type, see below). In either way, the thermal fluctuation of the dipoles leads to a zero net magnetization in the absence of outer fields. Under field and gradient influence, an alignment of the dipoles is achieved, while a suitable stabilization prevents the particles from agglomeration. As a consequence, magnetic colloids can be moved in droplets or set into position against gravity by the influence of outer fields.

In homogeneous static fields, the degree of alignment depends on the field strength and follows the Langevin law [64] (Eq. 2.1) for paramagnetic substances.

$$M = M_s \cdot [\mathrm{ctgh}(\alpha) - 1/\alpha] \tag{2.1}$$

where M is the sample magnetization, M_s is the saturation magnetization of the sample, and

$$\alpha = \frac{\mu_0 \cdot m \cdot H}{k_B \cdot T} \tag{2.2}$$

(μ_0, permeability of free space; m, magnetic moment of the particles; H, magnetic field strength; k_B, Boltzman constant; T = temperature).

The dipoles in commonly used magnetic colloids with up to 5 vol.% of magnetic material can be supposed to be free-rotating and non-interacting; however the involved magnetic moment of a single particle is in the order of three to four magnitudes higher that in conventional paramagnetics. This behavior is therefore referred to as *superparamagnetic*. As a consequence, the magnetization curve of magnetic colloids shows a symmetrical sigmoidal shape with no hysteresis (see Fig. 3) [64].

From the saturation magnetization, the content on magnetic material Φ_M can be calculated by relation to the specific

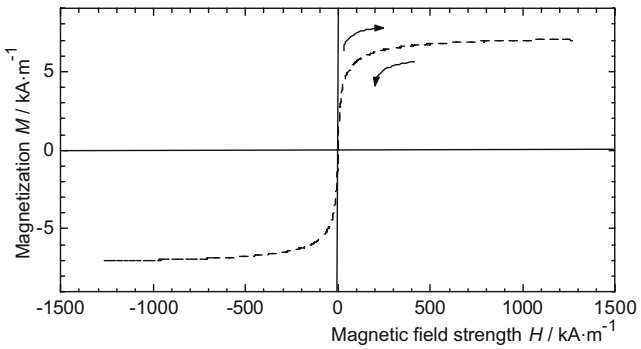

Fig. 3 Magnetization curve of a electrostatically stabilized Fe_3O_4-based magnetic colloid in water (1.8 vol.% Fe_3O_4)

spontaneous magnetization of the core material, M_0 (Eq. 2.2). For Fe_3O_4, M_0 is typically set to $4.50 \cdot 10^5$ A·m^{-1} respectively 90 A·m^2·kg^{-1}, [65] while for iron and cobalt a value of $7.90 \cdot 10^5$ A·m^{-1} [66] and $1.40 \cdot 10^6$ A·m^{-1} [67] are found.

$$V_M = \frac{M_s}{M_o} \tag{2.3}$$

The initial slope of the graphs gives the initial susceptibility χ_{ini} that allows the calculation of the involved magnetic dipole moments by using

$$M_{H\to 0} = \chi_{ini} \cdot H = \frac{M_s}{3} \frac{\mu_0 \cdot m}{k_B T} \cdot H \tag{2.4}$$

Magnetic relaxation and magnetic heating In dynamic magnetic fields, the difference in relaxation time dependency of the Néel type remagnetization mechanism and the Brownian type becomes important (see above) [68–71]. Both processes are ruled by the proportion of the respective activation energies and thermal energy.

For the "inner" (Néel type) remagnetization of the magnetic moment's direction against the crystallographic parameters, activation against the crystal anisotropy barrier in the lattice is necessary (Fig. 4a). The energy needed to overcome this barrier in an ideal spherical particle depends on the anisotropy constant K_{eff} of the crystalline magnetic material and the particle's volume V_c. In realistic materials, the impact of a shape anisotropy factor and of surface effects has to be considered additionally in many cases.

$$\Delta E = K_{eff} \cdot V_c = K_{eff} \cdot \frac{4}{3}\pi \cdot r^3 \quad , \tag{2.5}$$

giving a Néel-relaxation time τ_N of

$$\tau_N = \tau_0 \cdot e^{\frac{K_{eff}\frac{4}{3}\pi \cdot r^3}{K_B T}} \tag{2.6}$$

with $f_0 = 1/\tau_0$: Lamour frequency of the magnetization vector, of the order of 10^{-9} s^{-1}. Similarly, the Brownian motion has to be activated by thermal energy against the inner rotational viscosity in dispersion, that is, approximately against the viscosity η_0 of the carrier fluid. This energy barrier is thus depending on the carrier fluid's viscosity and on the hydrodynamic volume of the particle after the Stoke–Einstein law (Eq. 2.7; Fig. 4b).

$$D = \frac{K_B \cdot T}{6\pi\eta_0 \cdot r_h} \quad , \tag{2.7}$$

where D is the diffusion coefficient. Consequently, a relaxation time τ_B (Eq. 2.8) may be assumed.

$$\tau_B = \frac{4\pi\eta \cdot r^3}{K_B T} \tag{2.8}$$

It is worth to mention that the Néel relaxation time depends exponentially on the *core* volume, while the Brown mechanism involves the *hydrodynamic* volume of the particles that may differ from that of the crystalline cores due to the presence of a stabilizing shell or due to agglomeration. The resulting diameter dependency of the corresponsive relaxation times is presented in Fig. 5.

In realistic systems, the faster process will dominate the overall remagnetization process, and for similar time scales, both mechanisms will contribute (Eq. 2.9).

$$\tau_{eff} = \frac{\tau_N \tau_B}{\tau_N + \tau_B} \tag{2.9}$$

Furthermore, the particles may be far from being monodisperse, resulting in a distribution of magnetic moments in the particle ensemble with a distribution of relaxation times.

The dynamic magnetic losses can be detected by AC-susceptomery, in that the resulting course of the magnetic moment is recorded in response to the dynamic field. A real and an imaginary part of the initial susceptibility, χ' and χ'' can be calculated in dependency of the applied frequency (Fig. 6) A peak in χ''/χ' as well as a maximum in the phase shift angle δ is observed in the region of τ_{eff}.

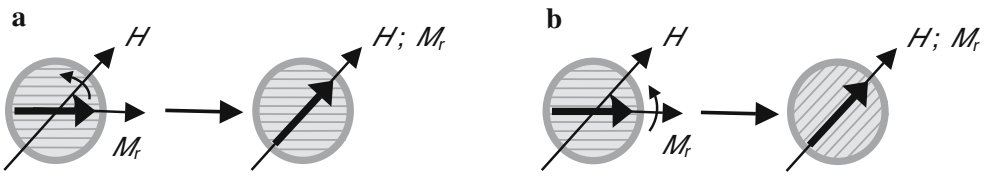

Fig. 4 Intrinsic (Néel) (**a**) and extrinsic (Brown) (**b**) remagnetization mechanism (schematic)

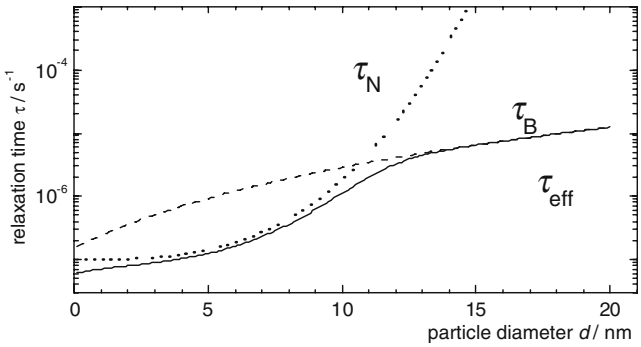

Fig. 5 Theoretical Néel (τ_N) and Brown (τ_B) relaxation times and effective relaxation time (τ_{eff}) for Fe_3O_4 versus particle diameter

Relaxational and hysteretic losses are responsible for the generation of heat by magnetic nanoparticles [68, 72, 73]. Exposed to a dynamic magnetic field, the particles are forced to conduct fast remagnetization correlated with thermal losses that can be used for a forced magnetic heating of the particles in AC fields of the kilo- to Gigahertz regime (see below). Within the validity range of linear response theory, the loss power density P is given by [74]

$$P(f,H) = \frac{(m \cdot H \cdot f \cdot \tau)^2}{(2 \cdot \tau \cdot k_B T \cdot V)(1 + f^2\tau^2)} \tag{2.10}$$

In real systems, the magnetic heatability of magnetic particles is greatly influenced by the particle size and the size distribution as well as field parameters. In AC fields that are accepted to be harmless for biological tissue [75] (e.g., 300–400 kHz, ~10 kA·m^{-1}), typical reported value for the specific heating power (SHP) of magnetite nanoparticles in the 10 nm range are below 100 W·g^{-1} [76, 77]. Clinical studies are performed regarding the application of the magnetic heatability of magnetite nanoparticles in tumor therapy by magnetic fluid hyperthermia [72, 78–82] (see below).

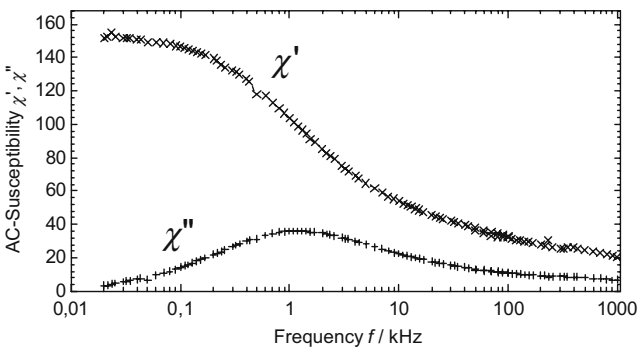

Fig. 6 Real (χ') and imaginary parts (χ'') of the specific susceptibility depending on the frequency for magnetite (d(XRD)=13 nm) suspended in water. Data reproduced from [162]. Copyright (2006) IOP Publishing

Other phenomena in magnetic colloids Clustering and chaining are present in many magnetic fluids due to magnetic interactions between the particles. In the absence of a magnetic field, particles that are big enough to show considerable magnetic interaction at a distance limited by the stabilizing shell of the particles are shown to form open-loop structures with no spatial orientation in theoretical expressions, [83, 84] Monte-Carlo and mean field simulations [85, 86] and in electron microscopy experiments [54, 87, 88]. In large applied field of 1 T, the particles form long chains oriented along the direction of the applied field. The extend of chain formation is of impact on physical properties, stability, and on optical properties of magnetic colloids based on strongly interacting or weakly stabilized magnetic particles.

The viscosity of a magnetic colloid in the absence of outer fields is, like in conventional colloidal dispersions, greater than that of the carrier liquid, as the presence of the suspended particles causes an increased rate of energy dissipation during viscous flow. In many cases, the behavior in the diluted regime can be approximated by Einstein's law: [89]

$$\frac{\eta}{\eta_0} = 1 + \frac{5}{2}\Phi \tag{2.11}$$

where η is the viscosity of the colloid, η_0 is the viscosity of the medium, Φ is the solid fraction, and adaptations for higher concentrations have been proposed by Batchtelor [90] and Rosensweig [91].

When an external field is applied, the colloid generally remains flowable, even when magnetized to saturation. Nonetheless, the rheology is affected by the presence of a field, [92, 93] possibly due to hindrance on the free rotation of the particles [94] or cluster respectively chain formation [95, 96]. As a result, when a magnetic colloid is subjected

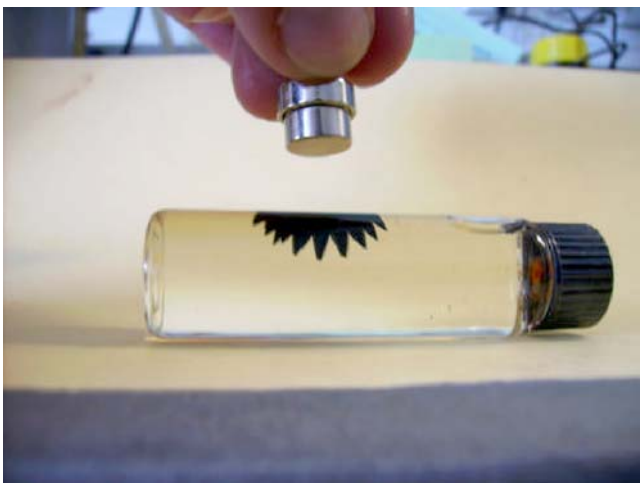

Fig. 7 Spike formation in a magnetic fluid under the influence of a permanent magnet

to perpendicular shear flow, larger gradients in the velocity field surrounding a particle are to be expected than if the particle was not aligned, and viscous dissipation increases in the sample as a whole. The magnetoviscous effect is strongly depending on the particles' magnetic moment, their size, and size distribution as well as on the concentration of particles, and leads to non-Newtonian behavior like viscoelasticity and shear-thinning of moderately concentrated magnetic fluids under field influence.

When subjected to a perpendicular field, a free surface of a concentrated magnetic colloid can form distinctive spikes that are known as the normal field— or Rosensweig instability (Fig. 7) [97]. Typically, there are organized in a static hexagonal pattern with a spike in each center of a hexagon. The magnetic field acts as the destabilizing mechanism for the surface, as the deformation is connected with a minimum of free energy by enhancing the overall magnetization of the colloid along the field [98]. The countercheck are gravitation and surface tension of the colloid, resulting in the presence of a critical field strength and a field dependency of the effect [99, 100]. Free surface instabilities are subject of several theoretical [99, 101], and experimental [102, 103] works.

Ferrofluid drops in small gaps, e.g., between glass plates show spiral- or labyrinth-like patterns due to instabilities in rotating fields [104]. A preliminary theory for ferrofluid labyrinth phenomena is based on a minimum free-energy analysis [105].

Application of magnetic colloids

Due to their unique physical properties, magnetic colloids are used in a broad range of applications [2, 3]. The most important by volume is the use in vacuum sealing rotary feedthroughs, e.g., in hard disk drives, and in high quality loudspeaker membranes. In both applications, the property of a viscous fluid (lubrication, and as damping and cooling liquid) is needed combined with the possibility to locate the fluid in space by a permanent magnet. Additionally, magnetic colloids are in use in dampers and separators and as additive in polishing agents. Actual investigations also concern nanomotors and nanoactuators [106].

The magnetic heatability of magnetic nanoparticles is furthermore exploited for glue formulations that can be activated by AC magnetic fields [107, 108].

In the biomedical field, magnetic nanoparticles and their dispersions play an important role for the development of new diagnostics and therapeutics [78]. Due to the limited stability and compatibility of metallic particles, in general oxidic ferrites are used, predominantly magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) with their accepted biocompatibility [109].

In vitro applications aim on the detection (magneto-relaxometry assays) or the separation (magnetic cell separation) [110] of biological species like proteins, [111, 112], oligonucleotides [113, 114], or cells. The application as a contrast enhancing agent in magnetic resonance imaging is based on the effect that the magnetic field induced by a particle results in modified relaxation times in the surrounding tissue. Therapeutic application potential is found in Magnetic Drug Targeting, [115] exploiting the magnetic moment of the particles for a preferred enrichment at the center of disease, e.g., a tumor, by the application of an outer permanent magnet. A predominantly local release of drugs like cytostatica is achieved, resulting in a decrease in side effects.

Hyperthermia is a therapeutic procedure to increase the temperature of a certain body region to decelerate the growth of tumor tissue, respectively to sensitize, damage or ideally destroy them. For magnetic fluid hypethermia, [72, 79] superparamagnetic particles are injected into the tumor, with the advantage that the heat development can be limited to the tumor region by magnetic heating of the particles in an applied AC field.

Magnetic colloids containing thermoresponsive polymers

The combination of magnetoresponsive and thermoresponsive properties is of interest from different points of view. The thermal properties can be used to complement or to control the features of magnetic fluids, or the physical properties of the nanomagnets can add the performance of thermoresponsive polymer systems. In this paragraph, the synthesis of thermoresponsive magnetic colloids is reviewed together with their interesting properties and their application potential.

Preparation of magnetic polymer hybrid colloids

By far, most of the thermoresponsive magnetic colloids described in literature are composed of nanocrystalline iron oxides (Fe_3O_4 or γ-Fe_2O_3) in combination with PNiPAAm or copolymers thereof. PNiPAAm is well known to possess a LCST in water around 32 °C that is of interest for fundamental investigations and for biomedical applications. Additionally, a few systems are realized that show an UCST in water [116] or organic solvents [117–120].

The different routes for the preparation of magnetic polymer particles can be divided into three principle methods: (1) synthesis of nanocrystalline particles on seed or porous polymer particles (polymer first), (2) adsorption of magnetic nanoparticles on seed latex or porous polymer microspheres followed by an encapsulation step using

appropriate monomers, (3) creation of a polymer shell in the presence of magnetic nanoparticles by emulsion or precipitation polymerization, and (4) formation of a surface-attached polymeric brush by surface-initiated polymerization processes.

Polymer-first methods

The strategy to prepare first polymeric particles that serve as seeds in the precipitation of magnetic nanoparticles is successful only in a few cases, as the precipitation process often is of high sensitivity toward the environmental conditions. Pich et al. [121] prepared polymeric microgels by surfactant-free emulsion copolymerization of acetoacetoxyethyl methacrylate (AAEM) and *N*-vinyl caprolactam (VCL) in water and the subsequent deposition of magnetite by coprecipitation of iron (II) chloride and iron (III) chloride (2:1) within the gel particles. The magnetite load can be controlled by the amount of added salts, and the thermosensitivity of the original particles was principally maintained. Suzuki et al. report the formation of PNiPAAm-co-glycidyl methacrylate microgels that allowed the precipitation of iron oxide nanoparticles within the core [122].

Encapsulation of particle adsorbates

The adsorption of magnetic particles to polymeric microgels or latexes can be made permanent by encapsulation with an additional polymeric shell. Sauzedde et al. [123] used polystyrene (PS) and PS-*co*-PNiPAAm latexes as seeds for the absorption of iron oxide nanoparticles with a diameter of 10 nm. Afterwards, the composite particles are encapsulated with PNiPAAm. Magnetite contents up to 22.5 wt% are realized, and the particles have been shown to be useful in enzyme-linked immuno sorbent assay (ELISA) for the detection of proteins (see below).

Wong et al. [124] use the layer-by-layer (LbL) method to deposit negatively charged magnetite nanoparticles on PNiPAAm microgels surface-modified with a positively charged polyelectrolyte (Fig. 8). A magnetite content of 33 wt% was achieved, while the thermoresponsive properties of the microgels and the magnetic characteristics of the particles, including magnetic heatability, are maintained.

Creation of a polymer shell by emulsion or precipitation polymerization

For NiPAAm, an emulsifier-free precipitation polymerization is possible by performing the process above the LCST and thus causing the oligomers to precipitate on the appropriately designed magnetic particle surface. In general, an intermediate step of surface-functionalization of the magnetic particles is necessary to enhance the compatibility and affinity of the polymer chains with the particles and thus achieve seed precipitation.

Kondo et al. [125] where among the first to show that it is possible to prepare magnetic thermoresponsive composite particles this way by copolymerization of NiPAAm, methacrylic acid (MAA), and *N*,*N*-methylene-bis-acrylamide (MBA) in the presence of Fe_3O_4 nanoparticles.

Ding et al. [126] used poly(ethylene glycol) (PEG) as a compatibilizer in the seed precipitation polymerization of NiPAAm/MBA at 70 °C in the presence of magnetic PS latexes and detected a thermoresponsive adsorption/desorption of proteins on the resulting polydisperse microspheres.

Similarly, Elaissari et al. [127] used magnetic PS latex in the seed polymerization of NiPAAm.

Alginate was used as a compatibilizing component in magnetite-containing interpenetrating network (IPN) gel beads with PNiPAAm by Xulu et al. [128] A functional bilayer of oleic acid/dodecyl benzene sulfonate was created on magnetite NP to allow deposition of *P*(NiPAAm-*co*-N-methacryloyl-N′-biotinylpropylenediamine) [129].

A versatile method to create nanoscopic (~100 nm) magnetite/PNiPAAm composite particles was employed by Deng et al. [130] by surface-modifying SiO_2-coated Fe_3O_4-nanoparticles with methacryloxypropyltrimethoxysilane (MPS) and subsequent seed precipitation polymerization of NiPAAm. Defined core-shell structures were obtained that could be further modified by SiO_2 etching resulting in mobile magnetite cores (see Fig. 9), further on by immobilization of a fluorescent dye [130], and by encapsulat gion of photoluminescent CdSe quantum dots [131].

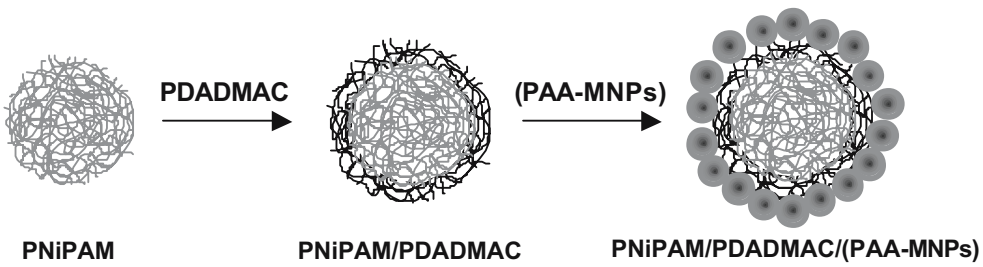

Fig. 8 LbL deposition of polyelectrolyte and magnetic nanoparticles on PNiPAAm microgel. Reprinted with permission from [123]. Copyright (2006) Elsevier

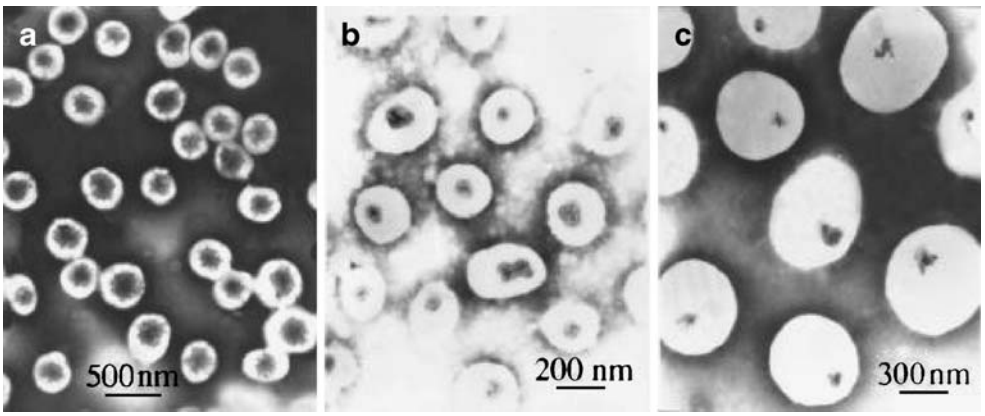

Fig. 9 TEM images of alkali-etched PNiPAAm microcapsules with mobile magnetic cores. The removed silica masses are 20.7 wt%, 55.3 wt%, and 83.9 wt% for the particles shown in images **a**, **b**, and **c**, respectively. Reprinted with permission from [130]. Copyright (2005) Wiley Interscience

Alternative methods are performed in organic media, e.g., by W/O miniemulsion polymerization of NiPAAm/MAA in cyclohexane in the presence of aqueous oligo(acrylic acid) stabilized Fe_3O_4 [132] and by an inverse suspension polymerization [133].

Formation of a surface-attached polymeric brush

Surface-initiated polymerization from inorganic nanoscopic features [134–137] is a relatively new pathway for the preparation of stabilizing or functional coatings and has recently been applied for the preparation of magnetic polymer brush particles (Fig. 10) [138, 139]. The technique is based on the growth of polymer molecules at the surface of a substrate in situ from surface-bound initiators and results in a irreversibly attached, covalently bound polymeric shell. Consequently, covalently anchored end-tethered polymeric chains with a high grafting density on the particle surface are formed. The approach offers the opportunity to form single-cored core-shell nanoparticles and to tailor dispersion properties like the minimum particle distance and the hydrodynamic particle volume.

By this method, thermoresponsive magnetic polymer brush particles have been obtained based on poly(ε-caprolactone) (PCL) by ring-opening polymerization, [117] and by atom-transfer radical polymerization resulting in poly(2-methoxyethyl methacrylatep; PMEMA)- [119] and PS-coated [120] Fe_3O_4 nanoparticles that show UCST behavior in dimethylsulfoxide (DMSO), [118] methanol, and cyclohexane, respectively.

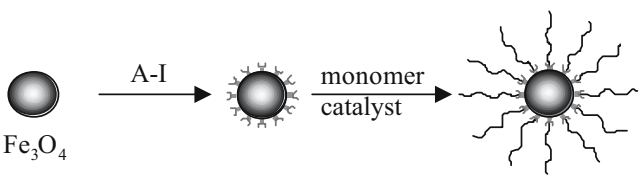

Fig. 10 Three-step synthesis of magnetic polymer brush particles. Reprinted with permission from [120]. Copyright (2006) IOP Publishing

The polymer shells are responsible for the good dispensability of the hybrid particles in good solvents for the polymeric arms up to several wt%. A direct correlation between the molar mass of the polymer arms as detected by GPC (after acidolysis of the core) and the hydrodynamic radius of magnetite nanoparticles in dynamic light scattering experiments of the hybrid core-shell particles has been found [120]. The architecture of such particles can be verified by visualization of the core-shell structure in TEM images (see Fig. 11).

Properties and potential applications of thermoresponsive magnetic colloids

By the combination of superparamagnetic nanoparticles with thermoresponsive polymers, the hybrid materials show the typical response of the particles to magnetic fields, that is, the property to manipulate the dispersions by permanent magnets and to heat the particles in AC fields. On the other

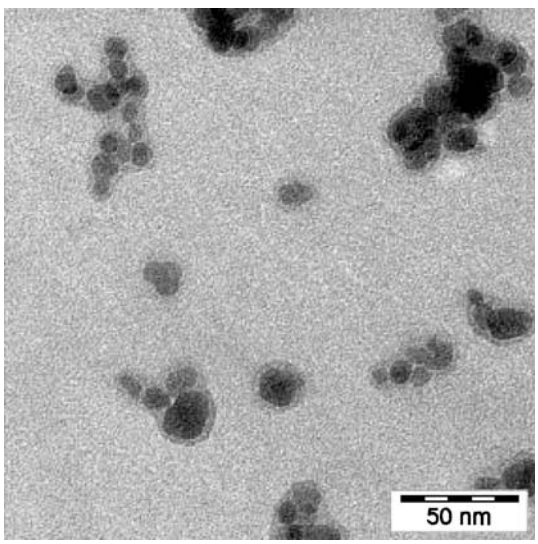

Fig. 11 TEM image of Fe_3O_4@PMEMA hybrid particles. Reprinted with permission from [117]. Copyright (2006) American Chemical Society

hand, the temperature responsive properties of the polymer are maintained and can be used to manipulate the material properties by conventional heating, or, of possibly even more interest, by magnetic heating (chapter 3.3).

Some a number of recent publications deal with the development and the properties of thermally manipulable hybrid magnetic colloids. In general, thermal and magnetic properties are utilized independently from each other, i.e., the thermoresponse of the polymeric component is used for a thermally induced effect or property change, while the magnetic properties are just an additional issue to magnetically control and to separate the particles. Such systems are most often based on Fe_3O_4 and PNiPAAm, with the temperature-sensitive property changes that can be used to reversibly disperse the hybrid particles, and to reversibly adsorb proteins due to hydrophilic–hydrophobic transition at T_{trans} (Fig. 12). Possible applications involve solid-phase supported immunoassays for the detection of alpha-foeto protein as an inflammatory marker, [123] systems for temperature-controlled protein separation of human [126, 140, 141] or bovine [142, 143] serum albumin, and contrast enhancers for magnetic resonance imaging (MRI) [144].

An interesting class of new materials aims at the manipulation of the magnetic properties by a change of temperature. A simple principle is based on the combination of magnetite nanoparticles with a polymer brush shell that exhibits a thermoresponsive solubility in combination with a suitable dispersion medium.

Below a critical solution temperature T_U (upper critical solution behavior) of the polymeric shell in the dispersant, the hybrid particles show a poor dispersibility due to the formation of polymer-mediated aggregates, whereas by rising the temperature above T_U, the polymer arms become stronger solvated and act as effective steric stabilizers against the agglomeration of particles. Consequently, the hybrid particles form stable magnetic dispersions above T_U. As shown in Fig. 13 for the system Fe_3O_4@PMEMA in methanol, [119] we observe the typical response of a magnetic fluid under the influence of a permanent magnet above T_U. Thus the response of the systems to a permanent magnet can be reversibly changed from a "bead suspension" to a "ferrofluid" behavior.

Similar behavior is observed for polystyrene-coated Fe_3O_4 nanoparticles in cyclohexane [120] and for particles with a poly(ε-caprolactone) shell in dimethylsulfoxide [118]. Thermoreversible stabilization of the particles offers an opportunity to combine dispensability and quasihomogeneous conditions for specific binding and catalytic activity, and easy magnetic separation at temperatures beyond the stabilizing conditions.

In biological and medical applications, the reversible flocculation and dispersion of the polymeric component with lower critical solution behavior in Fe_3O_4/PNiPAAm-based systems can be used for protein [125, 145, 146] and cell separation [128] purposes after affinity coupling.

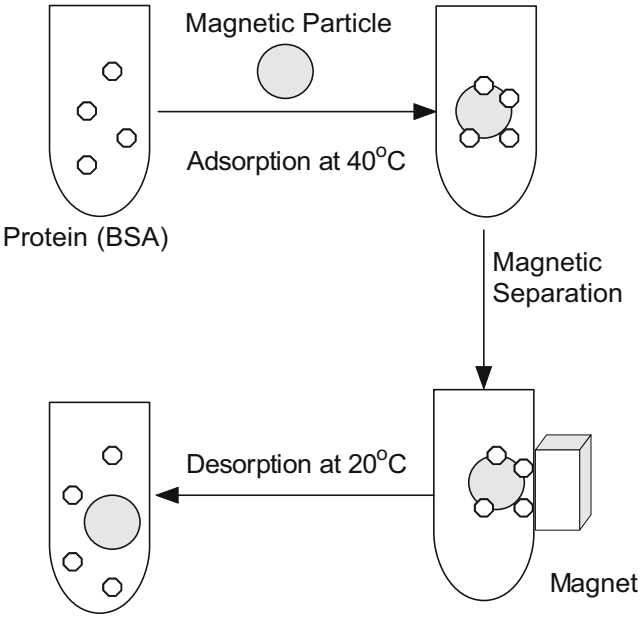

Fig. 12 Adsorption and desorption scheme of protein on thermosensitive-polymer coated magnetic particles. Reprinted with permission from [142]. Copyright (2006) Elsevier

Coupling of thermo- and magnetoresponsive behavior

A special feature is the magnetic heatability of superparamagnetic particles that can be used to initiate the transition of the volume transition in the polymeric shell. The issue is of interest as it offers the opportunity to activate thermal property changes remote-controlled within an accordingly designed materials system. The effect may be useful for medical applications in triggered drug release and may lead to a better understanding of the involved heat transfer mechanisms.

Two early reports deal with the direct visual observation of magnetically activated swelling and deswelling are described for two aqueous systems based on 16 wt% γ-Fe_2O_3 containing interpenetrating networks of polyacrylamide/polyacrylic acid that showed a swelling to 1.5 times the original volume after irradiation with a low-frequency field over a period of 1 h, [147] and a chemomechanical device based on PNiPAAm gel rods with 24 wt% γ-Fe_2O_3 [148]. The high magnetic load and the long irradiation times can be attributed to the use of multi-domain particles in the micrometer range.

Higher heating efficiency, quantified by the SHP can be found in single-domain particles in the nanometer range. Some recent reports concern the principal documentation and quantification of the magnetic heatability of previously described thermoresponsive magnetic colloids based on

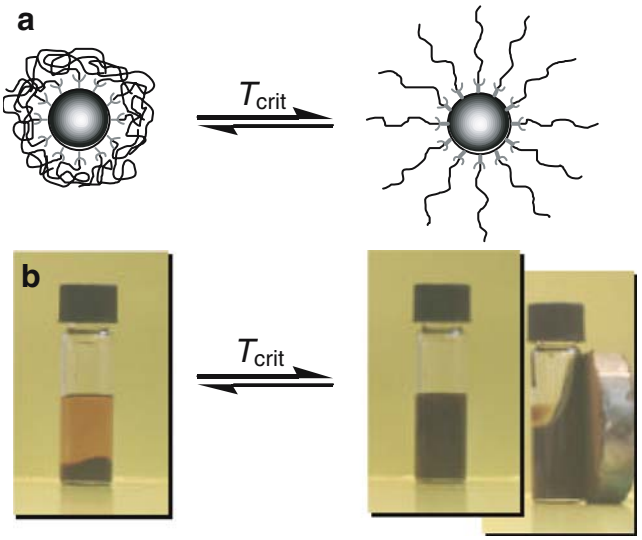

Fig. 13 Schematic behavior of polymer brush particles in thermoreversible magnetic fluids (**a**). Photographs of Fe_3O_4@PMEMA in methanol (**b**). The particles precipitate below T_U (at 20 °C, *left hand*). A particle dispersion is formed above T_U (at 50 °C, *right hand*) that reacts collectively under the influence of a permanent magnet. Reprinted from [117]. Copyright (2006) American Chemical Society

Fe_3O_4/PNiPAAm [123, 148] and Fe_3O_4/PS [119]. Magnetic thermoresponsive colloids can be loaded with low molecular substances like dyes or drugs and are of interest for magnetically activated drug release systems. The potential of the concept to contribute to the development of magnetically activatable drug release systems has principally been shown for model dyes (Fig. 14) [116, 132].

Thermo- and magnetoresponsive composites

Hybrid materials of macroscopic dimensions that include magnetic nanoparticles in a thermoresponsive polymer matrix are described for two classes of material, either based on thermoresponsive gels or on shape memory polymers.

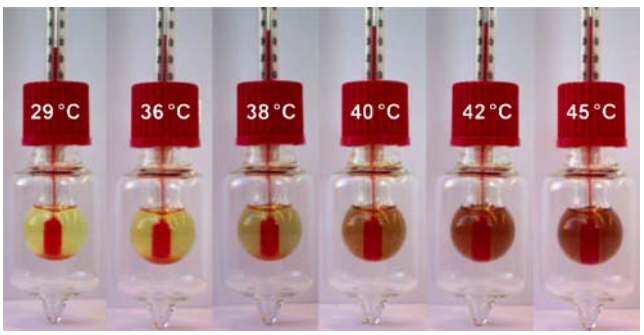

Fig. 14 Release of 1-methyl-4-[2-(4-oxocyclohexadienylidene)ethylidene)]-1,4-dihydropyridine (p-MOED) from loaded Fe_3O_4@PCL hybrid particles in DMSO by magnetic heating between 36 and 42 °C

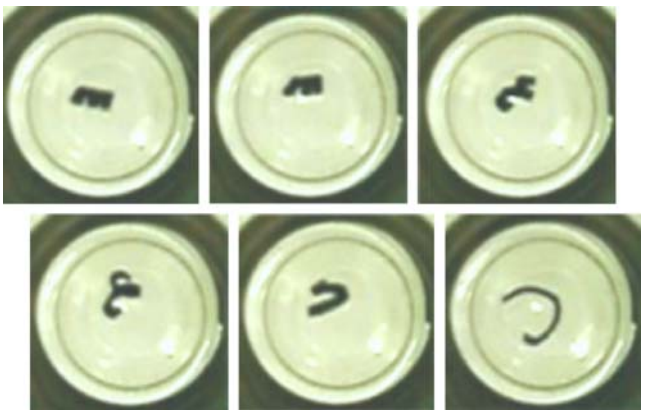

Fig. 15 Shape memory effect photos. Reprinted with permission from [157]. Copyright (2006) Wiley-VCH

The incorporation of magnetic nanoparticles into macroscopic hydrogels leads to magnetoresponsive gels called ferrogels [149, 150]. The polymeric matrices serve as highly flexible environment for the particles in the swollen state. Under the influence of an external static magnetic field, the magnetic dipoles become aligned along the magnetic field [151, 152] and an orientation of the gel [153]. Due to enhanced interparticle interactions, a volume contraction can be observed at sufficient field strength. The combination of elasticity and magnetic properties is of great interest for basic research [154].

Macroscopic thermoresponsive hydrogels based on PNiPAAm can be easily obtained by polymerizing the monomer in aqueous solution in at 25 °C in the presence of a crosslinker. The formation of macroscopic PNiPAAm gels containing Fe_3O_4 nanoparticles in contrast to magnetic colloids observed at 70 °C can be attributed to the good solubility of PNiPAAm in water at that temperature [127, 155, 156].

By embedding magnetic nanoparticles into a thermosensitive polymeric matrix, a possibility is provided to induce a thermal effect contactless by a specific "remote-control" [157]. Magnetic hydrogels where the magnetic heatability of the incorporated nanoparticles is explored for the induction of a volume transition are described in a few works. Kato et al. polymerized NiPAAm in the presence of maghemite nanoparticles and β-galactosidase to obtain gels that showed an enhanced catalytic activity for the enzymatic transformation of 2-nitrophenyl-*b*-galactopyranoside into galactose under the application of an AC field due to magnetic heating [159].

The formation of a physically crosslinked thermoreversible ferrogel based on a triblock-copolymer in paraffin oil is reported by Lattermann et al. [160] The thermoreversibility of the gel formation can be used to "freeze in" a Rosensweig instability by cooling down hot liquid magnetic colloids containing the gelator across the sol–gel-transition in the presence of a magnetic field.

One of the key challenges in realizing shape memory polymer devices for medical applications is the implementation of a safe and effective method of thermal actuation in vivo. Recently, the synthesis and properties of shape memory nanocomposites that can be activated by an external electromagnetic field have been reported [158, 161]. The magnetosensitivity is introduced to the material by the incorporation of superparamagnetic magnetite nanoparticles (Fe_3O_4, $d \approx 11$ nm) that are capable of inductive heating. The process of recovery of a magnetosensitive shape memory sample is shown in Fig. 15 [158].

A shape memory material based on Curie-thermoregulated magnetic heating of incorporated nickel zinc ferrites is presented by Buckley et al. [162].

Summary

Colloids that combine the unique properties of magnetic nanoparticles with thermoresponsive polymers are interesting materials for research and applications. During the past few years, this new class of materials has been described in a growing number of works in the field of physical chemistry, polymer science and material science. Up to now, systems are known that are either based on the presence of a critical solution behavior (volume transition materials), or of a shape transition temperature (shape memory materials).

Synthetic methods for the preparation of magnetic thermoresponsive colloids involve precipitation polymerization and the formation of a polymeric brush on the particle surface. Water-based systems often contain PNiPAAm as the thermoresponsive polymer component, and a few organic solvent-based systems are known. Their physical properties like thermoresponsive coagulation or thermosensitive adsorption of proteins are thereby complemented by the possibility to magnetically manipulate the objects. Additionally, the magnetic heatability of the cores can be used to initiate a thermal property change, and this way magnetically activated reaction systems, release effects, and shape transitions are realized. It may be expected that, taking into account the fast growing interest in this new class of material, present and future research on thermoresponsive magnetic colloids may contribute to the development of drug release systems, easily recoverable polymer-supported magnetic separation kits, and magnetically active catalysts, in sensor- or actuator applications and for microfluidic systems. Additionally, they are of interest as model fluids for the examination of relaxation behavior and magnetic particle interactions.

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