Hybrid Materials

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Room-Temperature, Strain-Tunable Orientation of Magnetization in a Hybrid Ferromagnetic Co Nanorod–Liquid Crystalline Elastomer Nanocomposite

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Abstract: *Hybrid nanocomposites based on magnetic nanoparticles dispersed in liquid crystalline elastomers are fascinating emerging materials. Their expected strong magneto-elastic coupling may open new applications as actuators, magnetic switches, and for reversible storage of magnetic information. We report here the synthesis of a novel hybrid ferromagnetic liquid crystalline elastomer. In this material, highly anisotropic Co nanorods are aligned through a cross-linking process performed in the presence of an external magnetic field. We obtain a highly anisotropic magnetic material which exhibits remarkable magneto-elastic coupling. The nanorod alignment can be switched at will at room temperature by weak mechanical stress, leading to a change of more than 50 % of the remnant magnetization ratio and of the coercive field.*

New applications involving composite materials aim at controlling different properties, such as electric polarization, magnetization, and shape, either directly or indirectly by various stimuli (electric, magnetic fields, or stress). Among the numerous possible combinations, an important one is that of piezo-magnetic materials showing the magneto-elastic coupling, that is, controlling the shape by a magnetic field and, conversely, the magnetization by stress.[1] Thus, composite materials obtained by inserting magnetic nanoparticles into deformable polymer matrices open new perspectives in the fields of biomedicine,[2] information storage,[3] and actuation.[4] Liquid crystalline elastomers (LCEs) have recently been proposed as promising matrices.[5] LCEs possess shape-memory properties due to the thermal transition of the liquid crystalline domains and exhibit large and reversible orientation of the mesogens when they are stretched in the liquid crystalline state.[6] These properties arise from the strong coupling between the orientational order of the liquid crystalline units, chemically bonded to the polymer matrix, and the rubber elasticity of the polymer network. Compared to conventional elastomers or shape-memory polymers, liquid crystalline materials offer the unique opportunity to spatially organize nanoparticle dispersions,[7] which is a decisive factor to improve their response to a magnetic field by exploiting collective behavior. This issue is crucial for obtaining efficient actuators or sensors.[8]

Two main studies proved that dispersing magnetic particles within LCE is an efficient way to induce a macroscopic magnetic reorganization, and the associated shape and magnetic memory features. Kaiser et al. prepared magnetic composites based on monodomain LCE matrices and magnetite spherical nanoparticles. Upon exposure to alternating magnetic field, the inductive local heating led to a 27 % reversible shape change.[5a] Haberl et al.[5b,c] prepared a nanocomposite with mutually cross-linked ellipsoidal silica coated iron oxide nanoparticles and LCE to form a covalent network. Initially, the sample is strained in the isotropic phase, at 80 °C, and then cooled down into the liquid crystalline phase in order to achieve an anisotropic soft magnet. Heating the sample brings it back to its initial disordered state. Nevertheless, these examples require crossing the liquid crystalline to isotropic transition, that is, the use of thermal energy, to exploit the magneto-elastic coupling. Therefore, they do not take advantage of the full potential of the liquid crystalline state.[9]

Here, we propose a novel strategy in which the system remains in the liquid crystalline state at room temperature, exploiting its ability of orienting/disorienting under mechanical stress, to switch the orientation of magnetic nanorods and therefore the magnetic properties of the composite. To elaborate such a material, strongly anisotropic and highly magnetic nanoparticles providing large magnetic torques must be embedded in the matrix. In this respect, long ferromagnetic metallic Co nanorods are presently the best choice for room-temperature applications. Their use, instead of weakly magnetic and anisotropic iron oxides, may give rise to larger magnetic torques with smaller nanometric particles upon minimal loading. Moreover, the use of rod-like ferromagnetic nanoparticles helps to achieve a strong orientational coupling with calamitic liquid crystalline moieties.[10] Indeed,

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we previously demonstrated that hybrids based on Co nanorods and liquid crystalline uncross-linked polymer exhibit improved magnetic properties compared to an amorphous matrix. This proves that the presence of the organized polymer increases the cooperative effects between the nanorods.[11] We showed that Co nanorods self-assemble into rows that further organize in a hexagonal lattice, giving rise to highly ordered bundled structures within the hybrid materials.[12] We also proved the feasibility of the synthesis of a liquid crystalline network starting from a hybrid magnetic liquid crystalline polymer.[13]

We describe here the synthesis of new highly magnetic hybrid elastomer materials (Figure 1): dispersion of preformed monodisperse cobalt nanorods into the liquid crystalline polymer, followed by alignment and cross-linking in the presence of an external magnetic field. The critical step is

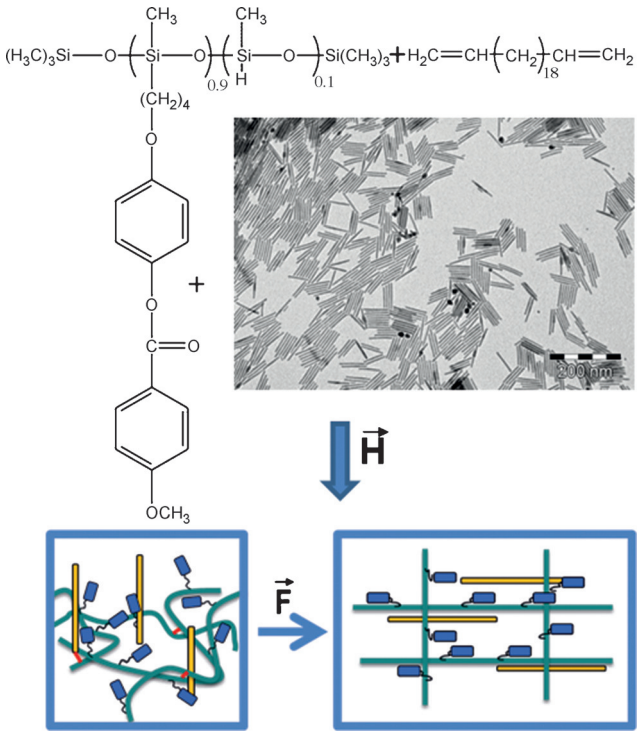

Figure 1. Top: Chemical formula of the liquid crystalline polymer and the cross-linker, and TEM image of the Co nanorods used for the synthesis of the hybrid material. Bottom: Schematic representation of the resulting material with strain-induced tunable orientation of the magnetic nanorods.

the nanorod alignment within the elastomer, required to achieve the highest remnant/saturation magnetization ratio, and obtain a strong anisotropic ferromagnet. This feature is specific of this new material and is necessary to obtain a strain-induced tunable orientation of the magnetic nanorods and therefore to develop nanoparticle-based materials with strain-tunable high remnant magnetization and high coercive field. Very importantly for future applications, these magnetic changes occur at room temperature and are reversible. We thus selected the liquid crystalline moiety and the polysiloxane backbone that is highly flexible at room temperature. The synthesis proposed here is simpler than the previously reported ones,[5b,c] in which the presence of a chemical link between the magnetic materials and the matrix was mandatory. Moreover, it allows for easy modulation of the nanoparticle content, without affecting the cross-linking density that controls the elasticity of the matrix.

In this Communication, we also report the stretching of samples cross-linked in the absence or presence of a magnetic field.

The metallic cobalt nanorods (NRs), 72 ± 7 nm long and 5.5 ± 0.5 nm wide, used here[14] display a magnetization at saturation close to the bulk value ($M_S = 160\ \mathrm{emu\,g^{-1}}$) and a strong uniaxial magnetic anisotropy due to the combination of the magnetocrystalline and shape contributions.[15]

The liquid crystalline elastomer was synthesized by a hydrosilylation[13,16] reaction at room temperature in a two-step procedure. The poly(methylhydrogenosiloxane) backbone was mixed with 0.9 silane equivalents of mesogens and the catalyst in a minimum quantity of toluene. A long aliphatic diene was then used to cross-link the remaining reactive silane functions; 0.5 wt% nanorods were also added in this second step. To obtain macroscopically oriented samples, a 1 T uniform magnetic field, produced by an electromagnet, was applied during cross-linking. Both oriented and non-oriented, 1 mm thick samples were prepared for comparison.

All the magnetic liquid crystalline elastomers exhibited a nematic phase. Their clearing and glass transition temperatures were around 90 °C and 0 °C, respectively (see Figure S3 and comments in the Supporting Information).

We investigated the influence of mechanical deformation, applied at room temperature, on the structural and magnetic behavior of both non-oriented and oriented elastomers.

X-ray scattering measurements provided us with a picture of the microscopic organization of the hybrid elastomers. For both the mesogenic side groups and the nanorods, the interferences of X-rays scattered in the plane perpendicular to their main axes were recorded at wide and small scattering angles (WAXS and SAXS, respectively). Through a classical procedure,[17] the nematic order parameter of the mesogenic side groups, S_{LC}, was obtained from an azimuthal scan of the X-ray-scattered intensity arising from the lateral interferences between the mesogens. In the same way, the presence of nanorod bundles[12] gives rise to a scattering signal from which we deduced the nematic order parameter of the nanorods, S_{NR}. The organization of the nanorods was also observed, at a larger scale, by TEM micrographs.

The magnetic properties of the hybrid elastomers were characterized by recording hysteresis curves. The hybrid elastomers synthesized without magnetic field were ferromagnetic at room temperature ($\mu_o H_c = 0.45$ T). The remnant ratio, $M_r/M_s \sim 0.5$, was characteristic of an assembly of dispersed nanorods randomly oriented (Figure 2).

Figure 3 shows the X-ray scattering patterns of the sample in the absence of strain, $\lambda = 1$, and stretched to more than twice its initial length, $\lambda = 2.5$. At wide angles, the initially isotropic diffuse scattering halo due to the mesogenic side groups (Figure 3a) became anisotropic when the sample was stretched (Figure 3c), which means that the mesogens aligned

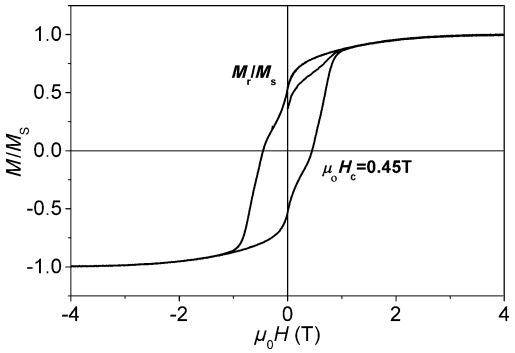

Figure 2. Hysteresis curve at room temperature of a non-oriented hybrid elastomer. $\mu_o Hc$ is the coercive field and M_r/M_s is the ratio between the remnant magnetization and the magnetization at saturation.

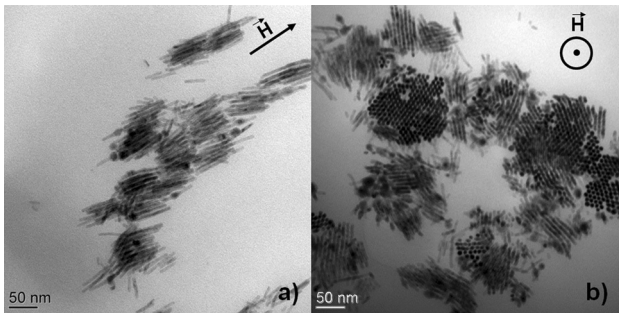

Figure 4. TEM micrographs of 80 nm thick cryo-microtomed slices of the oriented elastomer. Sample cut parallel (a) and perpendicular (b) to the magnetic field applied during the synthesis. Scale bar: 50 nm.

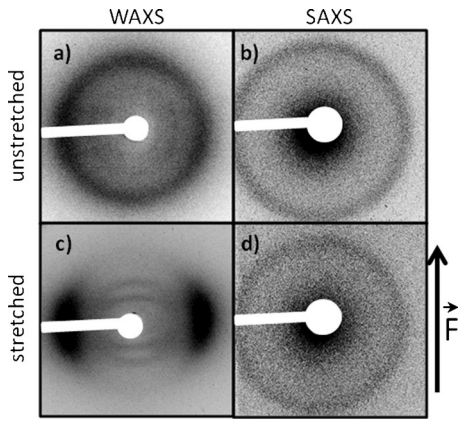

Figure 3. a,c) Wide- and b,d) small-angle X-ray scattering patterns, recorded at room temperature, of an a,b) unstretched ($\lambda = 1$) and c,d) stretched ($\lambda = 2.5$) magnetic liquid crystalline elastomer cross-linked in the absence of magnetic field. $\lambda = L/L_0$, where L_0 and L are the lengths of the sample at rest and under stretch, respectively.

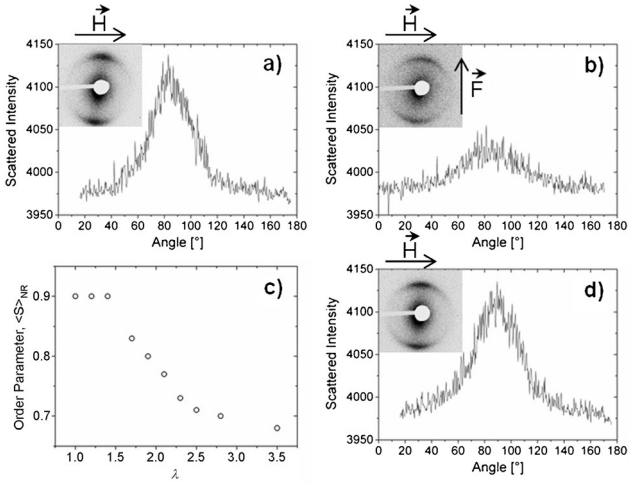

Figure 5. Azimuthal scans of the X-ray scattered intensity showing the nanorod orientation a) without strain ($\lambda = 1$) and b) under strain $\lambda = 2.75$ applied perpendicularly to the initial orientation. c) Nanorod order parameter, S_{NR}, versus elongation, λ. d) Azimuthal scan of the scattered intensity showing the nanorod orientation after relaxing without strain during one night. The insets are the corresponding SAXS patterns. The $\vec{H}$ denotes the direction of the magnetic field applied during cross-linking and the $\vec{F}$ the direction of the stress applied during the SAXS measurements shown in (b).

upon stretching. Doping does not affect the sample microstructure and elasticity, and, above all, the ability of the mesogens to align along the strain remains intact (Figure S4). In contrast, the SAXS patterns remained isotropic up to the maximum investigated elongation, indicating no effect of the strain on the nanorod orientation (Figure 3b and d).

The cross-linking reaction was then performed in the presence of a uniform magnetic field delivered by an electromagnet (Figure S1).

Figure 4 shows TEM micrographs of the sample cut parallel (Figure 4a) and perpendicular (Figure 4b) to the direction of the applied magnetic field. The nanorods organize in bundles in the material and all the bundles align along the direction of the magnetic field. No preferential orientation is observed on non-oriented samples (Figure S2).

The good alignment of the cobalt nanorods is also visible in the SAXS patterns (Figure 5a), with an order parameter of $S_{NR} = 0.9$. This high orientational order is also demonstrated by the hysteresis curves recorded at room temperature in two different sample orientations (Figure 6): the magnetic field lay either perpendicular or parallel to the direction of the magnetic field applied during cross-linking. In the latter case, the hysteresis curve was square and showed a 0.7 T coercive field and a squareness (M_r/M_s) of 0.7. This high ratio indicates that the nanorods were well aligned by the magnetic field applied during the synthesis and that they kept this alignment when the magnetic field was switched off. When the sample was placed in the perpendicular orientation, the hysteresis curve drastically changed, with a large reduction of the remnant ratio (0.3) and of the coercive field (0.29 T). The difficulty to saturate the magnetization in this orientation also proves that the applied magnetic field was actually perpendicular to the easy axis of the nanorods. These magnetic measurements prove that we have synthesized a highly anisotropic magnetic material.

To modulate the orientation of the nanorods, the samples were then stretched at room temperature perpendicularly to the initial nanorod orientation. SAXS experiments showed, together with the orientation of the mesogens (Figure S5),

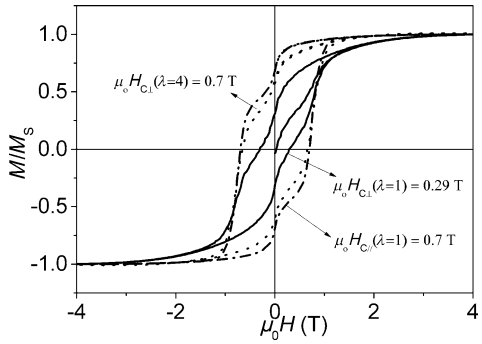

Figure 6. Hysteresis curves at room temperature of the hybrid elastomer prepared in the presence of a 1 T magnetic field. The nanorods in the samples were either perpendicular (solid line) or parallel (dot-dashed line) to the magnetic field applied during the magnetic measurement and no stress was applied ($\lambda = 1$). The dotted line is the hysteresis curve of the sample after applying a stress ($\lambda = 4$) perpendicular to the nanorod alignment and parallel to the magnetic field applied during the measurement. (The first measurement from $H = 0$ was recorded with nanorods perpendicular to the field during the measurement).

a decrease of the nanorod order parameter S_{NR}, upon increasing strain (Figure 5 a–c). Stretching the sample till $\lambda = 3.5$ induced a change in S_{NR} from 0.90 to 0.68 (Figure 5 c) and most of the change occurred between $\lambda = 1.4$ and 3. Interestingly, this variation in the mean nanorod orientation corresponds to a very significant change in the magnetic properties of the samples. By manually stretching samples to $\lambda = 4$, the hysteresis curve, initially thin and tilted (solid line in Figure 6), became wide and square (dotted line in Figure 6) with values of the remnant ratio and coercive field very close to those of the sample in the parallel configuration. This means that the nanorods have turned perpendicular to their initial direction upon stretching, leading to an increase of more than 50 % of the remnant magnetization and of the coercive field. We thus proved that it is possible to control the magnetic response of the sample at room temperature by applying a rather small mechanical stress.

These hybrid materials kept the elastic properties expected for silicone polymers at room temperature because they could be stretched till $\lambda = 3.5$–4 without breaking and they relaxed to their original size. This relaxation was accompanied by a rearrangement of the nanorods back to their initial alignment (Figure 5 d). The nanorod alignment appeared then completely reversible.

Furthermore, applying the magnetic field to samples a few micrometers thick during cross-linking resulted in monodomain elastomers with uniform mesogen orientation and nanorods well aligned in the same direction. Under these conditions, a change of sample shape and dimensions (by about 10–15 %) across the phase-transition temperature was observed. This shows that doping with Co nanorods does not suppress the shape change expected for such kind of liquid crystalline elastomers. The study of these monodomain samples is in progress.

In conclusion, we demonstrate the possibility to switch the orientation of nanorods, and hence, the magnetization direction of the material at room temperature by using a weak mechanical stress. This has been achieved by dispersing a low amount of metallic Co nanorods within a liquid crystalline polymer and by cross-linking under a magnetic field. This novel process provides a highly anisotropic ferromagnetic mesomorphous material in which the nanorod direction can be tuned at will at room temperature. A change of more than 50 % of both the coercive field and the remnant magnetization ratio with highly oriented nanorods ($M_r/M_s = 0.7$) was thus achieved. Due to their high magnetization and strong magnetic anisotropy, metallic Co nanorods lead to a strong magnetic readout and a good stability of the magnetic moment, respectively. This is particularly important in the context of new applications such as magnetic memories or actuators.

In this study, we proved the concept of strong magnetoelastic coupling by using anisotropic ferromagnetic nanoparticles. The hybrid nanocomposite/liquid crystalline elastomer approach may be easily extended to other kinds of anisotropic nanoparticles, leading to new possibilities in hybrid compounds, such as multiferroics,[1] operating at room temperature and coupling electric, magnetic, and elastic properties, allowing for instance manipulation of the magnetization direction by an electric field.

Experimental Section

Co nanorods were synthesized from $\{Co[N(SiMe_3)_2]_2(thf)\}$.[14] Hybrid liquid crystal elastomers were synthesized starting from poly(methylhydrogenosiloxane), the liquid crystal, the cross-linker, and the Co nanorods in a two-step procedure.

Differential scanning calorimetry measurements were performed with a DSC1 Star System (Mettler Toledo). X-ray scattering measurements were performed with a set-up equipped with a Cu rotating-anode generator. The detection was achieved with a Princeton CCD camera. TEM micrographs of the hybrid elastomers were performed on 80 nm thick cryo-microtomed slices using a Philips CM 120 operating at 120 kV. Magnetic measurements were performed using a Vibrating Sample Magnetometer (VSM).

Experimental details are reported in the Supporting Information.

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Keywords: cobalt nanorods · elastomers · hybrid materials · magnetic actuators · magnetization

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