Magnetic correlations of iron oxide nanoparticles as probed by polarized SANS in stretched magnetic nanoparticle–elastomer composites

Cite as: Appl. Phys. Lett. **120**, 052401 (2022); https://doi.org/10.1063/5.0081922 Submitted: 10 December 2021 • Accepted: 17 January 2022 • Published Online: 31 January 2022

🔟 S. D. Oberdick, 🔟 J. A. Borchers and K. L. Krycka





Shorten Setup Time Auto-Calibration More Qubits



GQBLOX

Fully-integrated Quantum Control Stacks Ultrastable DC to 18.5 GHz Synchronized <<1 ns

Ultralow noise



visit our website >

Appl. Phys. Lett. **120**, 052401 (2022); https://doi.org/10.1063/5.0081922 © 2022 Author(s).

Export Citatio

Tiow Onlin

Magnetic correlations of iron oxide nanoparticles as probed by polarized SANS in stretched magnetic nanoparticle-elastomer composites

Cite as: Appl. Phys. Lett. **120**, 052401 (2022); doi: 10.1063/5.0081922 Submitted: 10 December 2021 · Accepted: 17 January 2022 · Published Online: 31 January 2022

S. D. Oberdick,^{1,2,a)} (D J. A. Borchers,³ (D and K. L. Krycka³

AFFILIATIONS

¹Department of Physics, University of Colorado, Boulder, Colorado 80309, USA

²National Institute of Standards and Technology, Boulder, Colorado 80305, USA

³National Institute of Standards and Technology, NIST Center for Neutron Research, Gaithersburg, Maryland 20899, USA

^{a)}Author to whom correspondence should be addressed: samuel.oberdick@nist.gov

ABSTRACT

We have investigated the magnetic correlations among 7 nm iron oxide nanoparticles embedded in stretched silicone elastomers using polarized Small Angle Neutron Scattering (SANS). The magnetic nanoparticle (MNP)-elastomer composite can be stretched during experiments, and macroscopic deformations cause rearrangement of the iron oxide particles on the nanoscale. Polarized neutrons can be used to nondestructively probe the arrangement of magnetic nanoparticles before and after stretching, so that the relationship between applied stress and nanoscale magnetization can be interrogated. We find that stretching the MNP-elastomer composite past a certain threshold dramatically changes the structural and magnetic morphology of the system. The unstretched sample is modeled well by \sim 40 nm clusters of \sim 7 nm particles arranged in a hard sphere packing with a "volume fraction" parameter of 0.3. After the sample is stretched 3× its original size, however, the scattering data can be modeled by smaller, 16 nm clusters with a higher volume fraction of 0.4. We suggest that the effect can be understood by considering a stretching transformation on FCC-like crystallites of iron oxide nanoparticles embedded in an elastomeric medium.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0081922

Composite materials made of magnetic particles and polymeric materials are unique because they combine magnetic functionality with the "soft" characteristics of flexible polymers. Polymer materials have low elastic moduli, which can be engineered so that they deform in specific ways when subjected to applied stress. When magnetic particles are added to these materials, magnetic fields can be used to remotely control the applied stress, creating deformation and shape change. It is also possible to transduce a magnetic response from applied stress via the magnetoelastic effect, where deformations cause rearrangement of magnetic particles and influence magnetic polymer composite material. Due to these distinct characteristics, magnetic polymer composite materials have been used to create soft robotics,^{1–3} 3D printed magnetic materials,⁴ remote tools for drug delivery,⁵ and magnetorheological dampeners.⁶

Motivated by applications of such composites, we performed a series of experiments to investigate nanoscale magnetic correlations within deformable magnetic nanoparticle (MNP) elastomers. Specifically, we used polarized Small Angle Neutron Scattering (SANS) to study magnetic correlations of \sim 7 nm magnetite (Fe₃O₄) MNPs

embedded in strained silicone rubber. Neutron scattering has been employed previously to investigate stretched polymers⁷ and polymeric nanocomposites,^{8–11} but these studies used unpolarized neutrons to probe structural changes via nuclear scattering. The experiments described here use polarized neutrons to map magnetization of MNPs on length scales ranging from 0.1 to 100 nm.¹² This allows the strained MNP-elastomer composites to be probed locally, so that nanoparticle rearrangement and nanoscale magnetic domain deformation can be related to macroscale strain. Typically, MNP-elastomer composites are evaluated using "bulk" magneto-mechanical techniques, which include static and dynamic compression, tensile, and shear tests with and without applied magnetic fields.¹³ To fully realize the potential of these materials, however, it is critical to connect an understanding of their nanomagnetic properties to overall magnetic performance. The polarized scattering experiments described here suggest a quantifiable experimental pathway for doing so.

Polarized SANS has been successfully utilized to probe magnetization in many types of MNPs.^{14–17} With the exception of colloids and ferrofluids, nanoparticles in prior experiments were fixed in place over the course of the scattering experiments. Here, we employ the reconfigurable nature of the MNP-elastomer to control relative positions of nanoparticles while simultaneously probing changes in nanomagnetic correlations with polarized SANS. During a typical experiment, the MNP-elastomer composite is subjected to an in situ stretching force. The macroscopic change in shape is accompanied by deformation on the nanoscale, where polymer chains stretch and translate to accommodate a new equilibrium configuration. As a result, MNPs embedded in such an elastomeric matrix change their configuration as a function of applied stress [Fig. 1(a)]. When the force is removed, the particles return to their original positions and the sample assumes its original shape. We believe that this experimental scheme may prove useful for studying ensemble magnetization and interactions in MNP systems since it enables the spacing between particles to be tuned via applied stress. This system may also be useful for investigating biosensors that operate based on the reversible aggregation or relative motion of MNPs.¹⁸⁻²¹

The MNP-elastomer composite examined in this study is one of many possible manifestations of magnetic polymer systems. The magnetic response and performance of these systems can be engineered by picking different loading concentrations of magnetic particles, different polymer types, or different synthetic pathways for composite fabrication. For an overview of how these parameters can influence the magnetic properties of the magnetic polymer composites, we refer the interested reader to recent reviews on magnetic polymer materials.^{13,22,23} For the scattering experiments described herein, we chose to work with 7.4 nm iron oxide nanoparticles embedded in silicone rubber. Specifically, the particles were synthesized using thermal decomposition²⁴ and consist of a magnetite (Fe₃O₄) core coated by a thin layer of oleic acid (supplementary material). This particular method of thermal decomposition-the so-called Sun method-was chosen for this study because it produces monodispersed, singlecrystalline Fe₃O₄ nanoparticles with a higher magnetization than other methods.²⁵ The MNP-elastomer composite was prepared by curing the nanoparticles within a silicone elastomer network, which is known as the "blending" method for magnetic polymer preparation.²² This is different from other methods, such as in situ coprecipitation, where particles are grown inside of an already crosslinked polymer matrix.^{26,27} The oleic acid coated particles mixed well with the silicone



FIG. 1. (a) Schematic diagrams of magnetite nanoparticles embedded in a silicone rubber elastomer in unstretched (left) and uniaxially stretched (right) configurations. (b) TEM image of MNPs used in the experiment with inset showing histogram of size distribution. (c) Cross-sectional TEM image showing nanoparticles embedded in silicone rubber.

rubber precursor, showing no macroscale phase separation, allowing the particles to be stably cured within the silicone matrix. Figure 1(b) shows a transmission electron microscope (TEM) image of the particles, which are 6.9 ± 1.5 nm [inset of Fig. 1(b)]. Figure 1(c) shows a cross-sectional TEM image of the nanoparticles after they have been embedded in cured silicone elastomer. The particles form closepacked aggregates with random shapes and orientations, as seen in Fig. 1(c). While iron oxide particles and silicone were used for this study, the experimental system is not limited to these materials. Indeed, the experiments should be generalizable to other types of magnetic particle/polymer composites.

A small piece of the MNP-elastomer composite was removed and examined with magnetometry. Figure 2(a) shows a magnetization loop taken at 300 K, which roughly corresponds to the room temperature (~293 K) neutron scattering experiments. The loop has no coercivity and shows the characteristic shape associated with superparamagnetic particles. The data were fit to a single Langevin function, and the magnetic diameter of the particles was extracted, assuming saturation magnetization of magnetite (supplementary material). The magnetic diameter was found to be \sim 7 nm, consistent with TEM measurements. Figure 2(b) shows zero field-cooled (ZFC) and field-cooled (FC) curves for the samples. The dotted line indicates the peak of the ZFC curve, which occurs at $51.4 \text{ K} \pm 2.3 \text{ K}$. If we use this peak to extract the blocking temperature of the sample, then one can safely assume that the particles are superparamagnetic at room temperature. The authors acknowledge that extracting the blocking temperature is, in fact, more complex than simply evaluating the peak of the ZFC curve.²⁸⁻³⁰ The ZFC peak lies well below the temperature at which the neutron scattering experiments were performed (293 K). Thus, even without making a precise determination of the blocking temperature, we can safely say that the particles are superparamagnetic for the room temperature scattering experiments described herein.

Polarized SANS measurements were performed at the NIST Center for Neutron Research using the CHRNS vSANS beamline. Figure 3(a) shows the experimental configuration for polarization measurements. Incoming neutrons from the Z direction are scattered

off the sample and detected in the X-Y plane. The angle Θ denotes the angle between the scattering vector, Q, and the X direction in the detector plane. A double-V supermirror cavity polarizes the neutron spins in the incident beam, and a RF-neutron spin-flipper is used to select the up (+) or down (-) incident spin state. An electromagnet is used to apply magnetic fields in the X direction during experiments. Nuclear and magnetic scattering contribute to the overall measured scattering intensity, *I*. Simplified spin scattering rules can be applied to extract constituent contributions to the overall scattering.³¹ These spin rules allow for straightforward calculation of N^2 and M_{PARL}^2 which correspond to the square of the nuclear scattering and the magnetic scattering parallel to the applied field (which is proportional to the net magnetization),

$$N^{2}(Q_{X}) = I^{+}_{\theta=0^{\circ}} = I^{-}_{\theta=0^{\circ}}, \qquad (1)$$

$$M_{PARL}^{2}(Q_{Y}) = \frac{\left(I_{\theta=90^{\circ}}^{-} - I_{\theta=90^{\circ}}^{+}\right)^{2}}{8|N|^{2}}.$$
 (2)

(Note that these equations assume that the scattered intensity is normalized by the incident intensity for the + spin state, which is 1/2 of the incident intensity of the unpolarized beam.) As an aside, we also attempted polarized/analyzed measurements in which a ³He spin analyzer is placed between the sample and detector. Unfortunately, the abundance of hydrogen in the elastomer polymer chains dominated spin-flip scattering (supplementary material). Thus, most of the experiments were run in a half-polarized modality.

Figures 3(b) and 3(c) show the calculated values of N^2 and M_{PARL}^2 for scattering data from the unstretched MNP-elastomer. In Fig. 3(b), the electromagnet is off, and the sample experiences a remanent field of 0.009 T. Figure 3(c) shows data taken during application of a 1 T magnetic field. In both cases, the composite nuclear scattering over the entire Q range is dominated by scattering from the silicone gel, which has incoherent contributions from hydrogen, and the scattering from the embedded nanoparticles is obscured. This is consistent with the fact that the sample volume is largely comprised of silicone rubber. On the contrary, the calculation of M_{PARL}^2 [Eq. (2)] reveals the



FIG. 2. Magnetometry data on MNP-elastomer composite. (a) Magnetic moment as a function of applied field at 300 K and fit to a Langevin function. (b) Zero field-cooled and field-cooled curves. The cooling field for the field-cooled (FC) curve and the measurement field for the zero field-cooled (ZFC) curves was 1 mT.



FIG. 3. (a) Schematic showing vSANS experimental setup, which includes a double V polarizing supermirror cavity, a RF spin flipper, and three detector banks. (b) Data for N^2 and M_{PARL}^2 in the remanent field of ~0.009 T. (c) Data for N^2 and M_{PARL}^2 in an applied field of 1 T. Error bars displayed here and elsewhere indicate 1 standard deviation.

structure and net parallel magnetization of nanoparticles under application of a magnetic field. For the remanent field condition of 0.009 T, M_{PARL}^{2} is small and has no apparent structure. This behavior is consistent with a superparamagnetic ensemble of nanoparticles, where the magnetic moments of each particle are randomly oriented and the ensemble net magnetization averages to zero. At 0.009 T, the sample magnetization is 6% of the saturation magnetization and at 1T, the sample has 95% of the saturation magnetization, where the saturation magnetization was measured at 7 T. For the high field condition of 1 T, M_{PARL}^2 has a Bragg peak at ~0.075 Å⁻¹. This magnetic Bragg peak develops because the saturated magnetic moments from each particle are oriented uniformly in the X direction. The Bragg peak, which has been observed in other MNP systems,^{14–16} arises from diffraction from the (111) planes in close-packed FCC (face-centered cubic) crystallites of nanoparticles. Since the appearance of a (111) peak requires structural coherence over several nanoparticles, we conclude that the nanoparticles are clustered proximate to each other, consistent with the crosssectional TEM in Fig. 1(c). Assuming an effective diameter, d, of \sim 10 nm (7 nm core and 1.5 nm steric barrier from surfactant/silicone) gives an FCC lattice spacing of $a = \sqrt{2d} = 14.1$ nm or 141 Å. The (111) Bragg peak from a close-packed FCC lattice with this lattice spacing appears at $Q = 2\pi/(141 \text{ \AA}/\sqrt{3}) = 0.077 \text{ \AA}^{-1}$, which is consistent with the position that is observed.

To investigate the relationship between applied stress and nanoscale magnetic correlations, the sample was strained to different degrees and then scattering experiments were performed. The sample was stretched by factors of $2 \times$ and $3 \times$ its original size by mechanically pinning the ends of the elastomer across an opening of sufficient size for neutron beam transmission. After the sample was configured in a strained configuration, it was placed on the beamline for subsequent scattering experiments, at which point a magnetic field could be applied. In one set of measurements, the direction of stretching was parallel to the applied magnetic field (X - direction) and in the second set, it was perpendicular (Y-direction). Using SASView software,³ these data were fit to a model containing 7.4 nm, individual spheres that are hard-packed along with larger, multi-particle spherical clusters. Analysis of the SANS data indicates that MNPs are ordered locally into FCC-like assemblies of finite size that manifest as magnetic domains.

Figure 4 shows M_{PARL}^2 data for experiments in a 1 T magnetic field where the MNP-elastomer composite was stretched along the field direction 2× and 3× its original length. We fit the unstretched data [Fig. 4(a)] to a model containing 7.4 nm spheres that are hard packed alongside larger clusters, which are 44 nm in diameter (±10% polydispersity). The smaller, 7.4 nm spheres are packed within the clusters with an FCC-like structure and a "volume fraction" parameter



FIG. 4. Magnetic scattering, M_{PARL}^2 data for three configurations where the sample was stretched parallel to the 1 T applied field. (a) Unstretched configuration, fit to hard sphere model with 44 nm (±10%) clusters of NPs. (b) 2× stretched configuration, fit to hard sphere model with 44 nm (±20%) clusters of NPs. (c) 3× stretched configuration, fit to hard sphere model with 44 nm (±5%) clusters of NPs.

of 0.3. The aspects of this model were chosen based on observations from TEM and magnetometry. Indeed, the aggregate morphology accords well with observations from TEM, where the particles are arranged in \sim 50 nm clusters throughout the cured silicone elastomer. This cluster morphology produces fits that generally match the data, but there are noticeable regions where the fit does not match the data well. We attribute this to the fact that the actual system contains particle aggregates with random shapes and orientations. Despite the shortcomings of the model, it captures general changes in magnetic scattering as the sample is strained. This can be seen in Fig. 4(b), where the sample has been stretched $2\times$. The $2\times$ strain can be modeled by increasing the polydispersity of the large clusters from $\pm 10\%$ to \pm 20%. This change in polydispersity reflects a distortion of the magnetic domains as the sample is stretched. When the sample is stretched $3 \times$ in a direction parallel to the applied field [Fig. 4(c)], the magnetic morphology changes dramatically. The best model for these data is dominated by smaller spherical clusters with an effective diameter of 16 nm that emerge along the Y direction. The model also includes a small scattering contribution from the FCC-like structure, but the "volume fraction" parameter for these hard packed spheres increases from 0.3 to 0.4, suggestive of enhanced local ordering. Thus, stretching the sample $3\times$, its original size seems to condense nanoscopic magnetic domains within the sample.

Figure 5 depicts M_{PARL}^2 data for experiments in a 1 T magnetic field where the MNP-elastomer composite was stretched perpendicular to the field direction. The unstretched case [Fig. 5(a)] is the same as Fig. 4(a) and can be modeled by 44 nm clusters of particles (±10% polydispersity) with a "volume fraction" parameter of 0.3. The effect of 2× stretching in the perpendicular direction [Fig. 5(b)] can be modeled by an increase in polydispersity, from ±10% to ±20%, similar to the parallel stretching case. However, when the sample is stretched 3× in the perpendicular direction [Fig. 5(c)], the change in magnetic scattering is not as dramatic as when the sample is stretched in the parallel direction. These data can be modeled by 44 nm clusters of hard packed spheres with a further increase in overall polydispersity from ±20% to ±30%. A comparison of the results in Figs. 4 and 5 suggests that the parallel stretching direction is unique since that case generates an apparent reduction in magnetic domain size.

The changes in magnetic morphology between the stretched and unstretched cases can be understood in terms of a transformation of the relative positions among nanoparticles under applied stress. As the sample is stretched, interparticle spacing is extended in the direction



FIG. 5. Magnetic scattering, M_{PARL}^2 data for three configurations where the sample was stretched perpendicular to the 1 T applied field. (a) Unstretched configuration, fit to hard sphere model with 44 nm (±10%) clusters of NPs. (b) 2× stretched configuration, fit to hard sphere model with 44 nm (±20%) clusters of NPs. (c) 3× stretched configuration data, fit to hard sphere model with 44 nm (±30%) clusters of NPs.

scitation.org/journal/apl

parallel to the applied stress and contracted in directions perpendicular to the applied stress. These changes affect the magnetic properties of the system in ways that are detectable via magnetic scattering. For modest stretching, as in the cases where the sample is stretched $2 \times$ its original size, the clusters of MNPs are deformed slightly, leading to an increase in the overall polydispersity of the magnetic domains. The increased polydispersity indicates a greater distribution in the sizes of the magnetic domains in the clusters, as may be expected due to local variations in the magnitude of magnetic interactions introduced upon stretching. It is also notable that increased stretching (except for the $3 \times$ stretching along *X*) leads to an overall decrease in the magnitude of the magnetic scattering at all *Q*. The decrease in magnetic intensity may originate from increased frustration among the local nanoparticle moments, which reduces the magnitude of net magnetization parallel to the field direction.

In our experimental geometry, the effect of stretching $3 \times$ in a direction parallel to the applied field has a dramatic effect on M_{PARL}^{2} . To understand the origin of this effect, it is instructive to consider the action of stretching on an FCC-crystallite. Figure 6 has a schematic that depicts two planes of an idealized FCC-crystallite of ~7 nm particles with a \sim 3 nm edge-to-edge distance. The size of the two stacked planes is $\sim 40 \times \sim 50$ nm in the X-Y direction, matching the order of magnitude of crystallites observed in the actual sample. The schematic shows the effect of stretching $2 \times$ and $3 \times$ on the underlying lattice in a direction parallel to the applied field. It should be noted that Fig. 6 shows an oversimplified representation of the stretched sample. In actuality, the particles are not assembled into oriented, monodispersed FCC crystallites but, rather, are grouped into randomly oriented aggregates. Stretching extends interparticle distances along the X direction and causes contraction in the Y and Z direction. In Fig. 6, this has the effect of increasing the distance along X between shared Y-Z planes of nanoparticles, while decreasing the relative spacing between particles along the Y (and Z) direction. For a $2 \times$ stretch, this leads to an



FIG. 6. Schematic diagrams showing two stacked (111) planes of an FCC-like crystallite in (a) unstretched, (b) $2\times$ stretched, and (c) $3\times$ stretched configurations, for a geometry where the stretching force is applied parallel to the magnetic field.

increase in the overall polydispersity of the cluster size, but the average distance between particles remains mostly unchanged. When the sample is stretched $3 \times$ its original size, the spacing between particles in the Y (and Z) direction contracts so much that the neighboring particles are practically touching-separated only by a thin steric barrier. The distance between Y-Z planes along the X direction is free to extend unhindered, though, creating gaps between clusters of particles. The overall effect is to create condensed clusters of particles with smaller sizes than the original aggregates. In accordance with magnetic neutron scattering rules,³¹ the M_{PARL}^2 scattering [Eq. (2)] from these clusters is sensitive in a saturating field both to the magnitude of net magnetization parallel to the X axis and to magnetic correlations among the nanoparticles along the Y direction. Since the measurements were performed at saturation, the magnetic structure is expected to mirror the physical structure. Thus, the condensed clusters along Y generate M_{PARL}^2 scattering [Fig. 4(c)] that is well modeled by distinct, 16 nm magnetic domains. In addition, the scattering contribution from the individual hard packed spheres has a relative packing fraction that increases from 0.3 to 0.4, suggesting that the local FCClike packing of the nanoparticles in the cluster increases due to contraction of interparticle spacing in the Y direction. This effect is not seen when the sample is stretched in the perpendicular direction. For the perpendicular case [Fig. 5(c)], stretching causes an elongation of MNP clusters along the Y direction, as opposed to condensation into small 16 nm clusters. In this case, the data are best fit again by large, 44 nm clusters, with a further increase in polydispersity from $\pm 20\%$ at $2 \times$ to $\pm 30\%$ at $3 \times$.

In conclusion, we have performed a series of polarized SANS experiments to study the relationship between applied stress and nanoscale magnetic correlations within MNP-elastomer composites. MNPs embedded in the elastomer change their configuration as a function of applied stress, providing a method to adjust the average spacing between particles. The magnetic scattering data can be well modeled by hard-packed spheres within larger spherical clusters. Scattering data for different stretching configurations correspond to different degrees of cluster polydispersity, cluster size, and packing fraction. We suggest that the changes can be explained by considering the action of stretching on FCC-crystallites of MNPs in the sample. These polarized SANS experiments demonstrate that applied stress on the MNP-elastomer composite modulates the nanoscale structural properties and corresponding magnetic characteristics of MNPs in a pronounced, controllable manner.

See the supplementary material for details on nanoparticle synthesis, magnetometry, Langevin fitting, and additional scattering data. Also included is a compilation of tilt TEM images showing a nanoparticle cluster embedded in silicone resin. The stack of tilt TEM images has been rendered as a .avi animation to give the viewer a threedimensional impression of the iron oxide nanoparticle clusters.

S.D.O. would like to acknowledge support from NIST-PREP (Professional Research Experience Program), performed under the following financial assistance award 70NANB18H006 from U.S. Department of Commerce, National Institute of Standards and Technology. S.D.O. would also like to acknowledge NSF-CBET Award No. 2038046. Electron microscopy was done at the University of Colorado, Boulder EM Services Core Facility in the MCDB Department, with the technical assistance of facility staff. Access to vSANS was provided by the Center for High Resolution Neutron Scattering, a partnership between the National Institute of Standards and Technology and the National Science Foundation under Agreement No. DMR-2010792. The authors would also like to thank Cedric Gagnon for his technical assistance with the vSANS instrumentation as well as Hannah Burrall and Shannon Watson for providing and supporting the ³He spin filters for the vSANS polarization analysis. This work benefited from the use of the SasView application, originally developed under NSF Award No. DMR-0520547. SasView contains code developed with funding from the European Union's Horizon 2020 research and innovation program under the SINE2020 project, Grant Agreement No. 654000.

Any mention of commercial products is intended solely for fully detailing experiments; it does not imply recommendation or endorsement by NIST.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- ¹M. M. Schmauch, S. R. Mishra, B. A. Evans, O. D. Velev, and J. B. Tracy, ACS Appl. Mater. Interfaces **9**, 11895 (2017).
- ²X. Wang, G. Mao, J. Ge, M. Drack, G. S. Cañón Bermúdez, D. Wirthl, R. Illing, T. Kosub, L. Bischoff, C. Wang, J. Fassbender, M. Kaltenbrunner, and D. Makarov, Commun. Mater. 1, 67 (2020).
- ³W. Hu, G. Z. Lum, M. Mastrangeli, and M. Sitti, Nature 554, 81 (2018).
- ⁴Y. Kim, H. Yuk, R. Zhao, S. A. Chester, and X. Zhao, Nature 558, 274 (2018).
- ⁵T.-Y. Liu, S.-H. Hu, T.-Y. Liu, D.-M. Liu, and S.-Y. Chen, Langmuir 22, 5974 (2006).
- ⁶L. C. Davis, J. Appl. Phys. 85, 3348 (1999).
- ⁷M. Shibayama, Polym. J. 43, 18 (2011).
- ⁸T. Nishida, H. Endo, N. Osaka, H. Li, K. Haraguchi, and M. Shibayama, Phys. Rev. E **80**, 030801 (2009).
- ⁹M. Shibayama, S. Miyazaki, H. Endo, T. Karino, and K. Haraguchi, Macromol. Symp. 256, 131 (2007).
- ¹⁰M. Shibayama, T. Karino, S. Miyazaki, S. Okabe, T. Takehisa, and K. Haraguchi, Macromolecules 38, 10772 (2005).

- ¹¹H. Endo, S. Miyazaki, K. Haraguchi, and M. Shibayama, Macromolecules 41, 5406 (2008).
- ¹²K. L. Krycka, R. Booth, J. A. Borchers, W. C. Chen, C. Conlon, T. R. Gentile, C. Hogg, Y. Ijiri, M. Laver, B. B. Maranville, S. A. Majetich, J. J. Rhyne, and S. M. Watson, Phys. B: Condens. Matter **404**, 2561 (2009).
- ¹³A. K. Bastola, M. Paudel, L. Li, and W. Li, Smart Mater. Struct. 29, 123002 (2020).
- ¹⁴K. Hasz, Y. Ijiri, K. L. Krycka, J. A. Borchers, R. A. Booth, S. Oberdick, and S. A. Majetich, Phys. Rev. B **90**, 180405 (2014).
- ¹⁵K. L. Krycka, R. A. Booth, C. R. Hogg, Y. Ijiri, J. A. Borchers, W. C. Chen, S. M. Watson, M. Laver, T. R. Gentile, L. R. Dedon, S. Harris, J. J. Rhyne, and S. A. Majetich, Phys. Rev. Lett. **104**, 207203 (2010).
- ¹⁶S. D. Oberdick, A. Abdelgawad, C. Moya, S. Mesbahi-Vasey, D. Kepaptsoglou, V. K. Lazarov, R. F. L. Evans, D. Meilak, E. Skoropata, J. Lierop, I. Hunt-Isaak, H. Pan, Y. Ijiri, K. L. Krycka, J. A. Borchers, and S. A. Majetich, Sci. Rep. 8, 3425 (2018).
- ¹⁷Y. Ijiri, K. L. Krycka, I. Hunt-Isaak, H. Pan, J. Hsieh, J. A. Borchers, J. J. Rhyne, S. D. Oberdick, A. Abdelgawad, and S. A. Majetich, Phys. Rev. B **99**, 094421 (2019).
- ¹⁸T. Atanasijevic, M. Shusteff, P. Fam, and A. Jasanoff, Proc. Natl. Acad. Sci. 103, 14707 (2006).
- ¹⁹Y. Matsumoto and A. Jasanoff, Magn. Reson. Imaging 26, 994 (2008).
- ²⁰Z. Zhao and C. Rinaldi, Phys. Med. Biol. 65, 185013 (2020).
- ²¹Z. W. Tay, S. Savliwala, D. W. Hensley, K. L. B. Fung, C. Colson, B. D. Fellows, X. Zhou, Q. Huynh, Y. Lu, B. Zheng, P. Chandrasekharan, S. M. Rivera-Jimenez, C. M. Rinaldi-Ramos, and S. M. Conolly, Small Methods 5, 2100796 (2021).
- ²²Y. Li, G. Huang, X. Zhang, B. Li, Y. Chen, T. Lu, T. J. Lu, and F. Xu, Adv. Funct. Mater. 23, 660 (2013).
- ²³H.-J. Chung, A. M. Parsons, and L. Zheng, Adv. Intell. Syst. 3, 2000186 (2021).
- ²⁴S. Sun and H. Zeng, J. Am. Chem. Soc. **124**, 8204 (2002).
- ²⁵Z. Nedelkoski, D. Kepaptsoglou, L. Lari, T. Wen, R. A. Booth, S. D. Oberdick, P. L. Galindo, Q. M. Ramasse, R. F. L. Evans, S. Majetich, and V. K. Lazarov, Sci. Rep. 7, 45997 (2017).
- ²⁶M. Helminger, B. Wu, T. Kollmann, D. Benke, D. Schwahn, V. Pipich, D. Faivre, D. Zahn, and H. Cölfen, Adv. Funct. Mater. 24, 3187 (2014).
- 27S. D. Oberdick, S. E. Russek, M. E. Poorman, and G. Zabow, Soft Matter 16, 10244 (2020).
- ²⁸K. L. Livesey, S. Ruta, N. R. Anderson, D. Baldomir, R. W. Chantrell, and D. Serantes, Sci. Rep. 8, 11166 (2018).
- ²⁹I. J. Bruvera, P. Mendoza Zélis, M. Pilar Calatayud, G. F. Goya, and F. H. Sánchez, J. Appl. Phys. **118**, 184304 (2015).
- ³⁰H. Gabold, Z. Luan, N. Paul, M. Opel, P. Müller-Buschbaum, M. Law, and A. Paul, Sci. Rep. 8, 4835 (2018).
- ³¹K. Krycka, J. Borchers, Y. Ijiri, R. Booth, and S. Majetich, J. Appl. Cryst. 45, 554 (2012).
- ³²See www.sasview.org for more information regarding the SasView analysis software for small angle scattering data (2021).