# Long Time Response of Soft Magnetorheological Gels

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S *Supporting Information*

ABSTRACT: Swollen physical magnetorheological (MR) gels were obtained by self-assembling of triblock copolymers containing dispersed soft magnetic particles. The transient rheological responses of these systems were investigated experimentally. Upon sudden application of a homogeneous magnetic field step change, the storage modulus of MR gels continued to increase with time. Such increase trend of the storage modulus could be expressed by a double-exponential function with two distinct modes, a fast and a slow one. The result was compared with the transient rheological response of equivalent MR fluids (paraffin oil without copolymer) and a MR elastomer (PDMS) and interpreted as the consequence of strong rearrangement of the original particle network under magnetic field. Similar to the structure evolution of MR fluids, the ensemble of results suggests that "chaining" and "clustering" processes are also happening inside the gel and are responsible for the rheological behavior, provided they are happening on a smaller length scale (long chains and clusters are hindered). We show that response times of several minutes are typical for the slow response of MR gels. The characteristic time t_2 for the slow process is significantly dependent on the magnetic flux density, the matrix viscoelastic property, particle volume fraction, and sample's initial particle distribution. In order to validate our results, the role of dynamic strain history was clarified. We show that, in the linear viscoelastic region, the particle rearrangement of MR gels was not hindered or accelerated by the dynamic strain history.
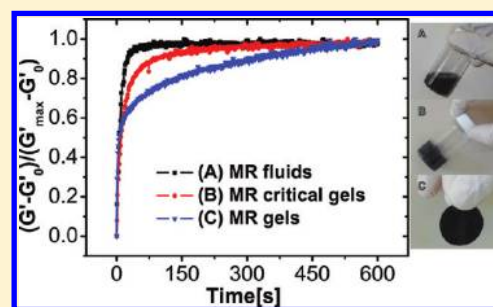
1. INTRODUCTION

While an increasing number of macroscopic studies continue to surface in the scientific literature, the aggregation of magnetic particles in the presence of a magnetic field remains the key issue to understand magnetorheological (MR) systems. For MR fluids, upon application of external fields, the induced structures cause significant anisotropies in fractal dimensions,[1] permeability,[2] conductivity, optical transmittance,[3,4] and rheological response. Various experimental techniques[5−11] and simulations[12−15] have already been employed to study the structure evolution with time. Aggregation kinetics at low solid fraction inside fluids were fairly understood by the diffusion-limited cluster aggregation (DLCA) theory.[16]

For highly concentrated systems, considering the difficulty of direct observation by optical methods, time-dependent rheological response was employed to indirectly characterize the microstructural evolution and predict the time response of the system. Previous researches have been carried out to explore the transient rheological response of magneto-[17−20] and electrorheological[21−26] fluids under stepwise field perturbations. Due to lack of precise meaning of response time and how to measure them experimentally, different groups focus on various quantities including storage modulus,[17] viscosity,[18] shear rate,[19] and shear stress.[20] The reported response time for MR fluids also varies a lot from 1 to 100 ms to several minutes.

Compared with well-known MR fluids and chemical cross-linked MR elastomers, we focus here on a new class of MR

systems called MR gels.[27] In a previous work,[27] we indirectly show that small amounts of rearrangement (structure evolution under field) of the original particle network are allowed even after synthesis likewise in fluids. Several groups also reported the possible rearrangement inside MR gels[28,29] and soft MR elastomers[30,31] to explain various rheological properties. However, the real structure information about particle network rearrangement of MR gels is very limited. Regarding MR gels, at least two questions need to be answered: what is the difference between the rearrangement of MR gels and structuration of MR fluids and what is the response time of the MR gels.

Below, we report on the transient rheological response of physical MR gels containing concentrated magnetic particles and try to answer these two questions. We follow the storage modulus and focus on the long time (>10 s) rheological response after the application of dc magnetic field. We found the increase trend of the storage modulus could be expressed by a double exponential with two distinct modes. The characteristic time t_2 for the slow process is significantly dependent on the matrix viscoelastic property, the magnetic flux density, and magnetic particle volume fraction as well as initial particle distribution. Besides the intrinsic importance for

applications of MR gels in effectively designing MR devices, this study may help to shed light on the structural change induced by an external field in other soft viscoelastic magnetic systems (soft MR elastomer, MR grease,[32] MR plastomer,[33] MR viscoelastic fluid[34]). The rearrangements of the particle networks in those systems are very often inevitable and result in strong rheological responses under field.

2. EXPERIMENTAL SECTION

Materials. Physical gels were obtained by self-assembling of triblock copolymer SEBS (Kraton G 1650E, kindly provided by Kraton Polymers). SEBS used had a molecular weight of $M_w \sim$ 104.000 g/mol and a styrene content of ca. 30 wt % (manufacturer information). The copolymer was swollen in paraffin oil (Sigma-Aldrich, 18512). The oil has a zero shear rate viscosity of 130 mPa·s and a density of 0.88 g/mL at 20 °C. Commercial carbonyl iron particles (HQ grade, kindly provided by BASF) were used as magnetic filler without further purification. The morphology of the particles was characterized using Philips XL 20 SEM operated at accelerating voltage of 15 kV. Figure 1 shows an SEM image of the HQ particles at a
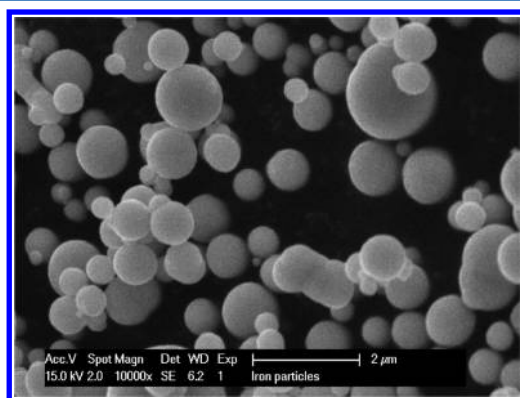

Figure 1. SEM image of carbonyl iron particles.

magnification of 10 000×. They are spherical and polydisperse, with average diameter ~1 μm.

Sample Preparation. Copolymer SEBS and paraffin oil were mixed with the iron particles under nitrogen at 170 °C and then quickly cooled down to 20 °C in a disk-shaped mold in the presence (or absence) of homogeneous magnetic field (20 mT). Samples were then pealed off their molds and the string (or bundle) structures of the particles retained in the gel

were kept. Two different types of magnetic particle ordering, isotropic (no magnetic field present during synthesis) and perpendicular to the plane of the gel film, were produced. Typical sample thickness was 0.7 mm. To make sure all the samples have similar thickness for rheology, we varied the total weight of the pure gel ($M_{gel} = M_{SEBS} + M_{oil}$) by a small amount. Weight concentration of the copolymer (M_{SEBS}/M_{gel}) was varied from 0 to 20 wt %. Higher polymer concentration means denser polymer network (formed by bridged copolymer midblock) and provides a higher G' and G'' with broad linear visoelastic region. The volume fraction of the magnetic particles was varied from 1 to 25 vol %. MR fluids as a reference system for this study were prepared with the same paraffin oil without SEBS. MR fluids samples were inspected at the end of each test, and significant sedimentation of the particle was not observed for 10 min.

Magnetorheology. A homemade plate—plate magneto cell was developed and mounted on a commercial rheometer (ARES, Rheometric Scientific Co.). Magnetic field (up to 650 mT) is generated by an electromagnet, which is composed by three customized solenoid coils (each one has a turnover number equal to 2000) and are connected to a dc power supply and a soft iron bar to enhance and guide the magnetic field perpendicular to the rheometer plates. The air gap between the iron bars enveloping the rheometer plate—plate is set to 5 mm, ensuring a high flux density on the sample while not interfering with the plate—plate cell. The hole was cleaved through the center of the yoke to allow the brass plates (diameter of 25 mm) to be inserted. The pieces can be reassembled with iron screws. All the experiments were carried out at room temperature, 20 °C. After every experiment, the magneto cell was demagnetized to keep the remanence lower than 1 mT. The field divergence was small enough (≈2%, 10 mT along the Z direction at 500 mT) such that particle migration was not observed during the experiments and the magnetic field can be regarded as homogeneous.

The relative particle alignment, dynamic oscillating shear direction, and homogeneous field direction during the rheological measurement are depicted in Figure 2. Two different types of magnetic particle orderings after synthesis were investigated: (a) isotropic and (b) perpendicular to the plane of the gel film.

3. RESULTS AND DISCUSSION

Time-dependent rheological response experiments were conducted under a fixed driving frequency of 10 rad/s. Lower
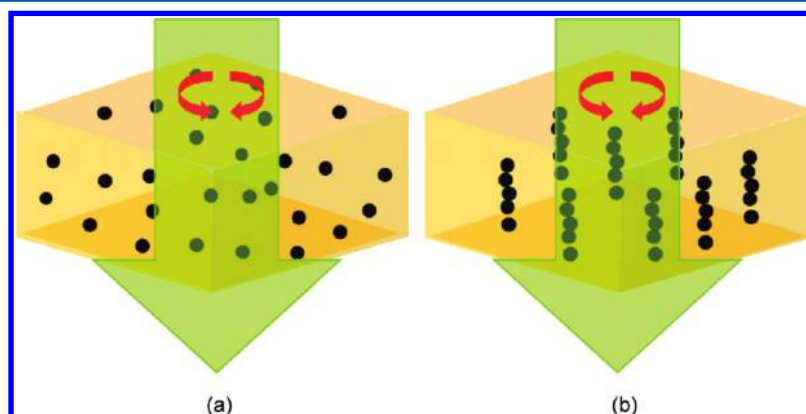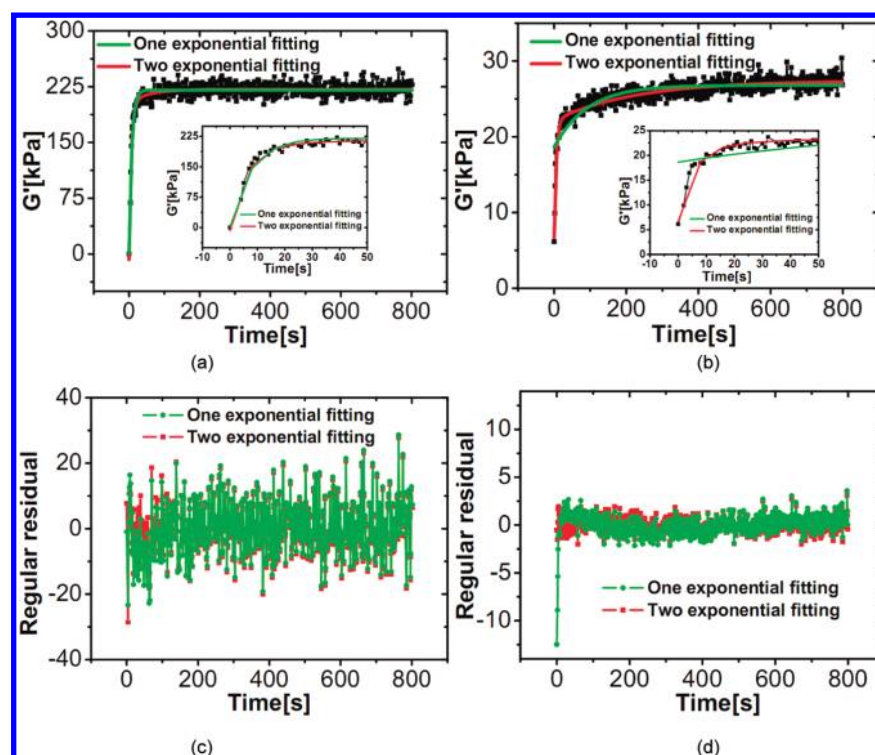

Figure 2. Schematic representation of original particle alignment, dynamic shear, and magnetic field direction during rheology characterization.

Figure 3. Evolution of the storage modulus with time in response to magnetic field step change (0 to 410 mT) for (a) MR fluid and (b) MR gel with 10 wt % SEBS in paraffin oil. Both systems contain randomly distributed particles at a volume fraction of Φ = 6 vol %. The insets show the short time response from 0 to 50 s. The regular residuals (the difference between the data and the estimated function value) of the two fitting methods were compared for (c) MR fluid and (d) MR gel.

frequencies are not appropriate since they have limited time resolution. Two different dynamic strain amplitudes were chosen: 0.05% and 0.2%. For MR fluids (without copolymer SEBS), the linear viscoelastic region is observed in a small window (up to 0.05%) as compared with MR gels (up to 0.3%) in the presence of magnetic field. The detailed study on the nonlinear viscoelastic behavior of MR gels will be discussed elsewhere. Besides copolymer concentration, the linear visocelastic region of MR gels is also significantly dependent on particle volume fraction, magnetic field intensity, and initial particle distribution. 0.05% of strain was small enough to ensure all data of this report (MR fluids and MR gels) fall in the linear viscoelastic regime unless mentioned otherwise. 0.2% of the strain was employed sometimes to give support information, especially for the loss modulus of MR gels where the small strain (0.05%) usually results in heavily scattered data.

After half minute of initial dynamic shear in the absence of magnetic field (off state), the voltage of the magneto cell was switched on to reach a desired magnetic field intensity and held constant for the following 800 s, during which the storage and loss moduli were recorded. For all measurements, a high level of reproducibility among the different batches of samples (5 batches) and various runs per sample (5 runs) was observed.

The current running through the magneto cell follows an exponential function with time due to the self-inductance of the electromagnet. After about 3 s, the current reaches a maximum, together with the magnetic flux density (Supporting Information, Figure S1). The rising time of the magnetic field is independent of the magnetic flux density.

Figure 3 illustrates the evolution of storage modulus with time in response to the stepwise magnetic field for paraffin oil based (a) MR fluid and (b) MR gel. The time origin represents the starting point when the current is abruptly applied. The MR gel here contains 10 wt % of SEBS in the paraffin oil and is compared with the equivalent MR fluid without addition of SEBS. Since the transient rheological dynamics of MR gels has never been studied before, it is reasonable to start with the equivalent MR fluid that will serve as a reference. Figure 3a displays the change in storage modulus associated to the stepwise change in magnetic field for the MR fluid. The rheology response fits well to the two-exponential increases.

$$G'(t) = G'_{max} - A_1 \exp\left(-\frac{t}{\tau_1}\right) - A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

$G'(t)$ is the storage modulus change with time, and G'_{max} is the equilibrium storage modulus at infinite time. For the MR fluid, starting from a low value at zero field shown in Figure 3a, $G'(t)$ shows an immediate increase that takes about several seconds after the application of magnetic field. Then it keeps constant until $G'(t)$ saturates around 225 kPa. The two-exponential fitting approach results in two time constants: a shorter t_1 of 5.7 s and a longer time t_2 of 52 s. Here, the second time constants t_2 are associated to the slow increase of storage modulus.

J. Claracq[15] shows that it is even possible to use one-exponential fitting to describe the rising storage modulus of MR fluids. They build a master curve in logarithmic scale with the characteristic time versus the magnetic intensity. We find here that the rising storage modulus could also be fitted with a one-exponential function for this specified fluid sample. Fitting results obtained from eq 2 for the rheological response of MR fluids are also displayed in Figure 3a.
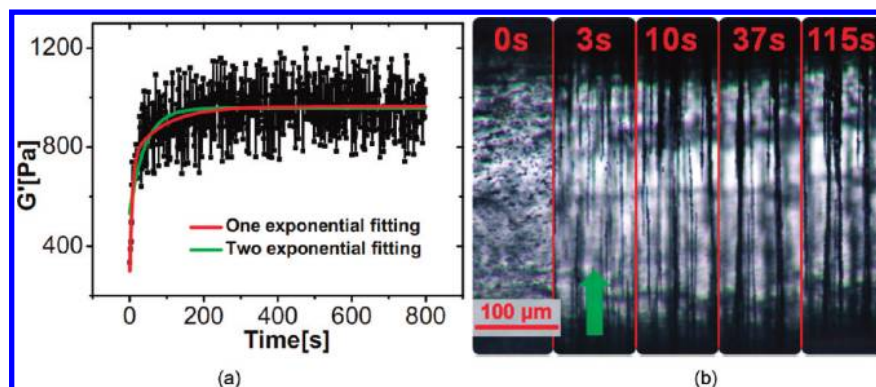
Figure 4. (a) Evolution of the storage modulus with time in response to magnetic field step change (0 to 80 mT) for a dilute MR fluid sample containing randomly distributed particles at a volume fraction of Φ = 1 vol %. (b) Snapshots of the aggregation of the same sample upon sudden application of a magnetic field of 80 mT. Direction of the field is indicated with a green arrow. The first snapshot was taken prior to magnetic field application. Other snapshots were taken in the presence of field. Time elapsed since field application is indicated in each snapshot.

$$G'(t) = G'_{max} - A_1 \exp\left(-\frac{t}{\tau_1}\right) \qquad (2)$$

A_1 is the difference between the starting and the equilibrium values, and t_1 is the structuring time. The fitting result gives t_1 around 7.5 s. The difference between one-exponential fitting and two-exponential fitting is very small for the MR fluid sample chosen. The regular residuals of those two methods are compared in Figure 3c. Both methods appear to fit the data well, and the residuals appear to be randomly distributed around zero. We want to stress that the possibility of using one-exponential fitting to describe the rheological response of MR fluids is not universal in this study. For MR fluids with lower volume fraction subjected to low magnetic flux density (one example will be shown later in Figure 4), the two-exponential fitting seems much more appropriate. For MR fluids with higher volume fraction (Φ = 10 vol %), the rheology response is synchronized with the stepwise magnetic field. The response is a step function and cannot be resolved by either one- or two-exponential fitting (Supporting Information, Figure S2). In this case, the time resolution of our rheometer is not fast enough to describe the dynamics of that concentrated system.

When it comes to the MR gel under similar conditions (particle volume fraction = 6 vol %, magnetic flux density = 410 mT) as shown in Figure 3b, one-exponential fitting is certainly not enough and the two-exponential fitting method has to be used. The regular residuals of those two methods were compared in Figure 3d. One-exponential fitting method generates poor residuals for short time, while the residuals from two-exponential fitting appear to be randomly distributed around zero. Starting from a low value (6 kPa) at zero magnetic field shown in Figure 3b, G' shows an immediate increase that takes about several seconds. Then, a slower increasing process is observed with $G'(t)$ saturating around 28 kPa. It is therefore natural to use a two-exponential function to fit the kinetics for MR gels. This approach results in t_1 of 5.5 s and t_2 of 227 s. The two time constants are, therefore, very different and the rheological response can be well described by the two-exponential fitting. In fact, all MR gels of this study had to be fitted with two-exponential function.

One reference sample of MR elastomer was made from PDMS (Dow Corning SYLGARD 184). The PDMS mixture was prepared by adding the curing agent to the base in a ratio of 1:10 by weight. The iron particles were mixed by hand at the same volume fraction of 6 vol %. After cross-linking (120 °C for 24 h), dynamic time sweep was employed to study the rheological properties. The storage modulus remains constant around 65 kPa, even when the sample was subjected to a stepwise magnetic field (410 mT) after half minute of initial shear (Supporting Information, Figure S3). This result suggests that no particle network rearrangement takes place inside the MR elastomer. The particles remain homogeneously dispersed under the application of field. The induced dipole interaction between particles is relatively small compared with the high resistance of the elastomer. Particles are still well separated and no anisotropy structure is formed under field. If particle rearrangements happen, they are small enough and unable to significantly contribute to an increase of G'.

Before the detailed study of the fast and slow rheological response dependence on various quantities (matrix, magnetic flux density, volume fraction), we would like to relate the two modes (fast and slow) to their microscopic structure origins if possible. A dilute MR fluid sample containing 1 vol % of particles was chosen. The selected volume fraction of iron particles must be concentrated enough to give detectable rheology response under field while dilute enough to be directly observed with optical microscope.

The evolution of the storage modulus of the dilute MR fluid sample is shown in Figure 4a. Despite of the noise, the (fast and slow) increasing trend of the storage modulus is confirmed. The one-exponential fitting is not able to describe the data here as we mentioned before. The one-exponential fitting is not even able to include the four points at the beginning. The two-exponential fitting yields values with t_1 = 6.65 s and t_2 = 89 s, suggesting the presence of two different structuration processes. There is almost no modulus change after 200 s. The same MR fluid sample was filled into a sample cell mounted on a microscope (Nikon, Model, Eclipse E600Wpol) and subjected to a magnetic field step change (0 to 80 mT) parallel to the microscopic stage. The sample cell was made of PMMA with a groove perpendicular to the field direction. The groove had a width of 0.7 mm (same as the gap during the rheology experiment), length of 10 mm, and height of 1 mm. A movie was recorded at a frame rate of 7.5 fps. The multimedia file is available online as Supporting Information. Five snapshots were taken from the movie as shown in Figure 4b. The numbers in the snapshots represent the elapsed time after the application of magnetic field. As suggested by Mohebi[35] using computer modeling, two structuration processes were also found out in
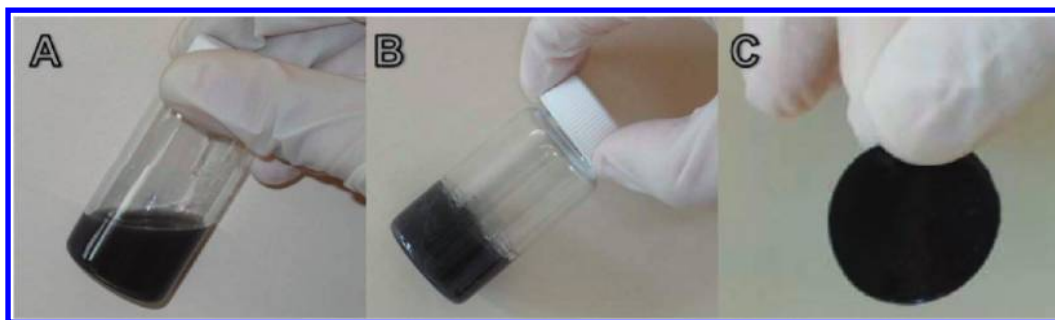
Figure 5. Images of (A) MR fluid and (B) MR critical gel, 2 wt % SEBS in the paraffin oil; (C) MR gel, 10 wt % SEBS in the paraffin oil. All samples contain randomly distributed particles at a volume fraction of $\Phi = 6$ vol %.
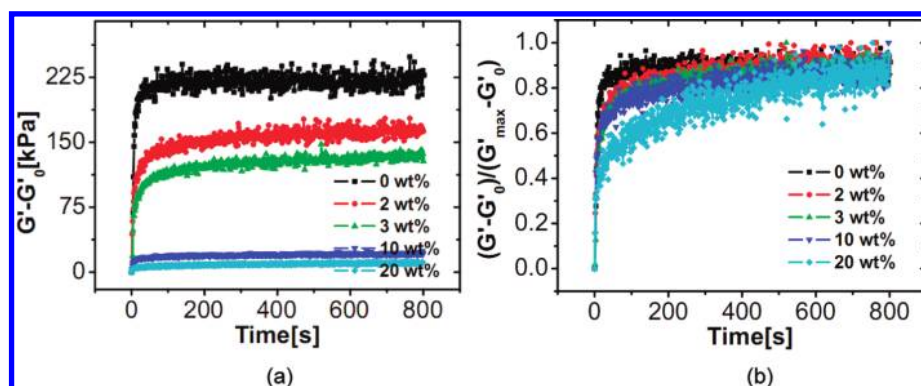
Figure 6. Evolution of (a) $\Delta G'$ with time in response to magnetic field step change (0 to 410 mT) for MR fluids and MR gels with different polymer concentration. Samples contain randomly distributed particles at a volume fraction of $\Phi = 6$ vol %. (b) $\Delta G'$ normalized by the on-state equilibrium value.

our movie. The fast one was associated to the formation of chains and the slower one to the migration of chains into thicker clusters. Chaining process finishes after 10 s, and the clustering process finishes around 120 s. The clusters are made of a concentrated solidlike material, which hinders the flow of the fluid, hence increasing the effective long time rheological response under field. At the end, the organized structure is periodic and spans the width of the cell (700 μm). Due to the similarity on the time scales between rheological response and the structuring process revealed by optical microscopy, we can state that the two different structural mechanisms (formation of individual chains and later coarsening) are directly correlated to the fast and slow rheological responses of MR fluids under the application of dc magnetic field.

We also prepared a MR gel at similar conditions (10 wt % of SEBS, 1 vol % iron particles) and subjected it to the same magnetic field (80 mT) under optical microscope. However, the rearrangement process is too weak to form any anisotropic structure that can be distinguished by human eye. The associated transient rheological response is also too small to be analyzed. For the concentrated sample (6 vol % as shown in Figure 3b), although the transient rheological response suggests the formation of anisotropic structure, the sample was too dark to be directly observed by optical microscope.

Due to the lack of structure information on MR gels, we cannot point out the specific structure responsible for the fast and slow increase of storage modulus to the last detail. Here we could assume a similar "chaining" and "clustering" process inside the gel, likewise in fluids, provided they are happening on a smaller length scale (long chains and clusters are hindered).

(1) Fast mode. The "chaining" process might not happen between individual particles in the gel under normal magnetic field, but, instead, the pre-existing particle aggregates at high volume fraction can overcome the resistance of polymer network and "regroup" in an irregular anisotropic structure in a short time (ref 20).

(2) Slow mode. Long time scale rheological response can be regarded as a densification process (adjustment of position order and orientation order) within the already formed irregular anisotropic structure without a significant increase of the length and diameter of the aggregates. For the fluids, the slow process t_2 is the time characteristic of clustering process. For the gel, t_2 can be regarded as the time it takes for the particles to interlock in a motionless state. The study below on MR gels will be carried out with this hypothesis in mind.

Dependence on Polymer Concentration. Figure 5 shows freshly made samples with different copolymer concentrations containing randomly distributed particles at a volume fraction of $\Phi = 6$ vol %. Three different macroscopic states could be observed. (A) MR fluids were prepared with no addition of SEBS. They still flow under gravity. (B) For copolymer concentration = 2 wt %, the "critical" gels are homogeneous, elastic, but difficult to be manipulated. They are in the limit of keeping their shape against their own weight. (C) At $C_{gelator} = 10$ wt % the gels are elastic and can be easily cut into a certain shape for rheological characterization. Similar dependence on SEBS copolymer concentration was also reported before with ferrogel-containing nanosized particles.[36]

It was noticed that after 1 month iron particles in a critical copolymer gel remain suspended while the particles in paraffin
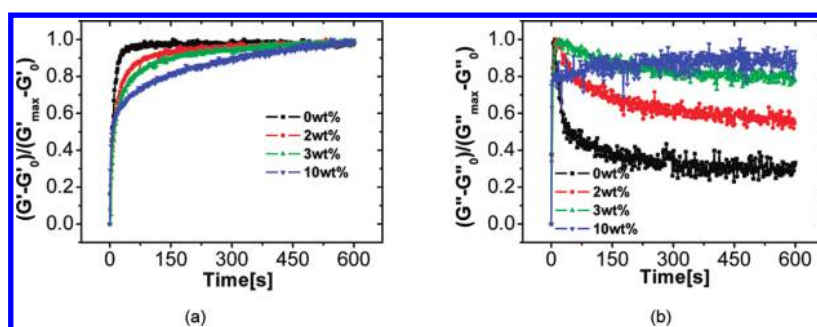
Figure 7. Evolution of (a) normalized $\Delta G'$ and (b) normalized $\Delta G''$ with time at strain value $r = 0.2\%$, in response to magnetic field step change (0 to 410 mT) for MR fluids and MR gels with different polymer concentration. Samples contain randomly distributed particles at a volume fraction of $\Phi = 6$ vol %.
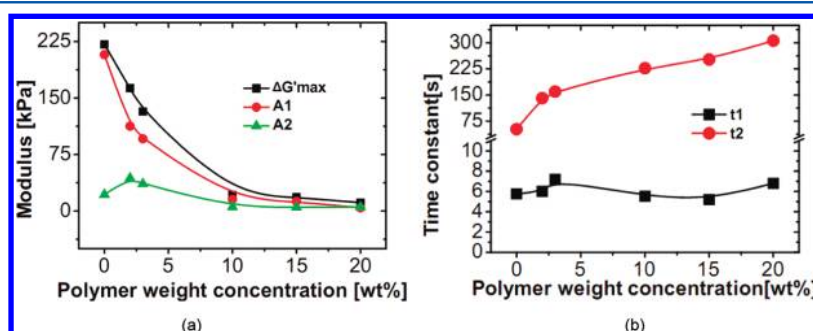
Figure 8. Fitting results including amplitudes ($\Delta G'_{max}$, A_1, A_2) and time constants (t_1 and t_2) plotted against polymer weight concentration from Figure 6a. Samples contain randomly distributed particles at a volume fraction of $\Phi = 6$ vol %.

Table 1. Fitting Results Including Amplitudes ($\Delta G'_{max}$, A_1, A_2) and Time Constants (t_1 and t_2) for MR Fluids and MR Gels with Different Copolymer Concentrations from Figure 6a

	G'_{matrix} (Pa)	G''_{matrix} (Pa)	$\Delta G'_{max}$ (kPa)	A_1 (kPa)	A_2 (kPa)	t_1 (s)	t_2 (s)
0 wt %	25	8.9	221	207.6	21.7	5.76	51.85
2 wt %	87	18	163	112.6	43.5	6	141
3 wt %	350	39	132	96	36	7.18	160
10 wt %	4680	136	21.2	15.5	5.3	5.52	227
15 wt %	9337	360	18.3	12.6	4.7	5.2	252
20 wt %	14 100	644	10.9	4	5.2	6.81	306

oil settle. Sedimentation of the iron particles due to the large density mismatch with the carrier liquid and difficulties in redispersion after caking have been regarded as a serious disadvantage of MR fluids regarding applications. The addition of SEBS copolymers in oil at concentrations ≈2 wt % allows for the formation of ultrasoft MR gels possessing a weak cross-linked 3-dimensional network that suppress particle sedimentation without compromising the MR response under field. When a strong shearing force is applied, the thixotropy polymer network is easily disrupted, encouraging the flow of material and the structuring of particle network under magnetic field. Quantities such as yield stress or storage modulus increment of MR gels under magnetic field remain reasonably high.

It is convenient in many cases to display data in absolute moduli difference $\Delta G' = G' - G'_0$, that is, the modulus under magnetic field G' subtracted by the off state value, G'_0. The same holds for $\Delta G''$. Figure 6a illustrates the evolution of $\Delta G'$ with time in response to magnetic field step change (0 to 410 mT) for MR fluids and MR gels with different copolymer concentrations. Although they all have the same off-state isotropic particle distribution, larger increment of storage modulus can be achieved with the decrease of copolymer concentration. The well-formed polymer network increases the

local resistance and hinders the formation of anisotropy structures. The particle network in the MR fluids or weak gel (2 wt %) will get more anisotropic (long and thick clusters parallel to the applied field) than the gel with higher polymer concentration (10 and 20 wt %). As a result, different rheological responses ($\Delta G'$) are shown in Figure 6a despite their similar initial particle distribution before the presence of magnetic field.

The rheological responses were normalized and the shapes of these curves can be easily compared in Figure 6b. For the gel (10 and 20 wt %), the increment of the storage modulus shows a shallow bend. This suggests a slower time response of MR gels as compared with MR fluids. It is expected that the addition of copolymer influences the dynamics of rearrangement process. Similar trend was also confirmed between samples with different copolymer concentration recorded with larger strain (0.2%) as shown in Figure 7a.

The loss modulus recorded with small strain (0.05%) was heavily scattered and very little valuable information can be found. The larger strain (0.2%) possesses a better signal/noise ratio as compared with smaller strain (0.05%), and both trends for the storage modulus and loss modulus can be observed after normalization. The difference between evolution of normalized

storage modulus with time for MR fluids and MR gels is very clear when Figure 7a is compared with Figure 6b. As shown in Figure 7b, immediately after the application of the field, a strong jump in G'' is observed at the beginning trigged by the strong dipole–dipole interactions. Beyond the maximum point, the long decreasing tails with time are obvious in MR fluids or critical MR gels (2 wt %), while no decreasing trend was found in the MR gels (10 wt %). The decreasing trends of G'' are the direct result of the rearrangement processes under magnetic field. The rearrangement process of particle network (particle location change) under magnetic field dissipates energy. The rearrangement process saturates with time resulting in the saturation of loss modulus.

To show the influence of copolymer on the dynamics of rearrangement processes between MR fluids and MR gels in Figure 6, the fitting amplitudes ($\Delta G'_{max}$, A_1, A_2) and the time constants (t_1 and t_2) are plotted against copolymer weight concentration as shown in Figure 8. The fitting results are also summarized in Table 1, where the moduli of pure matrix without magnetic particles recorded at (10 rad/s, 0.05% of strain) are also listed. The frequency sweep of the pure gel without particles can be found in the Supporting Information (Figure S4).

For the distinct amplitudes to the fast (A_1) and slow (A_2) processes of Figure 8a, A_1 decreases from 207 to 4 kPa, while A_2 only decreases from 21.7 to 5.2 kPa with increasing copolymer concentration. The relative contribution of the slow process (A_2) to $\Delta G'_{max}$ increases from 10% for MR fluids to 25% in the 10 wt % MR gel and eventually takes half of $\Delta G'_{max}$ for 20 wt % MR gel. If we associate A_1 and A_2 with the chaining and later clustering (densification for the gel), we might say the two processes had different dependences on the viscoelasticty of the matrix. For the MR fluids, the chaining process dominates the structuring of the particle network and contributes 90% of the rheology response under field. With the addition of copolymer, the formation of the long particle chain is very much hindered. Compare with that, the clustering process seems to be less influenced by the existence of polymer network and the total rheological response of MR gels comes more from the slower response (A_2).

The dependence of time constant (t_1) responsible for the fast process on copolymer weight concentration was not found, as shown in Figure 8b. All of the fitting results lay around 6 s within the experiment error. For our experiments, the dependence of t_1 is sometimes difficult to establish precisely because of the delayed rising of the required magnetic fields (~3 s) and the limited time resolution (1–2 s for one data point) at this frequency. Therefore, we mainly focus on the second time constant t_2 responsible for the slow process for what follows.

The second time constant t_2 increases with copolymer weight concentration as shown in Figure 8b. t_2 increases from 52 s for MR fluids to 306 s for 20 wt % MR gels. The value provides the possibility to indirectly quantify the dynamics of rearrangement process. We attribute the difference to the slowing down of the "clustering" process because of the high drag force coming from denser polymer network. To our knowledge, this is the first time the response time of the MR gels was systematically obtained and compared with MR fluids. It becomes even more important considering the concentrated particle volume fraction and the limited structure information about the "clustering" process within gel matrix. The X-axis of Figure 8b can also be changed into modulus of the pure matrix

without particles, but the general shape of Figure 8b remains the same. However, MR gels based on different types of matrixes with the same pure matrix modulus does not necessarily mean the magnetic particles within them have the same mobility under field.[29]

The transient rheological response experiments need to be strictly performed within the linear viscoelastic region. Otherwise, the large strain might yield a different value. As we stated before, two different dynamics strains were employed to explore the transient rheology response as shown in Figures 6b and 7a. Their fitting results t_2 are compared in Figure 9.
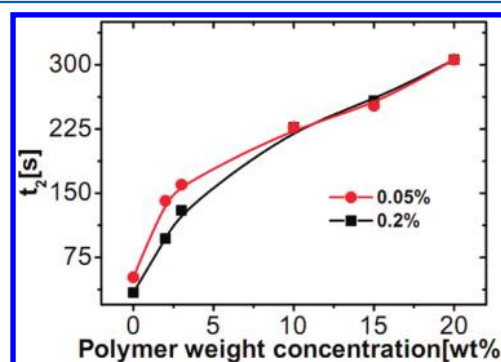

Figure 9. Second time constant t_2 for different polymer concentrations in response to a magnetic field step change (0 to 410 mT). Samples contain randomly distributed particles at a volume fraction of Φ = 6 vol %. Two different dynamics strains are employed.

Error bars are about one symbol size. In general, similar increasing trend of t_2 was found for two different dynamic strains. No difference of the fitting results t_2 was found for MR gels with high polymer concentration since the larger strain is still located in the linear viscoelastic region of MR gels. For the MR fluids and critical gels (=2 wt %), 0.2% of the strain (beyond the linear region) produces a smaller t_2 as compared with the small strain (0.05%). However, it does not necessarily indicate faster clustering processes with the help of larger strain. We believe the *Payne* effect associated with the larger strain suppresses the growth of $\Delta G'$ with time for the MR fluids and critical gels, naturally providing a smaller t_2.

Mechanical energy input might affect the particle rearrangement of MR gels in principle. Experiment was carried out to clarify the role of dynamic strain history during transient rheological response and validate our experimental method. For the chosen MR gel sample (10 wt %, 25 vol %) and a relatively large strain in the linear viscoelastic region (0.2%), the storage modulus was recorded after a stepwise magnetic flux density of 410 mT (Figure 10). The black curve was recorded with the strain input all the time. For the green curve, the rheometer (dynamic time sweep) was only switched on for the final 200 s, which is 400 s after the magnetic field was applied. For the red curve, the rheometer was switched on for the final 100 s. The maximum storage modulus is independent of the small dynamic strain history located in the linear viscoelastic region. We can conclude that the particle rearrangement in the MR gel under magnetic field was not drastically hindered or accelerated by the dynamic strain we use. Otherwise, the difference in anisotropy of particle network will be reflected by their rheological response.
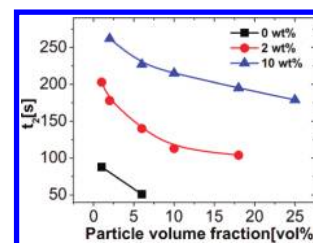
Dependence on Magnetic Flux Density. Figure 11a illustrates the evolution of normalized storage modulus with time in response to different magnetic flux density for critical
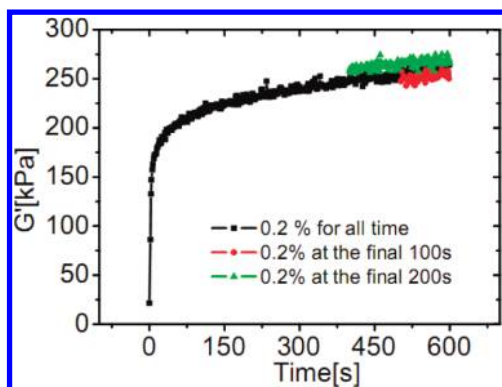
Figure 10. Evolution of the storage modulus G' with time in response to magnetic field step change (0 to 410 mT) for a MR gel, 10 wt % SEBS in the paraffin oil with randomly distributed particles at a volume fraction of $\Phi = 25$ vol %.
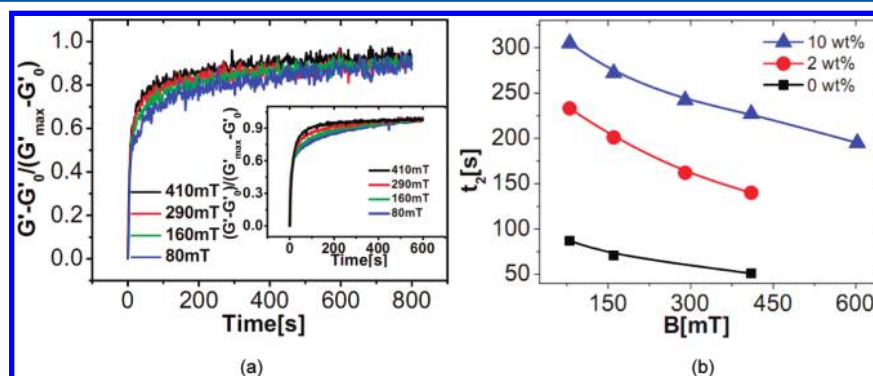

Figure 12. Second time constant t_2 as a function of particle volume fraction for three matrixes with different copolymer concentration containing randomly distributed particles in response to a magnetic field step change (0 to 410 mT).

MR gels with copolymer weight concentration of $c = 2$ wt %. It is noticed that, for the lowest flux density (80 mT), the increment of the storage modulus shows a clear shallower bend when compared with the others. The relative contribution from the slower structuring process (A_2) is larger under low magnetic flux density. Similar difference is better observed with large strain (0.2%) as shown in the inset of Figure 11a. The fitting results t_2 of Figure 11a (0.05% of strain) are plotted against magnetic flux density in Figure 11b. Error bars are about one symbol size for results below unless mentioned. It can be seen that t_2 decreases linearly with magnetic flux density for all three matrixes. MR fluids are shown here as reference. t_2 increases with copolymer concentrations as we explained before. For the same matrix, stronger interactions under higher field induce shorter t_2. This can be explained on the basis that, as the magnetic field is increased, well-defined energy minima are established which give rise to a faster agglomerates densification. The relevant time constants (t_1 and t_2) and amplitudes ($\Delta G'_{max}, A_1, A_2$) are summarized in Table S1 (2 wt %) and Table S2 (10 wt %) in the Supporting Information.

Dependence on Particle Volume Fraction and Sample Initial Particle Distribution. The transient dynamics is also influenced by the particle volume fraction. As particle volume fraction increases from 1 to 25 vol % in the critical MR gel with 2 wt % of the copolymer, t_2 decreases from 203 to 104 s as shown in Figure 12. Similar trend was also confirmed at higher

polymer concentration (10 wt %). MR fluids are also shown as reference where t_2 decreased from 88 to 52 s. It can be concluded that "clustering" (densification) of magnetic particles within MR gels is more effective when more particles per unit volume are involved. The relevant time constants (t_1 and t_2) and amplitudes ($\Delta G'_{max}, A_1, A_2$) are summarized in Table S3 (2 wt %) and Table S4 (10 wt %) in the Supporting Information.

MR gels provide the unique possibility to explore the influence of initial particle distribution on transient dynamics. Two types of samples with distinctive initial particle distributions are shown in Figure 2. Despite their large difference in the absolute values of $\Delta G'$ under field, their transient dynamics are very similar. The increment of the normalized storage modulus of the isotropic sample only shows a shallower bend when compared with the other as shown in Figure 13a. The difference between them is better observed with large strain (0.2%) as shown in the inset. The perpendicular distribution, which has previously frozen-in chains parallel to the magnetic field during rheology experiment, always exhibits smaller t_2 (difference around 20 s) as compared with the equivalent sample with isotropic distribution. The trend can be confirmed with all the volume fractions from 1 to 25 vol % as shown in Figure 13b. The relevant time constants (t_1 and t_2) and amplitudes ($\Delta G'_{max}, A_1, A_2$) are also summarized in Table S4 (isotropic) and Table S5 (perpendicular) in the Supporting Information.

The second time constants t_2 of the MR gels with two distinctive magnetic particle orderings are both larger than t_2 of MR fluids with no addition of copolymer (52 s). We believe the anisotropic chainlike structure formed during sample preparation still have many defects and are far away from the lowest

Figure 11. (a) Evolution of normalized $\Delta G'$ with time at strain value $r = 0.05\%$, in response to different magnetic flux density step change for critical MR gels with copolymer concentration of $c = 2$ wt %, contain randomly distributed particles at a volume fraction of $\Phi = 6$ vol %. Similar curves are also repeated at 0.2% as shown in the inset. (b) t_2 as a function of magnetic flux density for three matrixes with different copolymer concentrations containing randomly distributed particles at a concentration of $\Phi = 6$ vol %.
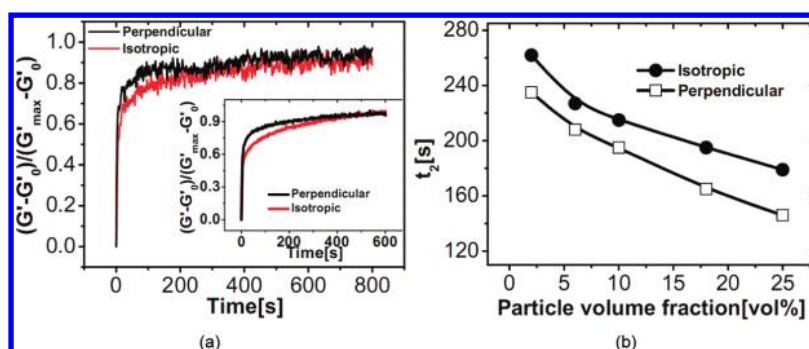
Figure 13. (a) Evolution of normalized $\Delta G'$ with time at strain value $r = 0.05\%$, in response to magnetic field step change (0 to 410 mT) for MR gels (10 wt %) with two different initial particle distributions at a constant particle concentration of $\Phi = 6$ vol %. Similar curves are also repeated at 0.2% as shown in the inset. (b) The second time constant t_2 as a function of particle volume fraction for two different initial particle distributions in response to magnetic field step change (0−410 mT).

ideal energy state. They can still enjoy their freedom toward a more ordered lattice bundle structure. The prealigned particle ordering has a better starting point as compared with the isotropic one, always providing a smaller t_2 toward the equilibrium state.

Finally, the reversibility of the particle network rearrangement within MR gel is illustrated in Figure 14. The MR gel
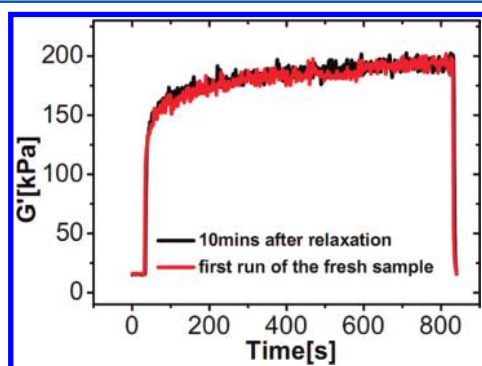
Figure 14. Evolution of storage modulus with time in response to magnetic field step change (0 to 410 mT) for MR gel (10 wt %). The sample contains previously frozen-in particle chains parallel to the magnetic field during rheology experiment at a volume fraction of $\Phi = 10$ vol %. The two sets of data were collected with 10 min interval.

contains previously frozen-in particle chains parallel to the magnetic field during rheology experiment at a volume fraction of $\Phi = 10$ vol %. After the magnet field (demagnetization) is shut down for 10 min, the transient rheological response experiment was repeated and compared with the first run of the fresh sample. Curves for both runs superimpose. Similar storage modulus increment and the fitting time constant t_2 (196.3 s for the first run as compared with 195.1 s for the second one) were obtained. It seems that the initial off-state distribution of the particles was restored due to elastic forces of the polymer matrix accumulated during the rearrangement. If the transient dynamics experiment was repeated in less than the required relaxation time (here 10 min), larger modulus increment and smaller time constant t_2 would be obtained for the second run due to the remaining change in anisotropy of the particle network.

When we compare the structuring process inside MR fluids and the "rearrangement" of the particle network inside the MR gels, three major differences can be summarized:

(1) The "rearrangement" of the MR gels can start from any different initial distribution of the particle network (isotropic, perpendicular as shown in Figure 2).

(2) The magnetic particles forming long chains or compact columnar structures in MR fluids can cause significant anisotropic structure. Unlike the liquid, the particles that are embedded within a gel only have a limited amount of freedom to rearrange because of the high viscoelastic forces from the polymer network. Long chains and clusters can hardly be observed due to the relatively small displacement of the particles.

(3) The rearrangement of particle network of MR gels is reversible. After the magnetic field is shut down, the initial off-state distribution of the particles will be restored due to elastic forces of polymer matrix accumulated during the rearrangement, irrespective of the sample initial distribution. For MR fluids, longer relaxation times are needed as the relaxation can only be restored by thermal motion. The relaxation can only lead to isotropic distribution of the particles at the end.

4. CONCLUSIONS

The purpose of this work was to examine the transient rheological response of MR gels subjected to step changes of an external homogeneous magnetic field. The result was compared with equivalent MR fluids and MR elastomer.

(1) For MR gels, the time increment of storage modulus could be expressed by a double exponential with two distinct modes. The loss modulus shows a long decreasing trend after an initial jump. It is suggested that rearrangement of the particle network at small length scales is largely responsible for the continue evolution of the moduli. This was compared with the structuring process inside MR. The two time constants found for the gel were associated to regrouping of larger aggregates into anisotropic structure (t_1) and later densification of those structures (t_2).

(2) Characteristic times of several minutes are typical for the slow response of the MR gels. The time constant for the slow process is significantly dependent on the matrix viscoelastic property, particle volume fraction, sample's initial particle distribution, and the stepwise magnetic flux density.

(3) The role of dynamic strain history was clarified. In the linear viscoelastic region, the particle rearrangement of

MR gel was not hindered or accelerated by the strain history.

(4) The fully reversible transient rheology response suggests the full restoration of magnetic particle network after rearrangement.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Rise of magnetic flux density with time. Evolution of G' with time in response to stepwise magnetic field for paraffin oil based MR fluids and PDMS-based MR elastomers. A movie recorded at a frame rate of 7.5 fps. Frequency sweep of the pure gel without particles. Time constants (t_1 and t_2) and amplitudes ($\Delta G'_{max}$, A_1, A_2) for 2 wt % and 10 wt % polymer concentrations. Time constants (t_1 and t_2) and amplitudes ($\Delta G'_{max}$, A_1, A_2) for isotropic and perpendicular distributions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Helgesen, G.; Skjeltorp, A. T.; Mors, P. M.; Botet, R.; Jullien, R. *Phys. Rev. Lett.* **1988**, *61*, 15.

(2) Ly, H. V.; Ito, K.; Banks, H. T.; Jolly, M. R.; Reitich, F. *Int. J. Mod. Phys. B* **2001**, *15*, 894.

(3) Pu, S. L.; Chen, X. F.; Di, Z. Y.; Xia, Y. X. *J. Appl. Phys.* **2007**, *101*, 053532.

(4) Helseth, L. E. *J. Phys. D: Appl. Phys.* **2009**, *42*, 105005.

(5) Melle, S.; Rubio, M. A.; Fuller, G. G. *Phys. Rev. Lett.* **2001**, *87*, 115501.

(6) Heinrich, D.; Goni, A. R.; Thomsen, C. *J. Chem. Phys.* **2007**, *126*, 124701.

(7) Promislow, J.; Gast, A. P.; Fermigier, M. *J. Chem. Phys.* **1995**, *102*, 5492.

(8) Martínez-Pedrero, F.; El-Harrak, A.; Fernandez-Tolenado, J. C.; Tirado-Miranda, M.; Baudry, J.; Schmitt, A.; Bibette, J.; Fernandez, J. C. *Phys. Rev. E* **2008**, *78*, 011403.

(9) Domínguez-García, P.; Melle, S.; Pastor, J. M.; Rubio, M. A. *Phys. Rev. E* **2007**, *76*, 051403.

(10) Sohn, D. *J. Magn. Magn. Mater.* **1997**, *173*, 305.

(11) Wiedenmann, A.; Keiderling, U.; Habicht, K.; Russina, M.; Gahler, R. *Phys. Rev. Lett.* **2006**, *97*, 057202.

(12) Duncan, P. D.; Camp, P. J. *J. Chem. Phys.* **2004**, *121*, 11322.

(13) Duncan, P. D.; Camp, P. J. *Phys. Rev. Lett.* **2006**, *97*, 107202.

(14) Ukai, T.; Maekawa, T. *Phys. Rev. E* **2004**, *69*, 032501.

(15) Carmen Miguel, M.; Pastor-Satorras, R. *Phys. Rev. E* **1999**, *59*, 826.

(16) Miyazima, S.; Meakin, P.; Family, F. *Phys. Rev. A* **1987**, *36*, 1421.

(17) Claracq, J.; Sarrazin, J.; Montfort, J. *Rheol. Acta* **2004**, *43*, 38.

(18) Donado, F.; Carrillo, J. L.; Mendoza, M. E. *J. Magn. Magn. Mater.* **2008**, *320*, e354.

(19) See, H.; Gordin, A. *J. Soc. Rheol.* **2008**, *36*, 59.

(20) Ulicny, J. C.; Golden, M. A.; Namuduri, C. S.; Klingberg, D. J. *J. Rheol.* **2005**, *49*, 87.

(21) Espín, M. J.; Delgado, Á. V.; González-Caballero, F. *Phys. Rev. E* **2006**, *73*, 041503.

(22) Wang, Z. W.; Lin, Z. F.; Fang, H. P.; Tao, R. B. *J. Appl. Phys.* **1998**, *82*, 1125.

(23) Tanaka, K.; Sahashi, A.; Akiyama, R.; Koyama, K. *Phys. Rev. E* **1995**, *52*, R3325.

(24) Nam, Y. J.; Park, M. K.; Yamane, R. *Exp. Fluids* **2008**, *44*, 915.

(25) Tian, Y.; Zeng, H.; Anderson, T. H.; Zhao, B.; McGuiggan, P.; Israelachvili, J. *Phys. Rev. E* **2007**, *75*, 011409.

(26) Wen, W. J.; Zheng, D. W.; Tu, K. N. *J. Appl. Phys.* **1999**, *85*, 530.

(27) An, H. N.; Picken, S. J.; Mendes, E. *Soft Matter* **2010**, *6*, 4497.

(28) Mitsumata, T.; Abe, N. *Chem. Lett.* **2009**, *38*, 922.

(29) Negami, K.; Mitsumata, T. *Chem. Lett.* **2010**, *39*, 550.

(30) Stepanov, G.; Abramchuk, S.; Grishin, D.; Nikitin, L. V.; Kramarenko, E.; Khokhlov, A. R. *Polymer* **2007**, *48*, 488.

(31) Stepanov, G.; Borin, D.; Odenbach, S. *J. Phys.: Conf. Ser.* **2009**, *149*, 012098.

(32) Rankin, P. J.; Horvath, A. T.; Klingenberg, D. J. *Rheol. Acta* **1999**, *38*, 471.

(33) Xu, Y. G.; Gong, X. L.; Xuan, S. H.; Zhang, W.; Fan, Y. C. *Soft Matter* **2011**, *7*, 5246.

(34) Kim, J. E.; Choi, H. J. *IEEE Trans. Magn.* **2011**, *47*, 3173.

(35) Mohebi, M.; Jamasbi, N.; Liu, J. *Phys. Rev. E* **1996**, *54*, 5407.

(36) Lattermann, G.; Krekhova, M. *Macromol. Rapid Commun.* **2006**, *27*, 1373.