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Reversible Photorheological Fluids Based on Spiropyran-Doped Reverse Micelles

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Supporting Information

ABSTRACT: We describe a new class of photorheological (PR) fluids whose rheological properties can be reversibly tuned by light. The fluids were obtained by doping lecithin/sodium deoxycholate (SDC) reverse micelles with a photochromic spiropyran (SP) compound. Initially, the lecithin/SDC/SP mixtures formed highly viscoelastic fluids, reflecting the presence of long, wormlike reverse micelles. Under UV irradiation, the SP was isomerized to the open merocyanine (MC) form, causing the fluid viscosity to decrease 10-fold. When the UV irradiation was switched off, the MC reverted to the SP form, and the viscosity recovered its initial value. This cycle could be repeated several times without loss of response. The rheological transitions are believed to reflect changes in the lengths of the reverse worms. To our knowledge, this is the first example of a simple, reversible PR fluid that can be made entirely from commercially available components.

Fluids whose rheological properties, such as viscosity, can be controlled by light are of interest to scientists and engineers.[1,2] Such fluids can be termed photorheological (PR) fluids.[3,4] Because light can be directed at a precise point with microscale accuracy, PR fluids may be useful in microfluidic devices as the basis for valves or flow sensors. Other applications have also been envisioned for PR fluids, including their use as drag-reducing fluids in recirculating systems for district heating and cooling, in microrobotics, and as patternable materials.

Our approach to PR fluids has differed from that of other research groups in one important aspect. Typically, researchers have focused on developing PR fluids using new, original types of photosensitive organic molecules.[5−10] However, we have emphasized the design of PR fluids using only commercially available molecules or particles.[4,11,12] The rationale for simpler PR fluids is that these could easily be recreated in the laboratory by scientists in both academia and industry without investing time and effort in organic synthesis. In turn, it is hoped that the greater availability and awareness of such PR systems will help advance new applications. Several examples of simple PR fluids have been published recently by our laboratory;[4,11,12] however, all of these fluids permit only one-way changes in rheological properties. Typically, the changes in rheology were induced by UV light, but these could not be subsequently reversed by irradiation at other wavelengths.

In this paper, we report a simple, photoreversible PR fluid based on reverse micelles doped with a photosensitive additive. We began with a formulation developed in our laboratory that gives rise to wormlike reverse micelles ("worms" for short),[13] which are long, flexible, cylindrical chains. The formulation combines the phospholipid lecithin and the bile salt sodium deoxycholate (SDC) in a nonpolar organic solvent such as cyclohexane (Figure 1).[14,15] While lecithin alone forms discrete, spherical reverse micelles in cyclohexane, the addition of SDC promotes the axial growth of lecithin micelles until these become long worms (diameter ∼4.4 nm and contour length >140 nm, as determined by small-angle neutron scattering).[14] These worms entangle to form a transient network[13] and thereby impart a high viscosity and viscoelasticity to the fluid. To endow these reverse worms with photoresponsive properties, we added a small concentration of the spiropyran (SP) derivative 1′,3′,3′-trimethyl-6-nitrospiro[1(2*H*)-benzopyran-2,2′-indoline]. SPs are well-known photochromic compounds that can be reversibly photoisomerized between the colorless SP form and the colored merocyanine (MC) form by irradiation at different wavelengths of light.[16,17] As shown in Figure 1, the closed SP form is hydrophobic and nonionic, whereas the open MC form is zwitterionic and hydrophilic. These two photoisomers are known to interact differently with the headgroups of lecithin.[18−20] As we will show below, they thus have different effects on the assembly of lecithin/SDC reverse worms. This leads to reversible light-induced changes in the rheological properties of the solutions.

Photorheological results for a typical formulation are shown below. The sample contained 100 mM lecithin, 35 mM SDC, and 15 mM SP in cyclohexane. It should be noted that the SP concentration is close to the maximum that can be dissolved in cyclohexane at ambient temperature. A photograph of this sample is shown in the left panel of Figure 2. The sample held its weight in the inverted vial, which is indicative of its viscoelastic character. Next, we subjected this sample to broad-band UV light from a 200 W mercury arc lamp. Within ∼5 min, the sample became noticeably less viscous and also changed color from yellow to red. This is shown by the photograph in the middle panel of Figure 2, which shows the red liquid flowing down the sides of the inverted vial. Such a color change is typical for the conversion of the closed SP form into the open MC form.[16,17] Thereafter, we switched off the UV light, and within ∼10 min, the sample recovered its initial viscosity and color. This is shown by the photograph in the right panel of Figure 2; it should be noted that the sample was again able to hold its weight in the

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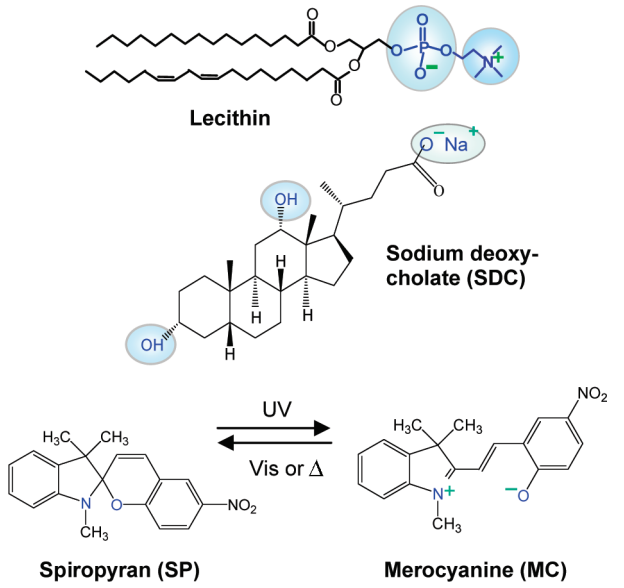

Figure 1. Components of a reversible PR fluid: the phospholipid lecithin is combined with the bile salt SDC and an SP derivative. The SP is initially in a closed form but can be photoisomerized to the open (MC) form by UV irradiation. This can be reversed by visible-light irradiation or heating.

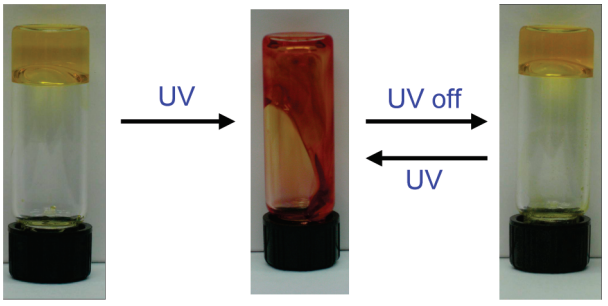

Figure 2. (left) Sample containing 100 mM lecithin, 35 mM SDC, and 15 mM SP in cyclohexane. (middle) After UV irradiation, the viscosity of the sample decreased, and its color changed from yellow to red. (right) When the UV irradiation was stopped, the sample viscosity and color reverted to their initial states. This cycle could be repeated several times.

inverted vial. The recovery of the sample viscosity and color indicates the inverse conversion of MC into SP. These data were reproducible, and the sample could be cycled more than 10 times without any deterioration of its response.

We quantified the above photorheological changes in real time using a rheometer with a built-in UV apparatus. The sample was placed between transparent parallel plates and irradiated with UV light at 365 nm with an intensity of 150 mW/cm^2. The sample was monitored under oscillatory shear at a frequency of 7 rad/s. At this frequency, significant rheological changes were observed and the measurements could be made rapidly (i.e., the time per measurement was low). The results are plotted in Figure 3 in terms of the complex viscosity η^*. Initially, the sample was viscous with η^* = 2.5 Pa s. Upon irradiation with UV light, the viscosity dropped quickly and reached a plateau value of ~0.2 Pa s (10-fold lower) within ~100 s. At the 200 s mark, the UV light was switched off, at which point the viscosity began to grow back. It recovered to nearly its initial value over the next 400 s.

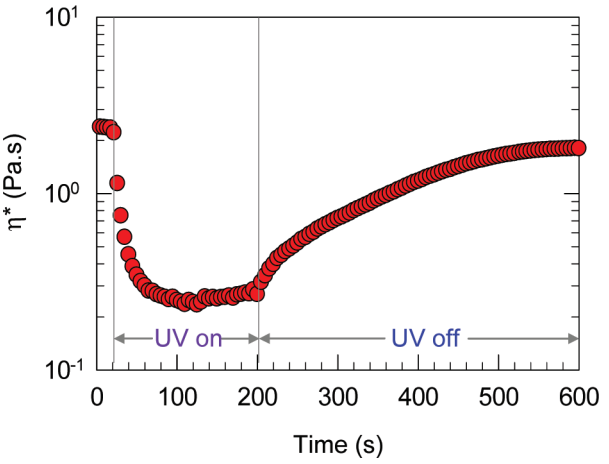

Figure 3. Real-time photorheology of a sample containing 100 mM lecithin, 35 mM SDC, and 15 mM SP in cyclohexane at ambient temperature. Upon UV irradiation for 150 s, the complex viscosity η^* decreased 10-fold relative to its initial value. The UV light was switched off at the 200 s mark, whereupon the sample recovered to nearly its original viscosity over the next 400 s.

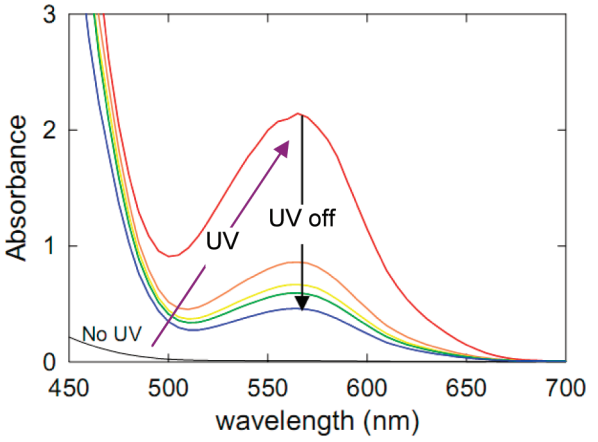

Figure 4. UV−vis spectra of a sample containing 25 mM lecithin, 8.75 mM SDC, and 3.75 mM SP sample in cyclohexane. A peak at 565 nm developed upon UV irradiation, indicating the conversion of SP to MC. The UV light was then switched off, and spectra were recorded after different wait times (at 0, 2, 6, 10, and 20 min top to bottom). The peak was observed to decrease, indicating the reversion of the MC to SP.

Dynamic frequency spectra (elastic modulus G' and viscous modulus G'' as functions of frequency ω) of the above sample were also measured [Figure S1 in the Supporting Information (SI)]. In all cases, the data were fit well by a Maxwell model with a single relaxation time (eq S1 in the SI), as is typical of wormlike micelles.[13,14] Initially (Figure S1a), the data revealed a typical viscoelastic response. That is, at high ω or short time scales, the sample showed elastic behavior with G' tending to a plateau and dominating over G''. On the other hand, at low ω or long time scales, the sample showed viscous behavior, with G'' exceeding G'. The parameters in the Maxwell model are the plateau modulus G_p and the relaxation time t_R. From the fits, the initial value of G_p was 455 Pa and the initial t_R value was 77 ms. We then ran the same frequency sweep under UV irradiation after the sample had been exposed to UV light for 180 s. The frequency

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spectra (Figure S1b) were shifted to higher frequencies (i.e., shorter time scales) as well as lower values of the moduli. From the fits, the new G_p was determined to be 122 Pa, and the corresponding t_R was 22 ms. Finally, we switched off the UV light and collected a frequency spectrum after 30 min, which was ample time to allow full recovery of the sample. The spectra (Figure S1c) reverted to close to their initial ones (G_p = 380 Pa and $t_R \approx$ 65 ms). All in all, the sample was observed to become less viscoelastic upon irradiation with UV and to recover its initial viscoelasticity after the UV light was switched off. The decrease in viscoelasticity suggests a UV-induced shortening of the reverse worms, allowing the worms to become less entangled and relax faster.[13,14] When the UV light was switched off, the worms appeared to regain their initial lengths.

UV−vis spectra (Figure 4) confirmed that the rheological changes were accompanied by the photoconversion of SP to MC and back. We used a diluted sample (25 mM lecithin, 8.75 mM SDC, and 3.75 mM SP) to ensure the proper levels of absorbance. The initial sample exhibited weak absorption over the range of wavelengths shown in Figure 4, which correlates with the colorless nature of the SP form. When irradiated with UV light for 3 min, the sample transformed to a red liquid, and correspondingly, a strong absorption peak appeared at 565 nm. This indicates the UV-induced conversion of the closed SP form into the open MC form. The UV light was then switched off, and we collected spectra after different wait times. Figure 4 reveals that the peak at 565 nm decreased as time progressed, and the sample correspondingly showed a transition in color from red to yellow. This occurred because the MC form in nonpolar solvents often is thermally unstable and thus reverts to the SP form even in the dark.[16,17] In short, the peak increase under UV irradiation indicates SP to MC conversion, while the peak decrease after the UV light was switched off indicates a reversion from MC to SP.

We now discuss why the viscosity of lecithin/SDC/SP micelles decreases when the SP is converted to MC. In this context, we note that the SP form is quite soluble in nonpolar solvents, whereas the MC form is relatively insoluble because of its hydrophilic nature. This is shown in Figure S2. First, 5 mM SP was solubilized in neat cyclohexane. However, upon UV irradiation, the SP was converted to MC, and the latter precipitated out of the cyclohexane. Next, we performed a variation of the same experiment for the case where lecithin was present in the cyclohexane. Once again, the SP was solubilized in the lecithin organosol, but in this case, upon UV irradiation, the solution remained homogeneous and took on a violet-red color. The homogeneity in the latter case shows that the MC must have been solubilized within lecithin micelles. Because of its hydrophilic and zwitterionic nature, it is likely that the MC binds to the zwitterionic phosphocholine headgroups of lecithin.[18−20]

We can therefore suggest a tentative mechanism to explain the different interactions of SP and MC with lecithin/SDC reverse worms. First, when SP is added to lecithin/SDC mixtures, it probably resides in the nonpolar solvent or next to the tails of lecithin, as shown in Figure S3. Lecithin and SDC would be expected to interact via hydrogen bonding between the hydroxyls of SDC and the headgroups of lecithin.[14,15] It is due to such interactions that the net geometry of the amphiphile favors the growth of reverse worms. Because of its nonpolar nature, SP has relatively no effect on the lecithin−SDC interactions. However, when SP is converted to MC, the zwitterionic MC is likely to bind to the lecithin headgroups,[18−20] displacing some of the SDC in the process (Figure S3). This causes the net geometry to be altered in a way that disfavors growth of worms (i.e., the micelles are induced to shorten).[14] The shorter worms evidently entangle less and relax faster,[13] which explains the reduction in viscosity.

In conclusion, we have demonstrated a PR system in which reversible viscosity changes can be induced by light. The system is based on mixtures of lecithin, the bile salt SDC, and a spiropyran; notably, all of these components are commercially available. The viscosity of the solution decreased 10-fold when UV light was switched on and recovered its initial value when the UV light was switched off. We suggest that these results are caused by the differential interaction of the zwitterionic lipid lecithin with the SP (nonpolar) and MC (zwitterionic) forms of the spiropyran.

■ ASSOCIATED CONTENT

Supporting Information. Details of experimental procedures, additional rheological and physicochemical data, and a schematic of the proposed mechanism for the PR effect. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information for

Reversible Photorheological Fluids Based on Spiropyran-Doped Reverse Micelles

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Experimental Section

Materials. Soybean lecithin (95% purity) was purchased from Avanti Polar Lipids, Inc. The bile salt, sodium deoxycholate (SDC, > 97% purity) was purchased from Sigma-Aldrich. The spiropyran, 1',3',3'-trimethyl-6-nitrospiro[1(2H)-benzopyran-2,2'-indoline] was obtained from TCI. Cyclohexane (> 99% purity) was from JT Baker.

Sample Preparation. Ground lecithin was dried in a vacuum oven at least for 48 h to remove residual water. Lecithin and SDC were mixed together in cyclohexane. The solutions became transparent and homogeneous by stirring and heating at 60°C. The sample was then cooled to room temperature and the spiropyran was added. The mixture was stirred till the spiropyran was completely dissolved.

Sample Response to Light. Samples were irradiated with UV light from an ORIEL 200 W mercury arc lamp. To access the UV wavelengths of the emitted light, a dichroic beam turner with a mirror reflectance range of 280-400 nm was used along with a < 400 nm filter. To nullify the effects of atmospheric moisture, the sample was contained in a capped quartz cell during UV irradiation. After UV irradiation, the colored dispersion was shaken and used for further studies. The sample was kept in a dark room to avoid contact with visible light. A Varian Cary 50 UV-Vis spectrophotometer was used to monitor the color transition of the sample in response to UV. The sample for UV-Vis spectrophotometer was diluted four times compared to the original sample to avoid too high a value of the absorbance.

Rheology. Dynamic rheological experiments were performed on an AR-G2 rheometer at the TA Instruments facility in Newark, DE. A high-pressure mercury lamp UV LED light source (150 mW/cm^2) having a 365 nm wavelength was fitted into the rheometer. This allowed real-time rheological measurements under UV irradiation, and subsequently in the absence of any irradiation. A parallel-plate geometry of 20 mm radius was used for all samples at ambient temperature. A solvent trap was used to minimize cyclohexane evaporation. Frequency spectra were conducted in the linear viscoelastic regime of the samples, as determined from dynamic strain sweep measurements.

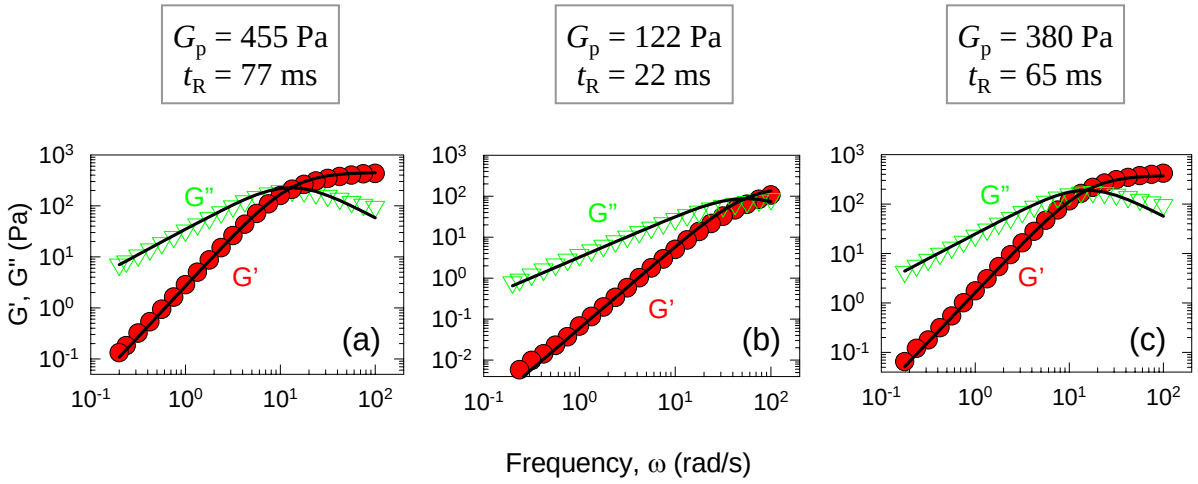

Figure S1. Dynamic rheology of a 100 mM Lecithin + 35 mM SDC + 15 mM SP sample in cyclohexane: (a) before UV irradiation, (b) during UV irradiation, and (c) 30 min after switching off the UV. Each plot shows the elastic modulus G' and the viscous modulus G'' as functions of frequency ω. The lines through the data are fits to the Maxwell model, which is shown below as eq S1. The parameters in the model are the plateau modulus G_p and the relaxation time t_R. Values of G_p and t_R for each plot are indicated in the boxes adjacent to the respective plots.

Eq S1

$$G'(\omega) = \frac{G_p \omega^2 t_R^2}{1+\omega^2 t_R^2} \qquad G''(\omega) = \frac{G_p \omega t_R}{1+\omega^2 t_R^2}$$

Maxwell model for $G'(\omega)$ and $G''(\omega)$
with a single relaxation time

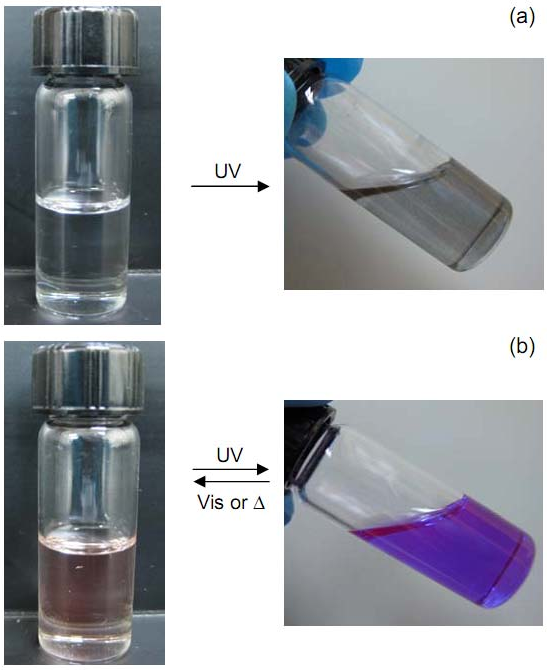

Figure S2. (a) 5 mM SP is solubilized in cyclohexane (left), but after UV irradiation, the MC precipitates out due to its polarity (right). (b) 3.75 mM SP solubilized in a 25 mM lecithin organosol in cyclohexane (left). After UV irradiation, the sample color changes to purple and it shows no precipitation (right). This indicates the binding of MC molecules to the lecithin headgroups within the reverse micelles.

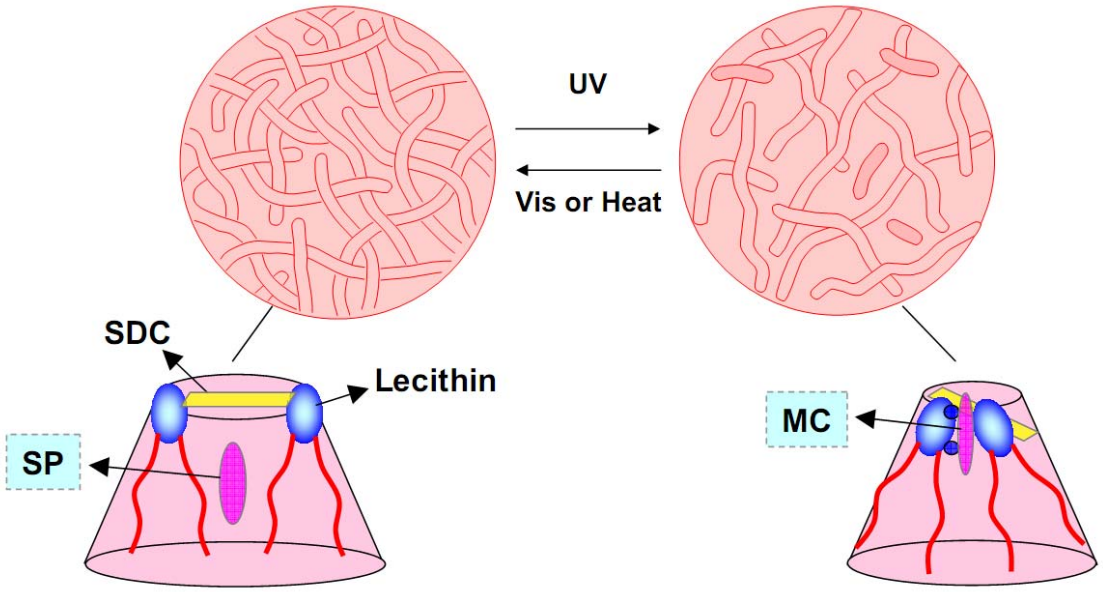

Figure S3. Mechanism of action in the case of lecithin/SDC/SP-based PR fluids. The mechanism relies on distinct effects of the SP and MC photoisomers on reverse self-assembly. Before UV irradiation (left), the SP remains in the hydrophobic area, surrounded either by the solvent or the hydrophobic tails of lecithin. The net molecular geometry is that of a truncated cone, which favors growth of micelles. Upon UV irradiation, the SP converts to MC, which shifts to the headgroup area of lecithin due to its hydrophilicity. The size of the headgroup area reduces resulting in a molecular geometry closer to a cone. In turn, the assemblies transform into shorter cylindrical micelles, which are less entangled and relax faster.