Langmuir
Article
pubs.acs.org/Langmuir

Nonaqueous Photorheological Fluids Based on Light-Responsive Reverse Wormlike Micelles

Rakesh Kumar, Aimee M. Ketner, and Srinivasa R. Raghavan*

Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland 20742-2111

Received October 9, 2009. Revised Manuscript Received December 7, 2009

Fluids whose flow properties can be altered by light are an emerging class of functional materials, with potential applications in microscale actuators and valves. While many such photorheological (PR) fluids have been developed over the years, most are based on specialized organized molecules that require synthesis. We have instead sought to develop PR fluids using inexpensive chemical components that are commercially available, and this approach has been successfully applied to aqueous systems. Here, we demonstrate a simple class of nonaqueous PR fluids based on the phospholipid, lecithin, and the organic derivative, *para*-coumaric acid (PCA). The combination of lecithin with the *trans* form of PCA results in reverse wormlike micelles, which are long, flexible chains that undergo entanglement, thereby giving rise to viscoelastic fluids. Upon UV irradiation, *trans*-PCA is photoisomerized to its *cis* form, which has a lower polarity and hydrogen-bonding tendency. This causes a significant reduction in the length of the micellar chains, and in turn, the fluid viscosity drops more than 1000-fold. We show that photoresponsive reverse micelles can be formed in a range of organic solvents including cyclohexane, *n*-alkanes, alkenes, and fatty acid esters.

1. Introduction

The term *photorheological* or PR fluid refers to those whose rheological properties, such as viscosity, can be tuned by irradiation with light.[1,2] These fluids are an enduring fascination for academic researchers, partly due to their applicability in emerging areas such as microscale robots or microfluidic systems. Over the past two decades many such photoresponsive fluids have been developed and characterized.[3−13] Most of these studies have relied on ingenious photoresponsive molecules, such as photosurfactants,[4,7,8] polymers,[6,9] or organogelators.[5,10,11] While these past approaches were indeed novel and successful, they cannot be easily replicated by other researchers who lack skills in organic synthesis. For applications to be devised with PR fluids, it is helpful to have PR formulations that can be made easily and at low cost by engineers and physical scientists (i.e., those who are more interested in the end-use rather than the chemistry behind the fluids). In other words, there is a need for simplicity, and this has guided our own work in this area.[2,14,15]

Previously, we have reported two aqueous PR fluids, each containing a surfactant and a cinnamic acid derivative.[2,14] Both compounds could be obtained from commercial vendors at low cost; thus, the fluids could be prepared by simple mixing and without additional synthesis. In both systems, UV irradiation sharply altered the viscosity: in one case,[2] the viscosity decreased by factors of 1 000 to 10 000 ("photothinning") while in the second case,[14] the viscosity was enhanced by a similar magnitude ("photogelling"). These UV-induced viscosity changes could not be reversed by irradiation at alternate wavelengths. Despite this limitation, our studies proved that PR effects could indeed be generated in simple aqueous formulations. The PR effects in the above cases relied on changes in the sizes of micelles in water.[2,14] Spherical or short cylindrical micelles gave a low viscosity, while long cylinders ("wormlike" chains) gave rise to high viscosities due to entanglements between the chains. The micelle length, in turn, was dictated by the binding of the cinnamic acid isomer (*trans* vs *cis*), which could be altered by light.

In the current paper, we turn our attention to the design of PR fluids based on nonpolar organic solvents. By analogy with our previous work, a working principle for such PR fluids could involve light-induced changes in the sizes of "reverse" micelles formed by amphiphiles in these solvents. The term "reverse" refers to the orientation of amphiphiles in the micelles: the nonpolar tails are directed outward into the solvent while the polar heads point inward − this is the opposite of normal micelles in water.[16] Reverse micelles that impart high viscosity to organic solvents are known: these are termed "reverse wormlike micelles" (reverse worms for short) and they are long, flexible cylindrical

*Corresponding author. E-mail: sraghava@umd.edu.

(1) Wolff, T.; Emming, C. S.; Suck, T. A.; Von Bunau, G. *J. Phys. Chem.* **1989**, *93*, 4894.
(2) Ketner, A. M.; Kumar, R.; Davies, T. S.; Elder, P. W.; Raghavan, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 1553.
(3) Wolff, T.; Klaussner, B. *Adv. Colloid Interface Sci.* **1995**, *59*, 31.
(4) Eastoe, J.; Vesperinas, A. *Soft Matter* **2005**, *1*, 338.
(5) Paulusse, J. M. J.; Sijbesma, R. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 2334.
(6) Yager, K. G.; Barrett, C. J. *J. Photochem. Photobiol., A: Chem.* **2006**, *182*, 250.
(7) Lee, C. T.; Smith, K. A.; Hatton, T. A. *Macromolecules* **2004**, *37*, 5397.
(8) Sakai, H.; Orihara, Y.; Kodashima, H.; Matsumura, A.; Ohkubo, T.; Tsuchiya, K.; Abe, M. *J. Am. Chem. Soc.* **2005**, *127*, 13454.
(9) Pouliquen, G.; Amiel, C.; Tribet, C. *J. Phys. Chem. B* **2007**, *111*, 5587.
(10) Yagai, S.; Nakajima, T.; Kishikawa, K.; Kohmoto, S.; Karatsu, T.; Kitamura, A. *J. Am. Chem. Soc.* **2005**, *127*, 11134.
(11) Matsumoto, S.; Yamaguchi, S.; Ueno, S.; Komatsu, H.; Ikeda, M.; Ishizuka, K.; Iko, Y.; Tabata, K. V.; Aoki, H.; Ito, S.; Noji, H.; Hamachi, I. *Chem.—Eur. J.* **2008**, *14*, 3977.
(12) Bonini, M.; Berti, D.; Di Meglio, J. M.; Almgren, M.; Teixeira, J.; Baglioni, P. *Soft Matter* **2005**, *1*, 444.
(13) Baglioni, P.; Braccalenti, E.; Carretti, E.; Germani, R.; Goracci, L.; Savelli, G.; Tiecco, M. *Langmuir* **2009**, *25*, 5467.
(14) Kumar, R.; Raghavan, S. R. *Soft Matter* **2009**, *5*, 797.
(15) Sun, K. S.; Kumar, R.; Falvey, D. E.; Raghavan, S. R. *J. Am. Chem. Soc.* **2009**, *131*, 7135.
(16) Evans, D. F.; Wennerstrom, H. *The Colloidal Domain*; Wiley-VCH: New York, 2001.

chains, much like their aqueous counterparts.[17−20] Our goal of engineering nonaqueous PR fluids can thus be reduced to the goal of generating light-responsive reverse worms. Importantly, we would like to design these fluids using chemicals that can be purchased from commercial vendors rather than new molecules that require synthesis in the laboratory.

The challenge in this context is that there are only a few known routes for forming reverse worms. (In comparison, aqueous worms can be assembled by a large number of surfactants along with a variety of salts.) The conventional "recipe" for reverse worms[17,18] is to combine the phospholipid, lecithin with a small amount of water. Lecithin−water mixtures give rise to reverse worms in many nonpolar solvents. While lecithin itself assembles into small spherical reverse micelles, it is the addition of water that induces growth of long, wormlike chains. Instead of water, a few other types of additives can have the same effect, these include strongly polar solvents like formamide,[18] biosurfactants like bile salts,[19,20] and certain sucrose esters.[21] The common thread with all these additives is their ability to form hydrogen bonds (H-bonds) with the headgroups of lecithin.[18,19]

To engineer photoresponsive reverse worms, a new route needs to be found whereby worms could be induced upon addition of photosensitive aromatic molecules such as phenylalkenes, stilbenes, or azobenzenes. Accordingly, we have explored the addition of various aromatic derivatives to lecithin organosols. Among more than 10 such derivatives tested, reverse worms were found in only one case − with *para*-coumaric acid (PCA). In this paper, we will describe the properties of lecithin/PCA mixtures in different organic solvents with focus on their rheological properties initially and after UV irradiation. We will demonstrate light-induced viscosity reduction by factors of 1000 or more in these mixtures. These rheological effects will be correlated with changes in the length of lecithin/PCA worms. In turn, these microstructural changes will be shown to be dictated by light-induced changes in the geometry of the PCA molecule. PCA is known to undergo *trans*−*cis* photoisomerization about its olefinic double bond.[22−24] In fact, PCA photoisomerization is integral to the function of proteins such as the photoactive yellow protein (PYP).[23,24] Our studies indicate the preferential ability of *trans*-PCA to cause reverse worm growth compared to *cis*-PCA, which is attributed to the higher polarity and thereby superior H-bonding capability of the former.[22,25]

2. Experimental Section

Materials. Soybean lecithin (95% purity) was purchased from Avanti Polar Lipids, Inc. and used as received.[19,20] The *trans* isomers of *para*-, *meta*-, and *ortho*-coumaric acids (denoted as PCA, MCA, and OCA, respectively) were purchased from Sigma-Aldrich and used as received (each was >98% in purity). Cyclohexane, iso-octane, and isopropyl palmitate were purchased from EM Sciences, Fisher Scientific and TCI America, respectively. *n*-hexane, 1-hexene, and *n*-decane were purchased from Sigma-Aldrich. Deuterated cyclohexane (99.5% D) was obtained from Cambridge Isotopes. Samples were prepared by dissolving weighed amounts of lecithin and the chosen coumaric acid in a given organic solvent. The solutions were then heated to ∼65 °C under continuous stirring for ∼1 h until they became homogeneous. The samples were then stirred continuously for 24 h and then left to equilibrate overnight in a desiccator at room temperature before any experiments were conducted.

Sample Response before and after UV Irradiation. 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, samples (5 mL) were placed in borosilicate glass vials with their caps on and were irradiated through vial walls for a specific duration under stirring. Irradiated samples did not undergo any changes when stored in the dark under ambient conditions (to be additionally careful, we covered sample vials with aluminum foil). This stable behavior made it easy to conduct subsequent tests on the samples. UV−vis spectroscopy studies before and after irradiation were carried out using a Varian Cary 50 spectrophotometer.

Rheological Studies. Steady and dynamic rheological experiments were performed using an AR2000 stress controlled rheometer (TA Instruments). Samples were studied at 25 °C on a cone-and plate geometry (40 mm diameter, 2° cone angle). A solvent trap was used to minimize solvent evaporation. Frequency spectra were conducted in the linear viscoelastic regime of the samples, as determined from dynamic strain sweep measurements. For the steady shear experiments, sufficient time was allowed before data collection at each shear rate to ensure that the viscosity reached its steady-state value.

Small Angle Neutron Scattering (SANS). SANS measurements were made on the NG-7 (30 m) beamline at NIST in Gaithersburg, MD. Neutrons with a wavelength of 6 Å were selected, and three different sample-to-detector distances were used to access a range of wave vectors q from 0.004 to 0.4 $Å^{-1}$. Samples were prepared with deuterated cyclohexane and were studied in 1 mm quartz cells at 25 °C. Scattering spectra were corrected and placed on an absolute scale using calibration standards provided by NIST. Data are presented as plots of the radially averaged scattered intensity I vs the wave vector $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the neutron wavelength and θ the scattering angle.

SANS Data Analysis. SANS data were analyzed by the indirect Fourier transform (IFT) method, which requires no *a priori* assumptions on the nature of the scatterers.[14,26] Here, a Fourier transformation of the scattering intensity $I(q)$ is performed to obtain the pair distance distribution function $p(r)$ in real space. $p(r)$ provides structural information about the scatterers, such as their shape and maximum dimension. IFT analysis was implemented using the commercial PCG software package.

3. Results and Discussion

We first studied mixtures in cyclohexane of lecithin and the isomers of coumaric acid, i.e., *para*-coumaric acid (PCA), *meta*-coumaric acid (MCA), and *ortho*-coumaric acid (OCA) (structures of all three are shown in Figure 1). All three compounds were insoluble in cyclohexane when added directly; however, each could be dissolved in the presence of lecithin. Among the three, only PCA increased the solution viscosity and the corresponding samples exhibited all the hallmarks of reverse

(17) Schurtenberger, P.; Scartazzini, R.; Luisi, P. L. *Rheol. Acta* **1989**, *28*, 372.
(18) Shchipunov, Y. A. *Colloid Surf. A* **2001**, *183*, 541.
(19) Tung, S. H.; Huang, Y. E.; Raghavan, S. R. *J. Am. Chem. Soc.* **2006**, *128*, 5751.
(20) Tung, S. H.; Huang, Y. E.; Raghavan, S. R. *Langmuir* **2007**, *23*, 372.
(21) Hashizaki, K.; Taguchi, H.; Saito, Y. *Colloid Polym. Sci.* **2009**, *287*, 1099.
(22) Caccamese, S.; Azzolina, R.; Davino, M. *Chromatographia* **1979**, *12*, 545.
(23) Kort, R.; Vonk, H.; Xu, X.; Hoff, W. D.; Crielaard, W.; Hellingwerf, K. J. *FEBS Lett.* **1996**, *382*, 73.
(24) Takeshita, K.; Hirota, N.; Terazima, M. *J. Photochem. Photobiol., A: Chem.* **2000**, *134*, 103.
(25) Lee, H. S. HPLC analysis of phenolic compounds. In *Food Analysis by HPLC*, 2nd ed.; Nollet, L. M. L., Ed.; Marcel Dekker: New York, 2000; p 775.
(26) Glatter, O. *J. Appl. Crystallogr.* **1977**, *10*, 415.

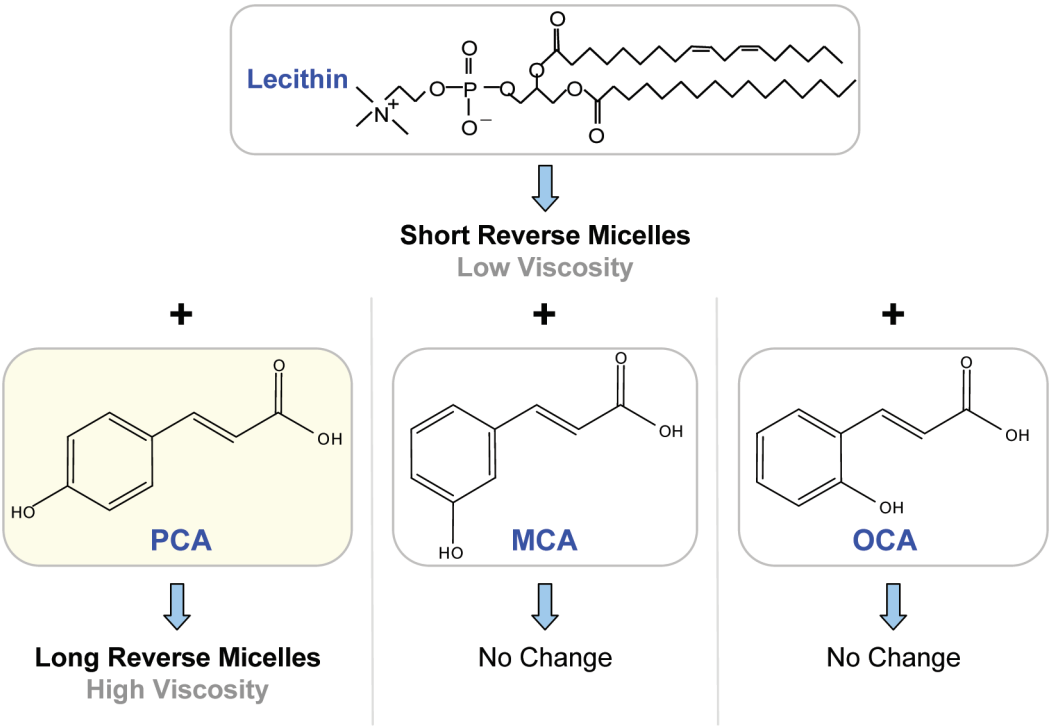

Figure 1. Effects of coumaric acid isomers on reverse micelles. The lipid, lecithin forms short (spherical or ellipsoidal) reverse micelles in organic liquids like cyclohexane. When *para*-coumaric acid (PCA) is added to this solution, the micelles grow into long (wormlike) chains. The other isomers, i.e., *meta*-coumaric acid (MCA) and *ortho*-coumaric acid (OCA), do not have this effect. Note that the olefenic double bond in all three coumaric acid isomers is in a *trans* configuration.

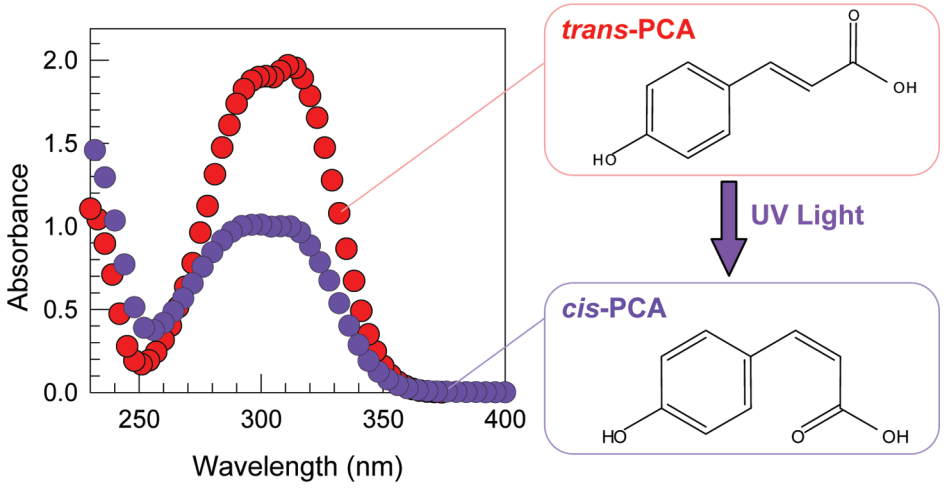

Figure 2. UV−vis spectra of lecithin/PCA samples before and after UV irradiation. The sample contains 1 mM PCA and 5 mM lecithin in cyclohexane. Initially, PCA is in its *trans* form. The drop in absorbance and slight blue shift in the spectrum after UV irradiation indicate that the molecule has been photoisomerized to its *cis* form. Lecithin was added to dissolve PCA in cyclohexane, and it did not affect the spectra.

wormlike micelles,[17−19] including viscoelasticity and flow-birefringence (see below). The reasons for the different effect of PCA relative to its other isomers will be discussed later. Further experiments were done solely on lecithin/PCA mixtures.

PCA is known to undergo photoisomerization about its double bond.[22−24] To confirm that this occurs in the presence of lecithin, we recorded UV−vis spectra on mixtures of 1 mM PCA (initially the double bond is in the *trans* state) and 5 mM lecithin in cyclohexane (Figure 2). The sample has an absorbance peak in the UV range (at 312 nm), which is clearly attributable to *trans*-PCA.[22,24,25,27] We then irradiated the above solution with UV light and recorded the spectrum again. The new spectrum shows a drop in peak intensity and a slight blue shift in the peak to a lower wavelength of ≈300 nm. This change in the spectrum is consistent with a UV-induced photoisomerization from *trans* to *cis*-PCA, and similar data have been reported previously.[22,24] The presence of lecithin had no effect on PCA spectra; similar data were obtained for solutions of PCA alone in solvents like ethanol and water.

The reverse isomerization of PCA (i.e., *cis* to *trans*) cannot be induced either by light or heat.[22,24] Indeed, it is worth noting from the UV−vis data that *cis*-PCA does not have a distinct absorption band where it has an appreciably higher absorbance than *trans*-PCA. This is unlike reversibly photoisomerizable compounds

(27) Putschogl, M.; Zirak, P.; Penzkofer, A. *Chem. Phys.* **2008**, *343*, 107.

such as the azobenzenes, where the *cis* isomer usually has a peak in the visible range, and irradiation at those wavelengths causes the reverse *cis* to *trans* photoisomerization. In the case of PCA, the data suggest a large potential barrier between the ground states of the *cis* and the *trans* isomers.[27] Another notable fact from Figure 2 is that both isomers of PCA have negligible absorbances in the visible ranges of their spectra. Thus, exposure to visible light does not affect the samples, and UV-irradiated samples remain unaltered when stored under ambient conditions in covered vials.

Having demonstrated that PCA can indeed be photoisomerized in the presence of lecithin, we studied the macroscopic effects of UV irradiation on lecithin/PCA samples in cyclohexane. The lecithin concentration was fixed at 100 mM, and varying amounts of PCA were tested. At PCA concentrations approximately equimolar to the lecithin, the fluid was appreciably viscoelastic and gel-like. An example of a sample with 110 mM PCA is shown in Figure 3a. In this case, the sample holds its weight for several minutes in the inverted vial. Note that the magnetic stirrer bar remains trapped in the sample. Flow-birefringence, i.e., bright streaks of light under crossed polarizers, was also seen when this gel-like sample was shaken. Both the viscoelasticity and flow-birefringence are indications of long reverse worms in this sample.[17−19] Next, the same sample after UV irradiation for 30 min is shown in Figure 3b. The sample has been transformed into a free-flowing, low-viscosity liquid: note that it flows easily upon tilting the vial and the bubbles have risen to the surface. No flow-birefringence was seen in this sample. We refer to the above light-induced macroscopic changes as "*photothinning*", i.e., conversion from a gel-like state to a thin, flowing liquid. The low viscosity and lack of flow-birefringence in the irradiated sample suggest that the micelles in it are considerably shorter than in the original case.[2]

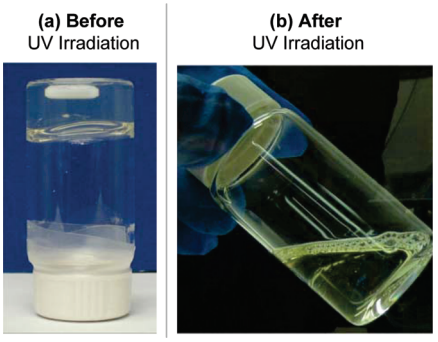

Figure 3. Photographs of a sample of 100 mM lecithin + 110 mM PCA in cyclohexane: (a) before and (b) after UV irradiation. Before irradiation, the sample is strongly viscoelastic and holds its weight along with a magnetic stir bar in the inverted vial. After UV irradiation for 30 min, the sample is transformed into a low viscosity fluid that flows easily and does not entrap air bubbles.

We then quantified our visual observations through dynamic and steady-shear rheological experiments on the above sample. First we discuss the data from dynamic rheology (Figure 4a), which is a more sensitive probe of the structure in complex fluids. The data are shown as plots of the elastic modulus G' and the viscous modulus G'' as functions of the angular frequency ω. Before irradiation, the lecithin/PCA sample exhibits a viscoelastic response typical of long, entangled reverse worms.[17−19] That is, at high frequencies or equivalently at short time scales, the behavior is largely elastic with $G' > G''$, whereas at low frequencies or long time scales, the behavior is mostly viscous with $G'' > G'$ and both moduli strongly dependent on frequency. A very different behavior is seen after 30 min of irradiation with UV light. The sample now exhibits a purely viscous response ($G'' \gg G'$) over the entire range of frequencies, a response similar to thin, runny liquids and consistent with short micelles.

The corresponding steady-shear rheological data are plotted in Figure 4b with data being shown for different periods of UV irradiation. Before irradiation, the sample shows a non-Newtonian and shear-thinning response: the viscosity tends to a plateau at low shear-rates followed by a precipitous drop at higher shear-rates. After 10 min of UV irradiation, the sample response is converted to a nearly Newtonian one (i.e., constant viscosity, independent of shear-rate) and the value of the viscosity is lowered by nearly 2 orders of magnitude. After 10 more min of irradiation (total 20 min), the viscosity is further lowered by an order of magnitude. Further irradiation beyond 20 min had negligible effect on the viscosity. Thus the extent of the viscosity drop (photothinning) can be controlled by the irradiation time. As mentioned in our earlier papers, the rate limiting step for these viscosity changes appears to be the absorption of UV light by the sample and we can shorten this time scale by using brighter lamps or smaller sample volumes.[2,14,15]

We now consider the effect of UV on a range of lecithin/PCA compositions in cyclohexane, with the [lecithin] fixed at 100 mM.

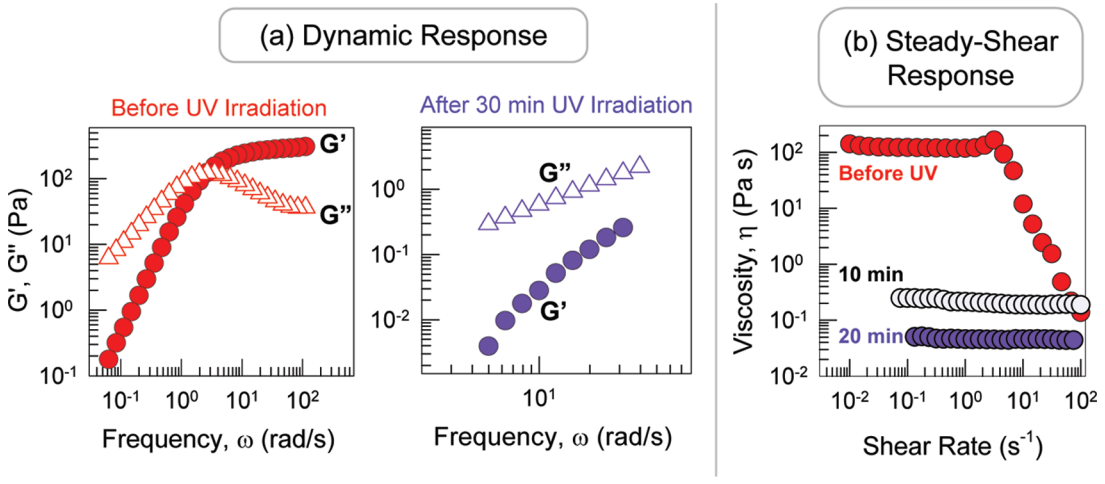

Figure 4. Effect of UV light on the rheology of a sample containing 100 mM lecithin + 110 mM PCA in cyclohexane: (a) dynamic rheology before and after UV irradiation for 30 min and (b) steady-shear rheology before and after UV irradiation for varying periods of time (indicated on the plot). The sample switches from a viscoelastic, shear-thinning fluid to a low-viscosity, Newtonian fluid upon UV irradiation.

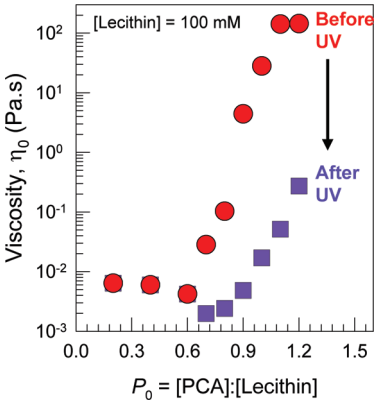

Figure 5. Zero shear viscosity η_0 of lecithin/PCA samples in cyclohexane as a function of P_0, the molar ratio of PCA/lecithin, with the [lecithin] held constant at 100 mM. Data are shown for samples both before irradiation (PCA in its *trans* form) and after 30 min of UV irradiation (PCA converted to its *cis* form).

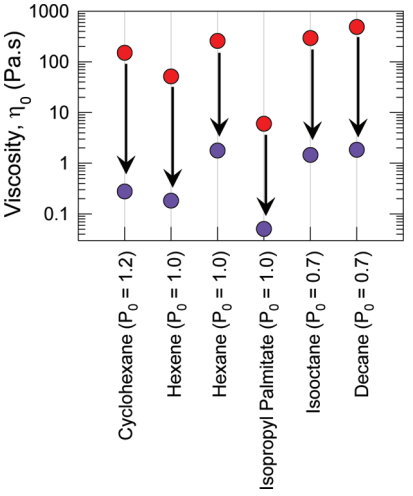

Figure 6. Zero shear viscosity η_0 of lecithin/PCA samples in six different organic solvents, before and after UV irradiation for 30 min. The [lecithin] is 100 mM in all cases, while the P_0 values for each solvent are specified on the plot. UV irradiation causes substantial drops in viscosity for each sample.

The molar ratio of PCA/lecithin, denoted by P_0, is the *x*-axis in Figure 5; note that the sample in Figures 3 and 4 corresponded to a P_0 of 1.1. The *y*-axis shows the zero-shear viscosity (η_0), which is the viscosity in the limit of low shear-rates, both before and after irradiation with UV light for 30 min. First, consider the behavior of lecithin/PCA/cyclohexane mixtures before irradiation. At low P_0 values (< 0.6), the samples have a low η_0, practically identical to that of a lecithin/cyclohexane solution without any PCA. As P_0 is increased from 0.6 to 1.2, η_0 grows by 5 orders of magnitude, implying the formation and growth of reverse worms. However, further addition of PCA (i.e., $P_0 > 1.2$) causes the sample to phase-separate into two isotropic liquid phases. Thus, we find that addition of PCA causes a rapid increase in viscosity up to a maximum, followed by phase separation. The same pattern was observed also in a study on lecithin−bile salt mixtures in cyclohexane,[19] where again the bile salt caused growth of lecithin worms followed by phase separation. As for the effect of UV irradiation on the above lecithin/PCA samples, a drop in viscosity occurs for all the viscous ones ($P_0 > 0.6$). The drop is particularly large (factor of 1000 or more) for samples near the peak viscosity ($P_0 \sim 1-1.2$). The results in Figure 5 show that the magnitude of photothinning can be modulated via the sample composition.

Following our studies on photothinning in cyclohexane, we were interested in extending these results to other organic solvents. We found that a variety of nonpolar solvents (*n*-alkanes, cycloalkanes, alkenes, fatty acid esters) could be rendered viscoelastic by mixtures of lecithin and PCA. In all cases, the viscosity increased up to a certain [PCA]/[lecithin] molar ratio P_0, followed by phase separation. For a [lecithin] of 100 mM, the maximum allowable P_0, i.e., the P_0 at the onset of phase separation, varied from 0.7 to 1.2 depending on the solvent. To compare the photoresponse between solvents in a uniform way, we picked samples in each solvent at their maximum allowable P_0 (which generally corresponded to the highest initial viscosities). The specific P_0 values are indicated in Figure 6. Significant UV-induced drops in zero-shear viscosity η_0 (i.e., photothinning) are observed for each of the six different solvents. The viscosity is reduced by factors ranging from 100 to 1000 in these samples.

The results so far suggest that lecithin and *trans*-PCA together form reverse worms, leading to viscoelastic samples. When *trans*-PCA is converted to *cis*-PCA by exposure to UV light, the worms shorten considerably and so the viscosity drops. To confirm the above scenario at the microstructural level, we conducted SANS experiments. Samples were made in deuterated cyclohexane to amplify the contrast between the micelles and the solvent; these samples were identical to those in cyclohexane. Parts a and b of Figure 7 show SANS spectra (I vs q) for two samples, both with 100 mM lecithin and with PCA concentrations of 60 and 70 mM, respectively. Data are provided both before and after UV irradiation for 30 min. In both cases, the spectra before irradiation have a shape reminiscent of cylindrical structures (slope close to -1 at low q).[2,14,28] Also, in both cases, a drop in the scattered intensity at low q is found after irradiation, which qualitatively signals a decrease in micelle length (overall size).[2,14] On the other hand, the data at high q are unaffected by irradiation, indicating a constant diameter for the micelles. Note that the SANS studies were deliberately done with samples having relatively low PCA concentrations compared to those studied in Figures 3−6. This was to ensure that the micelle sizes before and after irradiation fell within the size window probed by SANS.

To obtain more quantitative information, we modeled the SANS data using the IFT method, which permits analysis of the data without *a priori* assumptions on the nature of the scatterers.[14,26] Figure 7c shows the pair distance distribution functions $p(r)$ obtained from IFT modeling of the SANS data from the 60 mM PCA sample. The $p(r)$ before irradiation is asymmetrical and drops to zero around 95 Å. This shape of the $p(r)$ function is characteristic of cylindrical micelles, with 95 Å being a lower estimate for their contour length.[14,26] On the other hand, the $p(r)$ after irradiation is nearly symmetrical and this shape suggests ellipsoidal micelles with nearly equal length and diameter.[14,26] The point where $p(r)$ meets the *x*-axis gives the micelle length, which is about 55 Å in this case. Thus, the IFT analysis confirms a reduction in micelle size upon irradiation. Similar results were also obtained by analyzing the data from the 70 mM PCA sample (not shown).

The SANS data coupled with the rheology confirm that reverse cylindrical micelles (worms) exist in lecithin/PCA/oil samples and that the micelles shorten upon UV irradiation. In other words, the photothinning behavior occurs because of changes in molecular self-assembly. No covalent bonds are broken or formed in this process. Further proof for a self-assembly based mechanism comes from our ability to reverse photothinning by changing

(28) Pedersen, J. S. *Adv. Colloid Interface Sci.* **1997**, *70*, 171.

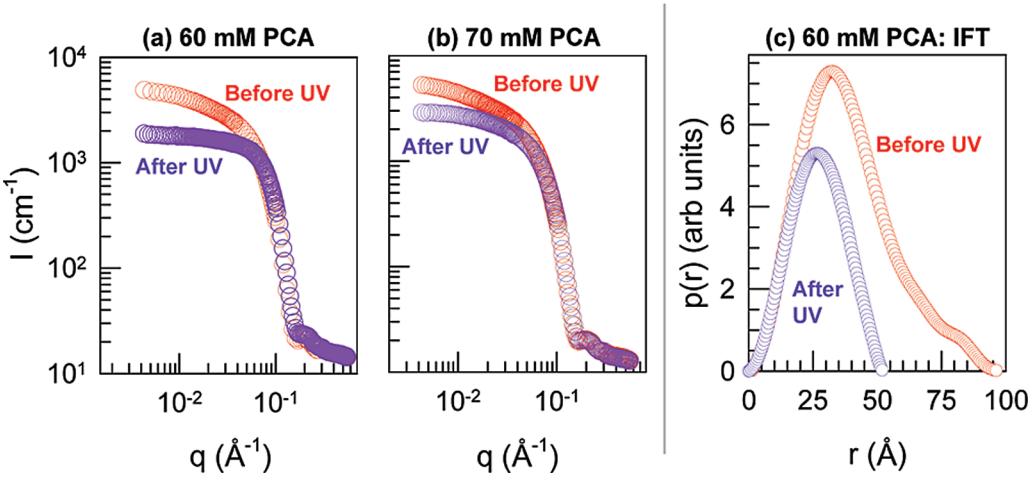

Figure 7. SANS data and analysis for lecithin/PCA samples in deuterated cyclohexane before and after 30 min of UV irradiation. Plots a and b show scattering spectra (intensity I vs wave vector q) for samples with 100 mM lecithin and PCA concentrations of 60 and 70 mM, respectively. Plot c is the analysis of the data for the 60 mM PCA sample using the IFT method. See the text for details.

the sample composition. For example, take the sample of 100 mM lecithin + 110 mM PCA in cyclohexane shown in Figure 3; its viscosity η_0 was reduced by a factor of 2800 by UV irradiation. Subsequently, if 30 mM of *trans*-PCA is added to the same sample, its η_0 can be increased more than 1500 times. In other words, the system still shows a sensitivity to composition, as expected of micellar fluids. Thus, our results can be rationalized in terms of molecular self-assembly in nonaqueous solvents, as was done previously in our work with aqueous PR fluids.[2,14]

The questions that still need to be addressed are at the molecular level, i.e., (1) why does PCA induce growth of reverse worms whereas its isomers (MCA and OCA) do not and (2) why do the worms shorten when PCA is converted from *trans* to *cis*. We believe the answers to these questions lie in the H-bonding capabilities of the different moieties. The H-bonding tendencies of the *trans* isomers of coumaric acid are known to follow the order PCA > MCA > OCA, as reflected in chromatographic retention factors, among other measures.[22,25] H-bonding is recognized to be critical to the growth of reverse micelles.[18,19] Other additives that can induce growth of lecithin worms, e.g., water and bile salts, do so by forming H-bonds with lecithin headgroups, which serves to increase the headgroup area without affecting the tail area.[18,19] Such a change in net molecular geometry favors the growth of cylindrical micelles at the expense of spherical micelles (see Figure 8). We believe that *trans*-PCA functions in a similar manner, i.e., the hydroxyl (−OH) groups of *trans*-PCA are optimally oriented to form H-bonds with the lecithin headgroups (Figure 8), and this leads to axial growth of cylindrical lecithin micelles. The other isomers, MCA and OCA, are less capable of such H-bonding and are therefore unable to cause micellar growth.

Next, we tackle the effects of UV irradiation. It is evident that PCA undergoes a UV-induced photoisomerization from *trans* to *cis* in the presence of lecithin. Indeed, photoisomerization of PCA is well-known[22,24] and our own UV−vis data (Figure 2) are consistent with the spectra reported for *trans*- and *cis*-PCA. Other possible light-induced effects in the case of coumaric or cinnamic acids such as photodimerization occur only at much higher concentrations of the derivatives,[29,30] besides these would not

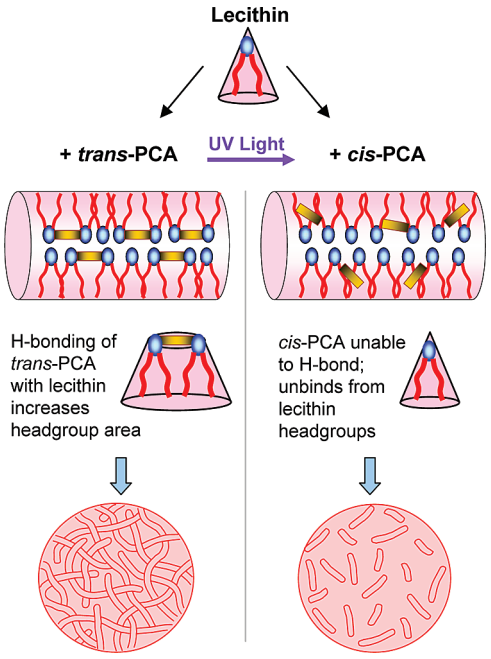

Figure 8. Mechanism for photothinning in lecithin/PCA/oil samples. The polar *trans*-PCA form H-bonds with the lecithin headgroups, increasing the effective headgroup area. This favors growth of reverse wormlike micelles and thereby leads to a high viscosity. When *trans*-PCA is photoisomerized, the less polar *cis*-PCA has only a weak H-bonding tendency and therefore unbinds from the headgroups. The lowered headgroup area favors the shortening of the micelles, and in turn the sample viscosity drops (photothinning).

be consistent with the UV−vis spectra. With regard to the *trans* and *cis* isomers of PCA, it is also known that they substantially differ in their polarity.[22,25] For example, *trans*-PCA is reported to have a dipole moment almost double that of *cis*-PCA.[24] We believe the greater polarity, and by extension, H-bonding ability of *trans*-PCA is the key to explaining the photothinning effect. As depicted in Figure 8, when the weakly polar *cis*-PCA is formed by UV irradiation, we postulate that it will unbind from the lecithin headgroups. As a result, the headgroup area will decrease to its original low size, and this will favor shortening of the reverse worms, in turn, explaining the drop in viscosity. Another factor

(29) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.
(30) Imae, T.; Tsubota, T.; Okamura, H.; Mori, O.; Takagi, K.; Itoh, M.; Sawaki, Y. *J. Phys. Chem.* **1995**, *99*, 6046.

that may contribute to the superior H-bonding ability of *trans*-PCA over its *cis* counterpart could be its greater planarity,[22] an attribute found also in the bile salts that are known to be effective at inducing lecithin micellar growth.[19] The above mechanism offers a tentative, but plausible, framework to interpret our results.

4. Conclusions

In this study, we have shown that PR fluids can be made using nonpolar organic liquids by employing two simple, inexpensive components, lecithin and PCA. The combination of lecithin with the *trans* form of PCA gives rise to reverse worms and thereby to viscoelastic fluids. *trans*-PCA induces growth of reverse worms because of its ability to form H-bonds with the headgroups of lecithin, which alters the net geometry of the amphiphile to one favoring cylindrical micelles at the expense of spherical ones. Upon UV irradiation, PCA undergoes a photoisomerization from *trans* to *cis*. The *cis* moiety, being considerably less polar, is less capable of H-bonding with lecithin; as a result, the micelles revert to much smaller sizes, leading to a substantial drop in viscosity. Such photothinning behavior has been achieved for samples in a range of organic solvents including *n*-alkanes, alkenes, and fatty acid esters.

Acknowledgment. This work was partially funded by a CAREER award from NSF-CBET. Additional discretionary funds to S.R.R. through the Patrick and Marguerite Sung Professorship in Chemical Engineering are gratefully acknowledged. We also acknowledge NIST NCNR for facilitating the SANS experiments performed as part of this work.