Photochromic and Optical Birefringence Properties of Azo-Dye-Doped Polymer-Grafted Lipid-Based Complex Fluids

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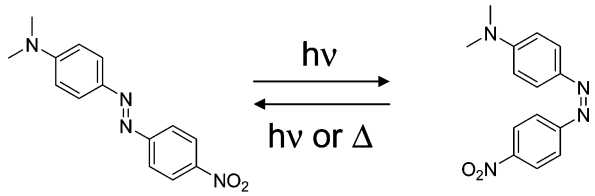
New materials designed to exhibit pronounced changes in absorbance or birefringence are of interest in the development of molecular-based all-optical devices.[1] Such devices have enormous potential in areas as diverse as holographic imaging, optical displays, switches, modulators, and data storage.[2−5] For optical information processing, photoisomerizable azo-dye derivatives have been the molecule of choice, since upon resonant illumination with linearly polarized light, they undergo a cycle of trans−cis isomerizations that cause the dye to orient perpendicular to the incident (polarized) light direction, thereby producing large changes in optical birefringence.[6] The selection of an appropriate host matrix for the photoisomerizable dye remains an important area of research.

To date, amorphorous polymeric (doped, side chain, and main chain functionalized) and nanostructured materials such as liquid crystals, Langmuir−Blodgett (LB), self-assembled monolayers (SAMS), or multilayer (LBL) thin films have been most frequently employed as hosts.[1,7−9] All suffer from various drawbacks, however, that limit their utility. For example, dye-doped or functionalized amorphorous polymers, despite extensive study, suffer from low attainable chromophore concentrations (due to solubility restrictions/dye aggregation) and rapid loss of photoinduced orientation (due to the high mobility of the relatively unconstrained chromophore molecules within the polymer).[10] The use of ordered, monomolecular systems such as LB films or SAMS is tedious and not amenable to large-scale processing. Moreover, LB films have been found to suppress photoselection (selective photoalignment), apparently due to steric factors inhibiting reorientation.[11] Furthermore, the amplitude of the photoinduced response has been found to decrease with the number of layers due to a decreased host ordering. To address these limitations, there is continued interest in developing new host materials as the basis for optical information processing/devices. Bulk samples are of interest since, in contrast to thin films, such architectures are more amenable to photoaddressability over three dimensions and thus can be used for multiplexed-volume holographic memories. Hosts that mimic the native biomembrane offer not only the opportunity to overcome those problems but also the possibility of exploiting membrane-bound biomolecules as optically active molecules (e.g., rhodospsins).

In this report, we evaluate the suitability of complex fluids (multicomponent, amphiphilic mixtures that are macroscopically homogeneous and microscopically disordered, but possess structure on a mesoscopic (nm to μm) length scale) as novel media for optical information processing and storage. The complex fluids comprise quaternary mixtures of a phospholipid (dimyristoylphosphatidycholine), a polymer-grafted phospholipid (PEGylated-dimyristoylphosphatidylethanolamine), and a cosurfactant (*N,N*-dimethyldodecylamine-*N*-oxide) dispersed in water that, at room temperature, self-assemble to form an elastic solid (gel) consisting of ordered microdomains of lamellae, Lαg.[12−14] As the sample is cooled below ca. 16 °C, the material reversibly converts to a low-viscosity state, converting to a 2-D hexagonal array of prolate micelles (H_1). Small-angle neutron and X-ray scattering studies have shown that the lamellar gel phase consists of alternating sheets of alkane bilayers 35 Å thick and aqueous channels 225 Å wide. It has also been shown that a wide range of small organic molecules (i.e., 4-nitro-4′-(dimethylamino)-azobenzene (**I**)) can be selectively introduced into the complex fluid by simply blending them into the preformed material and allowing them to partition into a chemically like region. Herein, we evaluate the ability of the complex fluid to serve as a novel host matrix allowing for both light-induced control of molecular orientation and temperature-induced control of architecture and physical properties.



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The azo-dye doped complex fluid is macroscopically uniform and optically transparent.[15] Both small-angle X-ray scattering (SAXS) and differential scanning calorimetry on complex fluids incorporating the azo-dye show no significant changes in either the structure of the gel or liquid phases or the temperature of the phase transition. The DSC heating profile (2 °C/min) collected on a sample with (0.18 mM dye) exhibits a pretransition centered at 15.9 °C and an endothermic peak (fwhm = 2.2 °C) centered at 22.5 °C (onset at 20.5 °C), as shown in Figure 1.[16] Small-angle scattering has indicated that within the phase transition region (∼16−23 °C) a mixed H_1/L_α architecture is present (Figure 1).[12]

The dye-doped complex fluid shows pronounced thermochromic behavior, exhibiting a color change from red to orange as the temperature is raised. This color change manifests itself in the UV−vis spectrum[17] as a shift in the absorption maximum from 515 nm in the cold phase, 2-D hexagonal liquid state (10 °C) to $\lambda = 509$ nm as the sample is warmed through the phase transition and finally, upon further warming to 28 °C (i.e., a temperature to fully place the sample into the lamellar, gel phase), to $\lambda = 493$ nm (Figure 2). For comparison, the absorption spectrum of the azo-dye dispersed into a glassy polymer, poly(methyl methacrylate), PMMA (2% w/w), or in octanol was recorded.[18] The absorption

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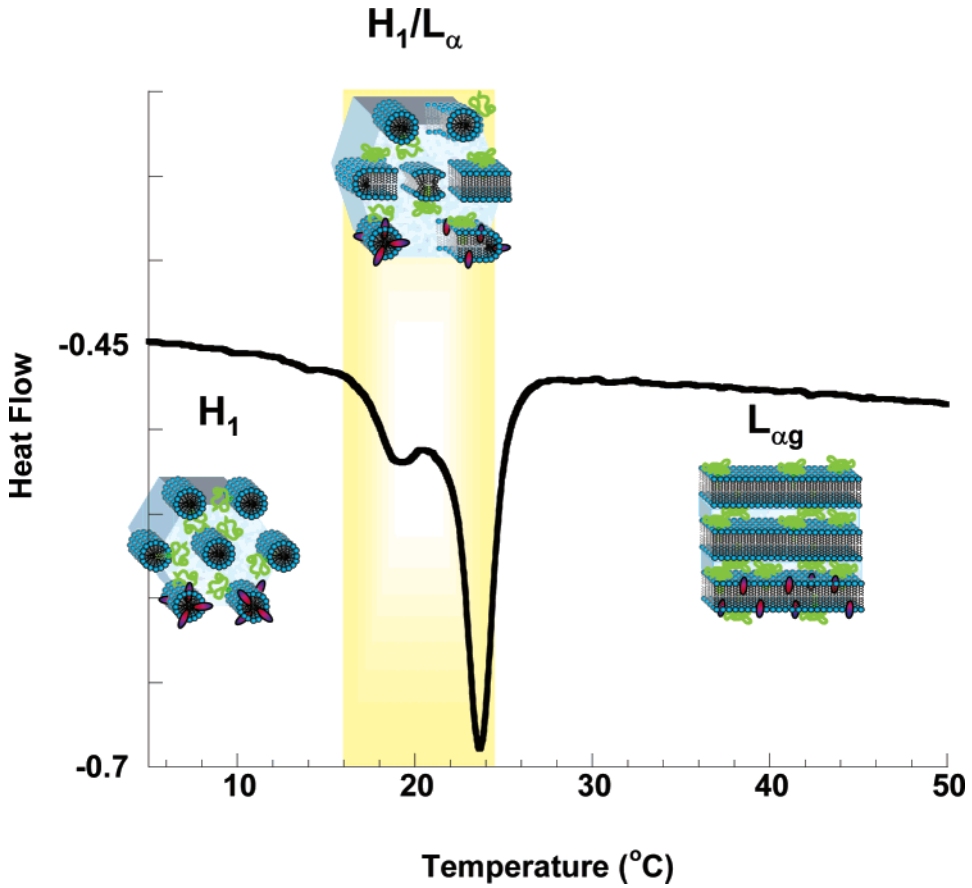

Figure 1. Calorimetric heating curve: 8 mol % PEG5000 grafted lipid-based complex fluid composition incorporating 0.18 mM azo-dye, scan rate 2 °C/min. Identical thermograms were obtained independent of the initial equilibration temperature. Schematic illustration of temperature-induced complex fluid (host) architecture (as previously determined by SAXS and SANS):[12] (A) cold (<16 °C) H_1 phase; (B) phase transition region (~16−22 °C) with mixed phase of micelles and lamellae; (C) warm (>23 °C) lamellar gel phase $L_{\alpha g}$.

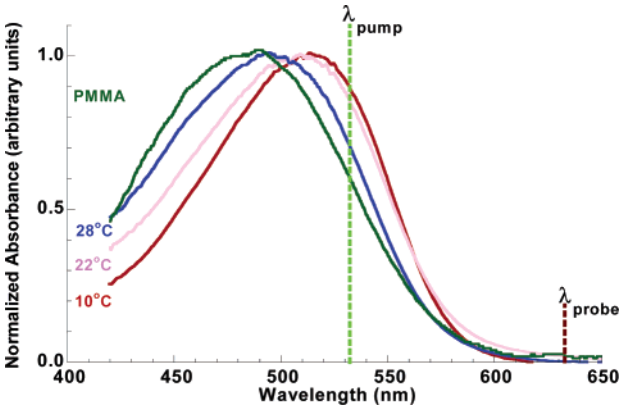

Figure 2. Normalized absorption spectra of an azo-dye doped (5.3 mM) PMMA polymer film and an azo-dye doped (0.18 mM) complex fluid at 10, 22, and 28 °C.

maxima, 488 and 470 nm, respectively, compare well with that observed for the azo-dye doped complex fluid in the lamellar, gel phase at 28 °C. The pronounced (20 nm) blue shift in the absorption maximum upon warming is completely reversible upon repeated cycling through the phase transition.

Azo-dyes are well-known to undergo solvatochromism (i.e., absorption shifts due to solvent environment).[19] Thus, the observed changes in λ_{max} may, in part, be ascribed to differences in the micropolarity/environment of the host matrix surrounding the chromophore in the various structural states of the complex fluids (schematically illustrated in Figure 1). Typically, the solvatochromic effect is observed as a red shift in the absorption or emission maximum as the solvent is changed from nonpolar (e.g., cyclohexane) to polar (e.g., water). The significant red shift in the absorption maximum observed in the 2-D hexagonal micellar state may arise from both the high-curvature micelle structure and the conformationally extended (away from the lipid headgroups due to temperature-induced alterations in the conformational state of the tethered polymer)[12] PEG chains, factors that serve to promote greater exposure of the azo-dye to the bulk water phase, thereby providing a more polar environment for it. Alternatively, in the lamellar, gel phase, the PEG chains adopt a more compacted brush conformational state with significant entanglement,[13] thus forming a "barrier" layer between the headgroup region and the bulk water channel and creating a less polar local environment for the chromophore. The temperature-induced shift in the position of the absorption maximum is observed over a wide range of concentrations (0.0053−0.18 mM). Comparison of the magnitude of the shifts between the highest (0.18 mM) and lowest (5.0 μM) chromophore concentrations shows that while the absorption band positions agreed very well (all centered ca. at λ = 515 nm) in the cold phase (10 °C) at higher temperatures (30 °C), which place the complex fluid well into the lamellar gel phase, the peak maximum is dependent on both chromophore concentration and the MW of the grafted polymer. Specifically, a blue shift in the absorption maximum from 500 nm at low chromophore concentrations (0.0053−0.043 mM) to λ = 493 nm at the highest concentration

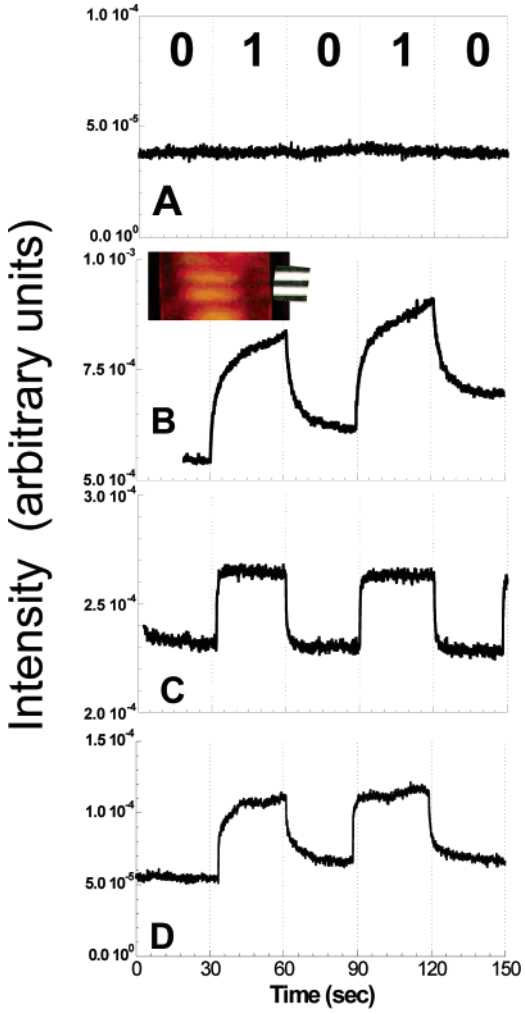

Figure 3. Time evolution of the optically induced birefringence during and after illumination with a 532 nm light recorded on azo-dye (0.18 mM) doped complex fluid at selected temperatures: (A) 12 and (B) 22 °C. Inset photo shows line patterns of increased birefringence written with a shadow mask throughout a 3 mm thick sample viewed through cross polarizers. (C) 28 °C. (D) Time evolution of the optically induced birefringence during and after illumination with a 532 nm light recorded on azo-dye doped PMMA thin film at room temperature.

studied (0.18 mM) is observed and may signal the onset of chromophore aggregation (i.e., the formation of H-aggregate structures).[20] In contrast, a red shift of the peak position (λ = 499−506 nm) was observed with decreasing molecular weight of the grafted PEG chains (from PEG5000 to PEG2000), for samples prepared with the same chromophore concentration (ca. 0.050 ± 0.001 mM). The MW-dependent shift in the position of the absorption band confirms that the local environment of the azo-dye in these systems is primarily controlled by the PEG chains.

The influence of the complex fluid architecture on the photoinduced response of the encapsulated azo-dye was evaluated using a standard pump (diode laser, λ = 532 nm)−probe (He−Ne, λ = 633 nm) laser system which permits determination of the time-dependent, photoinduced optical birefringence of the dye-doped complex fluid in three distinct structural states.[21] The variation in photoinduced response for the complex fluid-based materials evaluated below (T = 12 °C), at (T = 22 °C), and above (T = 28 °C) the phase transition temperature is presented in Figure 3, along with analogous results for azo-dye doped PMMA. When the complex fluid sample is maintained at 12 °C (i.e., in the 2D hexagonal structure), no photoinduced birefringence signal is observed upon illumination with 532 nm linearly polarized light. Thus, in this state, no preferred molecular orientation is achievable, and optical data storage is therefore not possible. The lack of photoinduced birefringence in this state is consistent with isotropically ordered chromophores with high rotational mobility (low-viscosity state) that cannot be ordered.

As the sample temperature is raised, a significant increase in the baseline signal is observed (arising from both scattering and intrinsic sample birefringence). In addition, a strong birefringence signal increase is "written into" the sample upon illumination with linearly polarized 532 nm light, generating a signature "sawtooth" pattern. Upon termination of photoexcitation, decay in the birefringence signal is observed, indicating molecular relaxation of the azo-dye molecules. The signal does not, however, return to baseline, indicating that some population of chromophores remains oriented and that information has been "written into" the material. Using a shadow mask in conjunction with illumination allows persistent patterns (areas of increased birefringence) to be written into this phase of the complex fluid (Figure 3B, inset). (It is noted that the formation of persistent photoimages in lyotropic liquid crystals (LLC) has been previously reported and has been attributed to a combination of the photoinduced alignment of the guest chromophore and its synergistic interaction with the LLC to promote orientation of the (LLC) aggregate structure.[2b] A similar mechanism may contribute to the formation of the observed persistent photoimage in the complex fluids. Further studies employing in-situ SAXS to monitor the phototriggered alignment of the complex fluid mesostructures (aggregates) will be the focus of future work.) The residual signal can readily be erased either by cooling the sample to below the phase transition temperature or by illuminating with circularly polarized light. As expected, the magnitude of the photoinduced optical birefringence is dependent upon the pump power and chromophore concentration. The time evolution of the optically induced birefringence is best modeled as a biexponential, suggesting a two-component (fast and slow) processes. Biphasic kinetics are common in glassy polymer dynamics and suggest the existence of populations of chromophores occupying two different host microenvironments: one that allows for facile molecular motion and a second that is more restrictive.[22] The slow component of the writing time (rise) under the experimental conditions is ca. 15 s, a value typically observed for azo-dye doped LBL films.[23,24] The optical response is, however, longer than that observed for dye-doped amorphous polymer thin films, such as the azo-dye doped PMMA, for which a value of 5.3 s was determined (Figure 3D). The decay of the optically induced birefringence after cessation of the pump laser was determined to be 7.8 s, a value that compares favorably with the dye-doped polymer (6.8 s).

Upon illumination of a sample that is completely in the lamellar gel phase (at 28 °C), a considerably weaker response that exhibits a rapid increase in the birefringence that reaches a plateau is observed. (Note that here the sample possesses intrinsic birefringence but scatters light less.) Once the pump beam is turned off, the signal rapidly returns to the baseline, indicating that informa-

tion is not stored in the material. Here, the material undergoes rapid "on"/"off" switching (ca. 2 s). This rapid switching seems to indicate that the intercalated dye molecules can rapidly orient and relax back, unhindered by the matrix or self-association. Both the weakness and fast kinetics of the optical response indicate major changes in chromophore local environment. The fast response could indicate that under these conditions only a small fraction of chromophores are able to undergoe local rotation upon illumination. Environmentally (host) constrained chromophores could presumably arise from confined/constrained molecules either through self-association or by densely grafted (here 8 mol %), entangled, membrane-associated PEG-grafted chains that would restrict the free volume and hence molecular freedom. The degree of chromophore orientation can thus be controlled by the host (complex fluid).

This work demonstrates the potential of hierarchical self-assembly as a means to prepare stimuli-responsive (here, thermoresponsive) materials that can be repeatedly cycled between three distinct architectures and that allow for control of the photochromic properties and photoresponse of dye doped materials. The complex fluid-based system described here offers several key advantages over amorphorous polymeric materials previously studied for encapsulation of a photoisomerizable dye, among them discrete physical/structural states that can be used to control the photoresponse (i.e., one optimized for optical storage and one for short write/erase cycles), good signal-to-noise ratios, and, most importantly, low-cost fabrication empolying self-assembly of molecular amphiphiles. In addition, the proven biocompatibility of these materials opens the possibility of developing photoaddressable materials based upon biomolecules (proteins) and will be the focus of future studies. Such a system, by permitting information to be stored throughout a three-dimensional volume, would provide a means to overcome a significant limitation of current polymer-based systems.

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(15) Complex fluids were prepared as quaternary compositions consisting of 0.823 ± 0.001 weight fraction water (Φ_w), 0.023 ± 0.0015 weight fraction surfactant (Φ_s), and 0.154 ± 0.021 weight fraction lipid (Φ_L). All samples were prepared such that the polymer-to-phospholipid ratio was held between 8 mol %. Hydration of the solid components in deionized water was accomplished by repeated cycles of heating (50 °C), vortex mixing, and cooling on an ice bath until sample uniformity was achieved. 4-Nitro-4′-(dimethylamino)azobenzene (TCI America, Portland, OR) was introduced as a solid into the preformed complex fluid and dissolution promoted by cycling through the phase transition. Dye-doped poly(methyl methacrylate), PMMA (MW 120 000, Sigma-Aldrich, St. Louis, MO), was prepared by dissolution of the polymer and chromophore at 2 wt % in toluene. Thin solid films were prepared by spin-coating the prefiltered solution onto clean glass substrates. After evaporation of the solvent at room temperature, the films were dried under vacuum to ensure removal of the casting solvent. Film thicknesses were between 0.5 and 1 μm thick as determined by measurement using a profilometer.
(16) Thermal properties were measured by differential scanning calorimetry (DSC) at heating rates of 2 °C/min on a TA Instruments Q100 interfaced to a refrigerated cooling system. Instrument calibration was performed using an indium standard. Weighed amounts (5−10 mg) of the complex fluids were sealed in aluminum pans and equilibrated at 0 °C for 10 min. Phase transitions were recorded over a range from −5 to 70 °C. Successive heating scans were found to yield identical results. The transition temperature (T_m) was taken as the temperature at the peak of the endothermic transition.
(17) UV−vis absorption spectra were recorded on a Cary model 5G UV−vis−NIR spectrophotometer or an Ocean Optics (Dunedin, FL) SD2000 fiber-optic spectrometer that was outfitted with a Peiltier capable of controlling the sample temperature between 10 and 35 °C ± 0.7 °C.
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(21) Optical induced birefringence experiments were performed using a diode laser (Edmund Optics, Barrington, NJ), $\lambda = 532$ nm. 1 mm incident beam diameter, max power ca. 2 mW, as the pump/write laser. Glan Taylor polarizers and quarter waveplates were inserted into the optical train to control polarization. He−Ne laser (JDS Uniphase), $\lambda = 633$ nm, 2mW, passed through the crossed polarizers was used as the probe/read beam. A silicon photodiode detector (unbiased, 100 mm^2 area, Edmund Optics) covered with a 630 nm interference band-pass filter (Oriel, Stanford, CT) was used to record the voltage (intensity) using an analog−digital converter (PMD-DAQ & SOFTwire program, Measurement Computing, Middleboro, MA). Measurements made on the complex fluids were carried out in a 3 mm square quartz cuvette employing a custom-built Peilter stage for temperature control (±1 °C).
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