Articles

Solid-State Solutions: Polymer-Encapsulated Reverse Micelles Containing Dye Solutions

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Monomer solutions of styrene and divinylbenzene containing the surfactant Aerosol-OT were found to form stable reverse micelle aggregates with the addition of water or formamide as a polar solvent. These aggregates were stable below ca. 40 °C, and thermally initiated, radical polymerizations carried out below this temperature resulted in highly transparent polymer monoliths. These polymeric solids were of optical quality and could be easily shaped and polished. The emission of tris(2,2′-bipyridyl)dichlororuthenium(II), placed inside these reverse micelles, was used as a semiquantitative probe of the chemical environment within the micellar aggregates and was studied by fluorescence spectroscopy. Both the spectral characteristics and the lifetime of the emission from polymeric samples indicated a solution environment for the dye inside the polymer-encapsulated reverse micelles. These materials should be good candidates for the incorporation of photoresponsive dyes requiring a solution-state environment to act effectively as signal transducers or memory elements.

Introduction

Our group has studied a wide range of synthetic dye systems based on polypyridine complexes of ruthenium(II).[1−6] Solutions of a number of these dyes have shown dramatic optical changes in response to relatively weak magnetic fields, and as such, have great potential as optical-magnetic sensors.[7] However, the photophysical processes responsible for the magnetic field sensitivity involve a large degree of intramolecular motion.[8,9] This degree of freedom for molecular motions is only afforded by a fluid environment. Simply freezing dye molecules of this type in a glassy polymer results in dramatically different photophysical properties exhibited by these dyes.[8] For this reason it is desirable to develop a solid-state material in which a dye solution is encapsulated. Ideally, this material would be of optical quality—not light scattering—and exhibit photophysical properties identical to that of the same dye in solution. The goal of this research was the development of just such a material.

To avoid the complications posed by a true solid, the material developed in this study contained both a solid and a liquid phase. The major phase is made up of a continuous cross-linked polystyrene network. Polystyrene was chosen because it is not highly absorbing in the visible region of the spectrum, it has excellent barrier properties to prevent oxygen gas permeation, and styrene is a sufficiently nonpolar monomer to phase-separate from a number of polar solvents.[10] The minor phase consists of discreet domains of polar solvent, either water or formamide and containing a probe dye. The fluorescence lifetime of tris(2,2′-bipyridyl)dichlororuthenium(II) (Rubpy) varies from 0.6 μs to 5 μs between a solution and solid-state environment, respectively, making it an excellent choice for a probe dye.[11]

The refractive indices of the major and minor phases are quite different (1.55 versus 1.33 for styrene and water, respectively), so the size of the dye-containing, polar solvent domains must be less than ca. 300 nm to avoid light scattering.[12] To ensure the proper formation of liquid domains of appropriate size, a reverse micelle-

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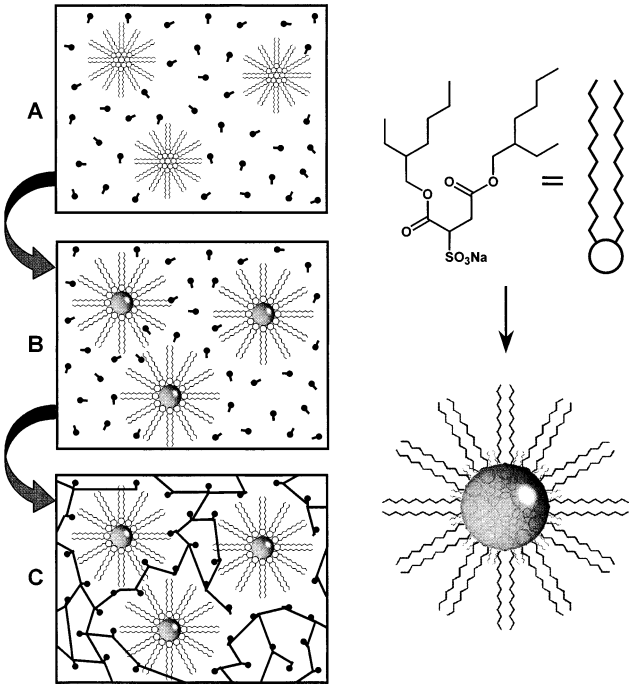

Figure 1. Materials synthesis strategy (left). First, surfactant is dissolved in the monomer (A), then dye solution is injected (B), and polymerization results in encapsulated reverse micelles (C). On the right is the structure of AOT along with a schematic representation of its structure and the structure of a reverse micelle.

forming surfactant is used to direct the phase segregation. This materials synthesis strategy is depicted schematically in Figure 1 (left).

The surfactant sodium bis(2-ethylhexyl)sulfosuccinate, also known as Aerosol-OT (AOT), has been well studied and is known to form spherical aggregates known as reverse micelles when dissolved in a number of nonpolar solvents.[13] Figure 1 (right) shows the structure of AOT along with a schematic representation of a reverse micelle. The minimum concentration of AOT at which these structures are formed—the critical micelle concentration (CMC)—depends on the solvent, but is generally in the 10^{-4} M range.[13] Concentrations of AOT well above the CMC are capable of sequestering water and a few other polar solvents in the ionic interior of the reverse micelle. In many cases, the size of the reverse micelle structure is directly proportional to the molar ratio of water to AOT (W_0), and the diameter of structures ranges from a few nanometers to tens of nanometers.[14]

Zhu et al. used AOT to form reverse micelles in styrene−divinylbenzene mixtures.[15−18] They found that by varying W_0, the reverse micelle size imprinted a porosity into the material that was easily controlled. UV-initiated radical polymerization resulted in highly cross-linked polymer solids which were finely ground and washed. Characterization of the powders revealed a pore volume that scaled proportionally with W_0. The stated purpose of these materials was as gel permeation chromatography column materials, and as such, no mention was made of the optical properties of the materials. Nonetheless, this work provided an excellent starting point for the development of the materials in this study. An adaptation of this procedure was used to obtain solid-state materials exhibiting the photophysical properties of the corresponding dye solutions. This adaptation involved the thermal-initiated radical polymerization of styrene and divinylbenzene to encapsulate reverse micelles containing dye solutions.

Experimental Section

Materials. All solvents other than deionized water were purchased from Fisher at spectroscopic grade or better purity. Activated neutral alumina, sodium bis(2-ethylhexyl)sulfosuccinate (AOT), tris(2,2′-bipyridyl)dichlororuthenium(II) hexahydrate (Rubpy), 2,2′-azobisisobutyronitrile (AIBN), styrene, and divinylbenzene at ≥97% purity were purchased from Aldrich and used as received. 2,2′-azobis(2,4-dimethylpentanenitrile) (ADPN) was kindly donated by Professor Marc M. Greenberg.

Monomer and Dye Solution Preparation. Both styrene and divinylbenzene (DVB) were inhibited with ca. 10 ppm of 4-*tert*-butylcatechol as received. Just prior to use, the monomers were "dehibited" using a short column of Dehibit-100 (Polysciences Inc.) followed by a short column of alumina. The freshly dehibited styrene and DVB were mixed in a 2:1 volume ratio in a 5-mL glass vial, and the surfactant AOT was added to a concentration of 50 mM. A dye solution of 15 mM Rubpy in either water or formamide was injected via microliter syringe in varying amounts (2−36 μL) to the surfactant-containing monomer mixture (typically 2 mL). As a final component, ca. 1 wt % of the radical initiator, AIBN or ADPN, was added to the mixture. Samples prepared in this way were degassed with dry nitrogen and vigorously stirred for ca. 10 min on a Vari-Whirl mixer (VWR).

Reverse Micelle Analysis. Dynamic light scattering (DLS) was used to measure the size of the reverse micelles formed in the above solutions. The radical initiator was left out of the solution until after the measurements were taken. All samples were filtered into the sample cuvette to remove interfering particulate matter. The filtration was accomplished using a 250-μL syringe equipped with a Teflon-housed 0.02-μm Anodisc 13 membrane (Whatman).

Polymerization. Thermal initiation of polymerization was carried out using a variac-controlled heating mantle filled with sand and monitored by a mercury thermometer. This apparatus was brought up to the desired temperature prior to sample introduction. The polymerization temperature was 35−37 °C. All samples were cured for a minimum of 48 h at the above temperatures. The resulting polymeric monoliths were removed by carefully breaking the glass vial in which they were contained. These monoliths were cylindrical in shape, but grinding and polishing afforded flat orthogonal surfaces of high quality for optical measurements.

Fluorescence Lifetime Measurements. The lifetime of fluorescent emission from Rubpy contained within polymer-encapsulated reverse micelles was measured on the following instrumentation (see S. I.1 in Supporting Information for details). The frequency-tripled output of a Spectra-Physics LAB-190 Nd:YAG laser produced a train of ca. 8 ns pulses at 30 Hz and ca. 1.5 W of power. This output pumped a methanolic solution of Coumarin 450 (Exciton) dye in a Spectra-Physics PDL-3 dye laser. The typical output from the dye laser was a corresponding train of pulses ca. 50 mW in power at 450 nm.

The excitation beam was directed onto the sample—a quartz cuvette containing a solution or a shaped and polished

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monolith—parallel to the surface-normal of one face. The fluorescence emission was collected from a face with a surface-normal orthogonal to the excitation beam. This emission was collimated and focused through an appropriate cutoff filter onto the entrance slit of a Jarrell Ash model 82-410 monochromator set to pass 600-nm light. The light that exited the monochromator was detected with a Hamamatsu model R2496 photomultiplier tube operated at ca. 500 V.

The output from the photomultiplier tube was sent to a Tektronix TDS 620B digital oscilloscope. A Thorlabs DET210 fast photodiode monitoring scattered laser light was used to trigger the oscilloscope. Signal averaging of 200 sets of decay curves was used to improve signal-to-noise levels. The output from the oscilloscope was saved to disk as $x-y$ data pairs in ASCII format. Using a computer running Microsoft Windows XP, these data were organized and truncated in Microsoft Excel; and graphical and single-exponential regression analysis was carried out in SigmaPlot version 2000.

Instrumental. A DynaPro molecular sizing instrument (Protein Solutions, Inc.) was used to obtain DLS data for the determination of reverse micelle size in solution. Thin sectioning of polymeric samples was accomplished with a Reichert Ultracut E ultramicrotome using a freshly made glass knife. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2000 EX-II microscope. Shaping and polishing of samples was accomplished on a Buehler variable-speed polishing wheel with a variety of abrasive surfaces. Fluorescence emission spectra were obtained using a Horiba Fluorolog-3 spectrofluorometer.

Results and Discussion

AOT−Monomer Solutions. Reverse micellar structures formed from AOT and water are usually studied in aliphatic, nonpolar solvents such as isooctane.[13,14] Despite the foreknowledge of the work of Zhu et al. it was necessary to confirm that reverse micelle structures could reliably be formed in styrene/DVB mixtures. To test this and to test formamide as an alternative polar solvent, samples were prepared in which 8 μL of either polar solvent was injected into 2 mL of AOT-containing styrene/DVB. The initial injected volume of polar solvent phase separated from the monomer, but after mixing, the solution appeared macroscopically homogeneous and was completely transparent—a good indication that reverse micelles had formed.

Figure 2 shows the raw data that were obtained from the DLS sizing instrument for the above samples. Ten data samplings were obtained for each solution. The horizontal error bars represent the range of sizes of all observed particles within the sampling time frame. The data points themselves are simply the median values of this range. For consistency, the average of all median data points was taken as the average measured radius.

Treating the DLS data in this way, a number of other samples were prepared in which W_0 was varied and the average radius was determined. Figure 3 shows the two plots for samples containing water or formamide. The average radius is plotted as a function of W_0 for each set of samples. Although the relationship between size and W_0 does not appear to be linear, there is clearly a trend of increasing size with added polar solvent. This "nonideal" behavior has been observed both with nonaliphatic solvents—such as benzene and toluene—as the major phase and with polar solvents other than water in the minor phase.[13,14] Nonetheless, these data demonstrate the formation of reverse micelles using water and formamide as the minor phase in AOT-styrene/DVB solutions.

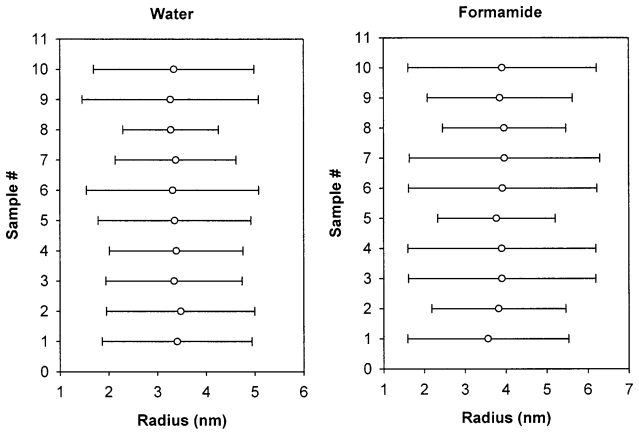

Figure 2. Raw data obtained from DLS determination of reverse micelle size. These two samples were prepared by injecting 8 μL of the corresponding polar solvent into a 2-mL sample of AOT-containing monomer. Ten data samplings were obtained for each monomer sample. The error bars represent the range of sizes observed by the instrument within the sampling time, and the data points are the median values of this range.

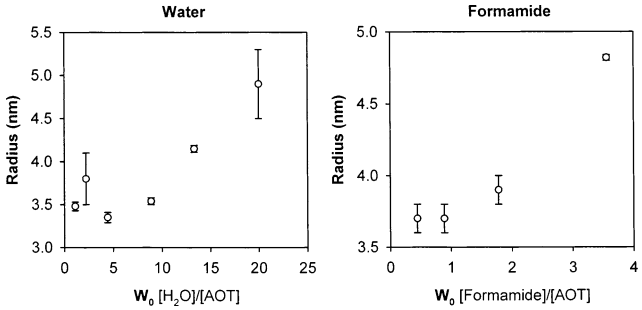

Figure 3. Plots of reverse micelle radius as a function of W_0 for water and formamide as the polar solvent inside reverse micelles. The radius values were calculated as the average of the median values from the DLS data. The error bars represent one standard deviation.

Polymerization Conditions. Thermal initiation was employed in these studies because it requires no special UV-exposure apparatus. Samples can simply be prepared in standard glass vials, heat-cured, and removed. The thermal initiator most commonly employed in thermally initiated polymerization is AIBN. However, the decomposition kinetics of AIBN make it necessary to run a radical initiation reaction at temperatures above 40 °C, and temperatures of 60−70 °C are commonly used.[10] However, all attempts to encapsulate reverse micelles under standard AIBN initiated conditions failed. The polymer monoliths that resulted were highly light scattering and opaque.

The thermal decomposition kinetics of ADPN make it an effective initiator at 35 °C. We found that polymerizations run below 40 °C using ADPN as the radical initiator resulted in polymer monoliths that were transparent and identical to the appearance of the starting monomer solution. All subsequent polymeric samples employed in the following research were prepared using ADPN as the initiator.

Monolith Characterization. TEM was used in an attempt to visualize the pore structure of polymer monoliths. Ultramicrotome sections of ca. 100-nm thickness were obtained, but these sections proved to be too thick to obtain images at the magnification necessary

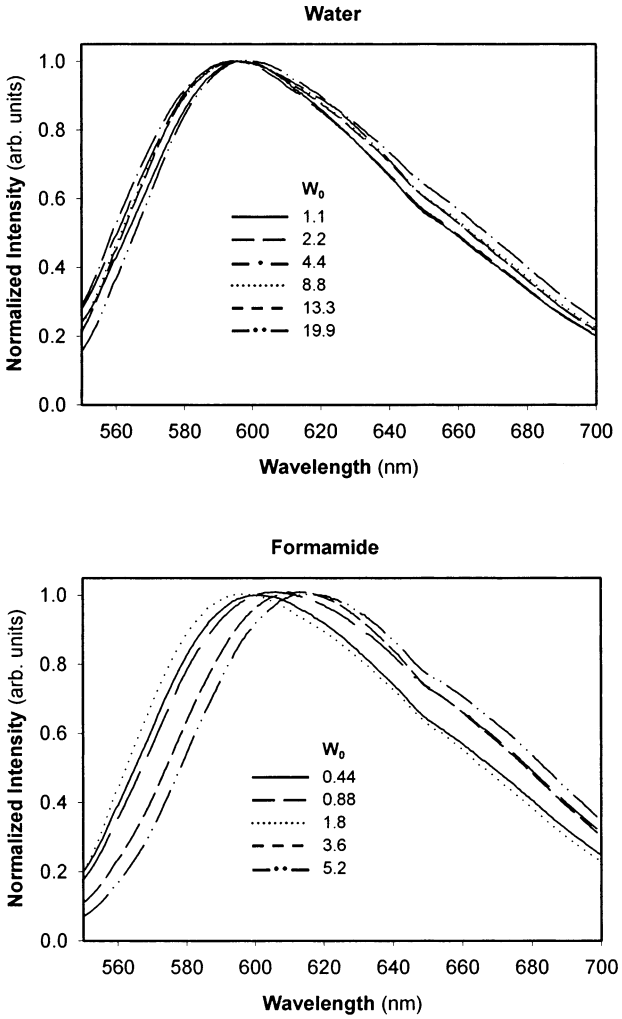

Figure 4. Emission spectra of polymer-encapsulated reverse micelles containing Rubpy in water (top) or in formamide (bottom). Each spectrum corresponds to a sample with differing W_0 (see legends).

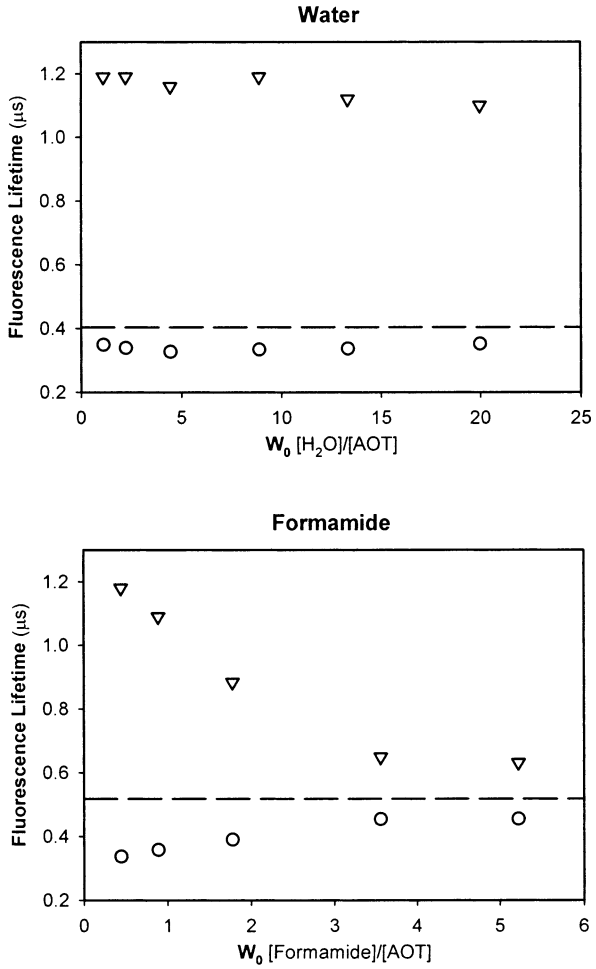

Figure 5. Plots of the fluorescence lifetime of Rubpy in water (top) or formamide (bottom) as a function of W_0. The lifetime measurements were made both prior to polymerization (○) and after polymerization (▽). The dashed line in each graph represents the measured fluorescence lifetime of Rubpy in the respective bulk solvent.

to resolve individual reverse micelle-imprinted pores. The best micrograph image obtained was taken in a very thin portion of a cut section, but no pore structure could be resolved (see S. I. 2 in the Supporting Information for micrographs).

Fluorescence Spectroscopy. Figure 4 contains the emission spectra from two sets of monoliths: one containing aqueous Rubpy (top) inside the reverse micelles, and the other containing Rubpy in formamide (bottom). The samples within each polar solvent set were prepared with a range of W_0 values, and thus contained increasing amounts of Rubpy as W_0 increased. We expected the peak intensity of the emission to scale with W_0, however, the irreproducible placement of samples in the spectrofluorometer resulted in a large degree of variance in the measured intensity for each sample. To simplify visual comparison of spectra, each set of data was normalized at its peak intensity (λ_{max}). Basically, the emission characteristics of these samples—a single broad emission band with a lack of fine structure—indicate a solution environment for the dye in both water and formamide.[11] Water-containing samples show almost no spectral changes—λ_{max} varies by at most 6 nm—as a function of W_0; whereas formamide-containing samples show a very clear redshift of 20 nm with W_0 values between 0.44 and 5.2. These data are in qualitative agreement with the fluorescent lifetime data discussed below.

Fluorescence Lifetime. The fluorescence lifetime of Rubpy in solutions encapsulated by reverse micelles was measured and used as a semiquantitative indicator of the nature of the environment surrounding the dye—this lifetime being a few hundred nanoseconds in solution and a few microseconds in solid (vide supra). It is also known that the fluorescence of Rubpy decays with a single exponential in solution and a multiexponential in the solid -state.[19] In the data that follow, all decay curves fit well ($R^2 > 0.95$) to a single exponential. Figure 5 shows the fluorescence lifetime data obtained as a function of W_0 for both water (top graph) and formamide (bottom graph) as the polar solvent. To determine the effect of polymerization, data were obtained both prior to and after polymerization for each sample. As a basis for comparison, the fluorescence lifetime was also measured in bulk water and formamide; this value is represented in the respective graphs as a dashed line.

When water is used as the polar solvent, the monomer solutions exhibit a fluorescence lifetime that is within

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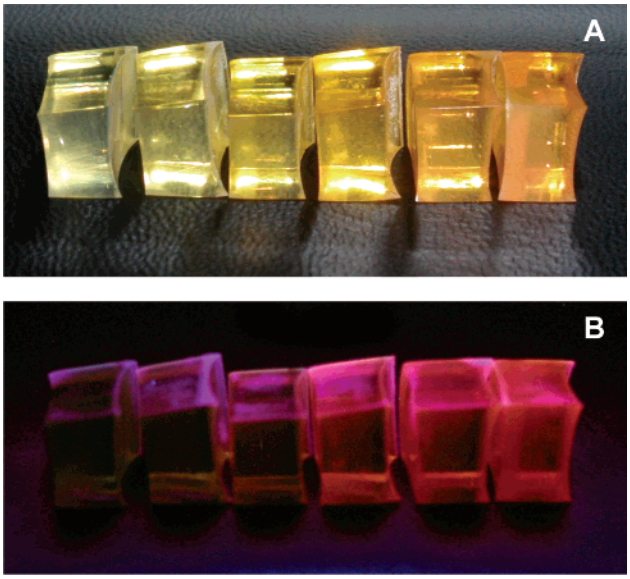

Figure 6. Polished monoliths of polymer-encapsulated reverse micelles containing increasing (left-to-right) concentrations of aqueous Rubpy solution under normal (A) and UV (B) illumination.

ca. 60 ns of the lifetime measured in bulk water. This is true irrespective of the W_0 value of the sample—within the measured range. After polymerization, this lifetime increases to ca. 1.15 μs, and again is relatively invariable as a function of W_0. These data suggest two things: (1) the chemical environment surrounding the dye is relatively unchanged by the addition of more dye solution (i.e., larger reverse micelles), and (2) polymerization results in a longer lived excited state (by ca. 800 ns) indicating a chemical environment intermediate between solution and solid.

Monomer solutions and polymeric solids containing formamide dye solutions exhibited somewhat different characteristics. Monomer solutions again exhibited fluorescence lifetimes close to the lifetime measured in bulk formamide. However, there appears to be a trend in which the lifetime increases and approaches the bulk solvent value as a function of W_0. Again, polymerization results in an approximately 800 ns increase in the lifetime. However, as W_0 increases, the lifetime decreases and approaches to within ca. 110 ns of the bulk solvent value. For both monomeric and polymeric samples these data suggests that, as the reverse micelle's size increases, the chemical environment surrounding the dye becomes increasingly similar to bulk solvent conditions.

Although the results obtained with water-containing samples are not presently understood, the results from formamide-containing samples were qualitatively as expected. It is intuitive that the dye's environment approaches bulk solvent properties as the reverse micelles increase in size. Notwithstanding the less intuitive results obtained with water, both sets of materials exhibit characteristics that fulfill the requirements established at the outset of this research. Figure 6 shows photographs of the series of water-containing monoliths under room light (A) and UV (B) illumination. These photographs clearly demonstrate the excellent optical quality of the materials developed in this study.

Conclusions

The primary objective of this effort was the development of a solid optical material incorporating a dye whose photophysical properties correspond to that of the dye in a fluid environment. This was achieved through the polymer encapsulation of reverse micelles containing dye solutions. AOT−monomer solutions were found to form stable reverse micelle aggregates with the addition of water or formamide as a polar solvent. These aggregates were stable below ca. 40 °C, and polymerizations carried out below this temperature resulted in highly transparent polymer monoliths.

Both the fluorescence spectra and lifetime of emission of Rubpy in polar solvent containing reverse micelles indicated a solution environment for the dye. The observed emission characteristics differed before and after polymerization, and differed between the water- and formamide-containing samples, but in each case the results support the conclusion that the dye is surrounded by a fluid environment.

Other optically responsive dyes, for example ones that exhibit sensor or memory element characteristics in solution but not in the solid-state, could now be investigated for use in solid-state applications. These materials combine the freedom of motion on a molecular scale afforded by a solution environment, with the advantages of a solid polymer material.

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Supporting Information Available: A diagram of the instrumentation used to obtain fluorescence lifetimes and TEM micrographs of monolith sections (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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