# Dynamics of Spin-Correlated Radical Pairs in Non-Ionic Surfactant Solutions

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*Received: July 24, 2002; In Final Form: February 14, 2003*

Time-resolved (CW) electron paramagnetic resonance spectroscopy (TREPR) has been used to investigate the diffusional dynamics of radical pairs created in micelles made from nonionic, poly(ethylene glycol) (PEG)-based surfactants (Brij-35, Triton X-100, and Cremophor EL). Photoexcitation of solubilized perdeuterated benzophenone (BP) at 308 nm leads to hydrogen atom abstraction by triplet BP from the surfactant chains. Spectral simulation and comparison to other PEG radicals shows that H-atom abstraction is taking place in the PEG *outer shell* of Brij-35 and Triton X-100 micelles rather than in the alkyl chain core. The TREPR spectra exhibit a temperature-dependent superposition of chemically induced electron spin polarization (CIDEP) patterns. In Brij-35 solutions, radical pair mechanism (RPM) multiplet polarization is predominant at room temperature, but strong spin-correlated radical pair (SCRP) polarization is observed at temperatures above 40 °C. In Triton X-100, the triplet mechanism (TM) dominates at all temperatures and delay times, with some evidence of $S-T^-$ SCRP polarization at longer delay times. The results are discussed qualitatively in terms of a spectral exchange model that uses spin product operators. Using known micellar dimensions, the diffusion coefficient of the radicals in the micelle interior and their escape rates can be estimated. Radicals of identical structure produced from pure PEG and aqueous PEG solutions show ordinary RPM polarization at all temperatures, and these spectra are used to confirm the photochemical mechanism and to provide characterization data (hyperfine couplings) for the radicals. The BP/Cremophor EL system was TREPR silent most likely because of triplet quenching impurities.

## Introduction

A detailed understanding of dynamic effects in magnetic resonance spectra of interacting radicals is gradually emerging from our laboratory[1−3] and several others.[4−6] Many of these studies involve the time-resolved electron paramagnetic resonance (TREPR) observation of interacting radical pairs created in micellar solution.[7−9] Micellar solubilization is convenient for restricting free radical diffusion and increasing the probability of radical encounters. When radical pairs are created using a pulsed laser and detected in a time-resolved fashion, several mechanisms of chemically induced electron spin polarization (CIDEP)[10] can be observed: the triplet mechanism (TM),[11] the radical pair mechanism (RPM),[12,13] and the spin-correlated radical pair mechanism (SCRP).[14] All three mechanisms exhibit unique intensity patterns which are easily distinguished by spectral simulation.

In previous work from our laboratory, we reported TREPR results from photochemically active surfactants which were large (60 × 30 Å ellipses) and internally viscous (∼70 cP).[9,15] The ensuing radical pairs were devoid of escape processes, and under these conditions, an interesting phenomenon was observed: the "ordinary" RPM polarization normally associated with noninteracting radicals was observed at early delay times after the laser flash or at low temperatures, whereas the antiphase structure (APS) attributed to the SCRP mechanism was observed at later delay times or at higher temperatures. The APS is quite distinct from the RPM multiplet pattern (low field emissive, high field absorptive) in that each individual hyperfine line in the spectrum is split into an emissive/absorptive doublet by the exchange interaction *J*. However, in many cases, the SCRP and RPM patterns are superimposed in any given spectrum, depending on the delay time, temperature, and micelle size.

The SCRP/RPM superposition phenomenon has recently been modeled theoretically using spin product operators and a spectral exchange technique, and the model acurrately accounts for the time evolution of the interacting and noninteracting states of the radical pair.[16] From such an analysis, a diffusion coefficient for the radicals in the micelle of interest can be extracted. In general, the superposition phenomenon is observed in systems undergoing slow motion with a weak exchange interaction. The SCRP polarization remains EPR silent until the rate of encounters increases or enough time has elapsed that the majority of the radicals exist at long distances where the exchange interaction is small (this is called the "filling out" of the micelle).

The superposition pattern is most typically observed in large micelles with anionic headgroups, and although it was not recognized as such at the time, it is clearly visible in TREPR spectra of correlated radical pairs created in cationic micelles reported by Levstein and van Willigen in 1993.[17] The micelles used for that study were also large and internally viscous. For more common anionic micelles such as sodium dodecyl sulfate (SDS), the structures are small and not extremely viscous; therefore, the motion is never very slow, even at room temperature.[18] Also, in SDS the time taken to fill out the micelle is short and escape processes are significant. For these reasons, the superposition phenomenon is not observed in small systems. In this paper, we extend our investigation of RPM/SCRP superposition to surfactants with nonionic headgroups. The surfactants consist of a hydrophobic alkyl chain and a hydro-

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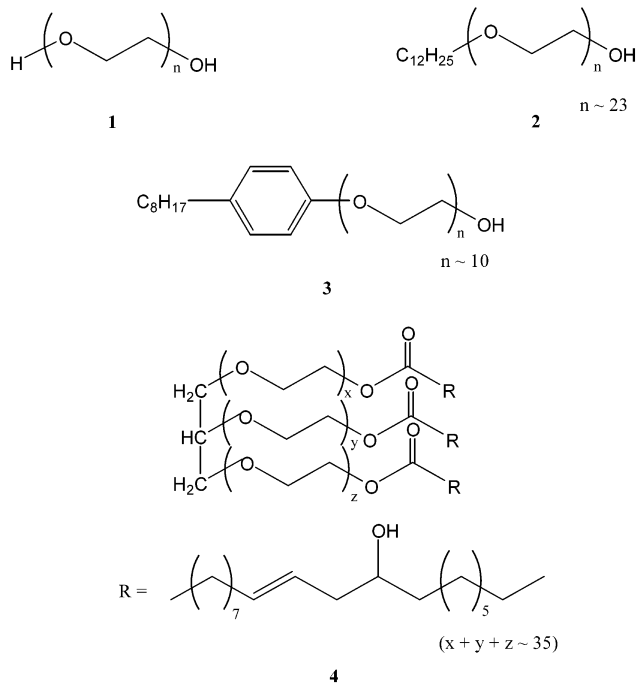
10.1021/jp026601p CCC: $25.00 
Published on Web 04/11/2003

**SCHEME 1**




philic shell made up of poly(ethylene glycol) (PEG) chains. The structures we have investigated are shown in Scheme 1. Many TREPR experiments have been carried out in these surfactants previously,[19−23] but the structure and dynamics of radicals created from the micelle itself have not been reported. Batchelor et al. have studied MARY and RYDMR spectra from radical pairs produced in surfactant **3.**[24] To the best of our knowledge, TREPR characterization data has not been published for surfactant free radicals arising from H-atom abstraction in PEG-based micelles.

The molecules in Scheme 1 have a variety of interesting commercial uses, particularly in the pharmaceutical and food industries. Compound **1** is PEG itself, which is used as a suppository base in many medications[25] and to modify transport properties in electrochemical reactions.[26] Compound **2** is available commercially under the trade name Brij-35 and consists of a PEG hydrophilic chain covalently linked to a $C_{12}$ alkyl chain. It is used in fragrance emulsions,[27] in dialysis applications,[28] and in the food industry as an adhesion modifier in sausage casings.[29] Compound **3** is called Triton X-100, which is used extensively in biochemical extractions to solubilize membrane proteins[30] and is also used as a spermicide.[31] Compound **4**, Cremophor EL (CrEL), is used in the pharmaceutical industry as a drug delivery agent for water-insoluble medications.[32] Because of these diverse and biologically relevant applications, a study of diffusion and escape properties of solubilized molecules in these structures is warranted.

We seek to assess the generality of the SCRP/RPM superposition phenomenon as a function of headgroup structure and charge (or lack thereof) and micelle shape and size. For example, by studying the TREPR spectra of the free radicals as a function of temperature and time, we can estimate the influence of the headgroup on the escape rate or the reencounter rate. If the superposition is indeed present for radical pairs created in these structures, we also want to determine if its appearance can be manipulated by raising or lowering the temperature of the solution and if a diffusion coefficient can be estimated from the temperature and time dependence of the spectra.

## Experimental Section

Continuous wave TREPR experiments were performed as previously described.[33] All spectra were recorded on a JEOL USA Inc. JES RE-1X X-Band (9.5 GHz) EPR spectrometer outfitted with a fast preamplifier and a low noise GaAs FET microwave amplifier (25 dB gain). The microwave power incident on the samples was 10 mW for all experiments. Solutions were bubbled with nitrogen and circulated through a flat cell of 0.4 mm optical path length centered in a rectangular Varian $TE_{103}$ optical transmission cavity. Flowing prevented sample depletion and heating. Laser excitation at 308 nm used a Lambda-Physik LPX 100i excimer laser, with a repetition rate of 60 Hz, which ensured complete radical decay between successive laser shots. The pulse energy hitting the sample was ~20 mJ. Spectra were collected at a fixed delay time after the laser flash using a Stanford Research Systems boxcar integrator (100 ns gates), and the external magnetic field was swept over 2 to 4 min. All spectra and simulations shown have a sweep width of 80 G except as noted.

For variable temperature experiments, the sample was circulated through Teflon PFA 1/8″ tubing insulated with polyurethane foam tape. The tubing passed from the pump through a copper coil wrapped with heating tape, which was placed immediately below the entrance to the microwave resonator. Temperature was controlled using a feedback circuit between a variable power temperature controller (Omega, Inc.) and thermocouples positioned at the entrance and exit of the flow cell. Temperatures reported are averages of measurements at the top and bottom of the cell. Temperature gradients of 2 °C were typical, and all temperatures reported here are ±1 °C.

PEG, Triton X-100, and Brij-53 (Aldrich), and CrEL (Sigma) were used as received. Water was purified by passage through a Millipore Milli-Q water purification system. Benzophenone-$d_{10}$ (BP) was prepared from benzene-$d_6$ (Aldrich, 99.5%-d) according to literature methods[34] and was purified by crystallization from hexane. Surfactant solutions were prepared to final concentrations of 6.0 wt % in water. Benzophenone-$d_{10}$ was added to warmed surfactant solutions with vigorous stirring for approximately 1 h to a final concentration of 1.6 mM.

## Results and Discussion

The rationale for this study centers on the concept of micellar confinement and observation of the resulting CIDEP polarization patterns. However, it is instructive to first investigate the behavior of radicals of similar structure in free solution, a condition under which SCRP polarization should be absent. Scheme 2 outlines the expected photochemistry for BP dissolved in PEG. Figure 1A shows a TREPR spectrum obtained during photolysis of 1.6 mM BP in neat PEG (mw ~ 400) acquired at a 0.5 $\mu$s delay time. From the simulation shown in Figure 1B, we conclude that the radicals exhibit some RPM polarization but that TM polarization is dominant. This is typical for highly viscous solutions. The intense central peak is due to the hydroxydiphenylmethyl-$d_{10}$ radical (Scheme 2) which was simulated using magnetic parameters from the literature.[35] The PEG radical is simulated using a $g$ factor of 2.0026, one $\alpha$-hyperfine coupling of 17.7 G, two $\beta$-hyperfine couplings of 9.3 G, and two long range $\gamma$-hyperfine couplings of 2.0 G. These hyperfine values are consistent with those reported by Gilbert et al. for smaller radicals of similar structure.[36] Figure 1C shows the same system at an elevated temperature (55 °C) where less TM is observed because the viscosity is lower.

Figure 1D shows the TREPR spectrum obtained after 308 nm photolysis of a PEG solution in water (50% v/v) containing

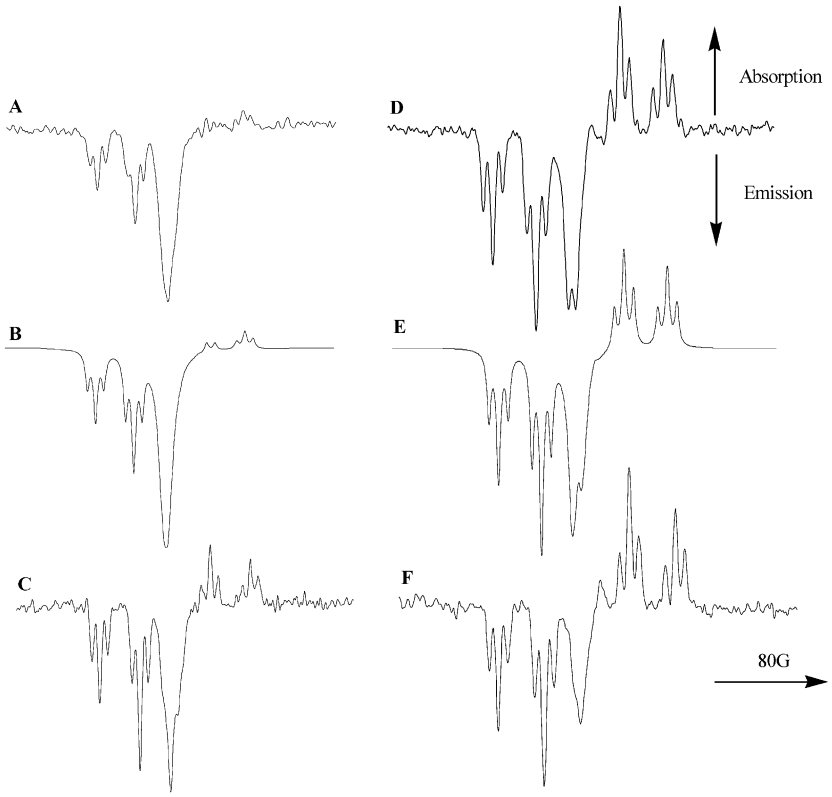
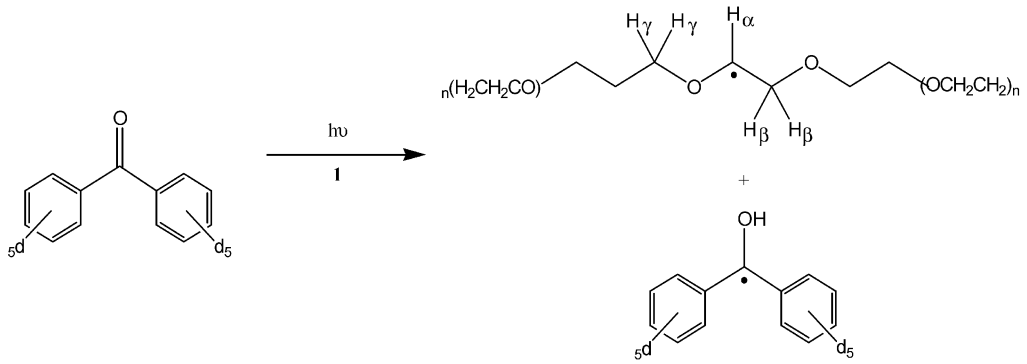



**Figure 1.** (A) Experimental TREPR spectrum of neat PEG solution at 25 °C with BP (1.6 mM) at 0.5 $\mu$s delay time. (B) Simulation of the spectrum in A using $a_H = 17.7$ G, $a_{CH2} = 9.3$ G, and $a_{OCH2} = 2.0$ G. (C) Experimental TREPR spectrum of BP/neat PEG solution at 0.5 $\mu$s delay time and 55.0 °C. (D) Experimental TREPR spectrum of low molecular weight PEG solution in water (50% v/v) with BP (1.6 mM) at 0.5 $\mu$s delay time. (E) Simulation of the spectrum in D using $a_H = 17.09$ G, $a_{CH2} = 9.0$ G, and $a_{OCH2} = 2.0$ G. (F) Experimental TREPR spectrum of BP/aqueous PEG solution at 0.5 $\mu$s delay time and 55.0 °C. The magnetic field sweep width for all spectra is 80 G. In all spectra, lines below the baseline are in emission, and lines above the baseline are absorption.

**SCHEME 2**




BP (1.6 mM). This spectrum was also obtained at a delay time of 0.5 $\mu$s. The simulation shown in Figure 1E uses the same hyperfine couplings and *g* factors as in Figure 1B. The emissive/absorptive (E/A) pattern about the center of the spectrum is characteristic of the RPM. There is also a small amount of net emission from the TM. At higher temperatures (Figure 1F) there is little change in the spectral shape or splitting patterns. There is no evidence for SCRP polarization at any delay time or temperature for neat or dilute PEG solutions. The time dependencies of all of the experimental spectra in Figure 1 (not shown) were unremarkable, showing only decay by spin lattice relaxation.

From Figure 1 it can be concluded that (1) the primary photochemical reaction of BP in PEG is that of H-atom abstraction by the excited triplet state of BP from the PEG chain, (2) the TREPR signal carriers are the free radicals shown in Scheme 2, and (3) no significant confinement of the radical pairs is taking place in this system. Figure 1 also demonstrates that in the absence of SCRP polarization, the relative magnitudes of the RPM and TM can be manipulated by adjusting the viscosity of the solution. These results are in line with predictions from well-established CIDEP theoretical models.[10]

Brij-type micelles are reported to be "core-shell" type structures with a dense hydrocarbon interior and an outer shell structure with significant water penetration.[37] In aqueous solution at 6 wt % Brij-35, **2** forms elliptical micelles with approximate semiaxis radii of 35 Å for the shell and 16.6 Å for the core.[38] These micelles differ in shape and are overall much larger in size compared to the anionic micelles of SDS. However, their core radii are similar in magnitude. If the shell radius is included in the measurement, the particular Brij molecule studied here produces micelles that are similar in size to the two-tailed

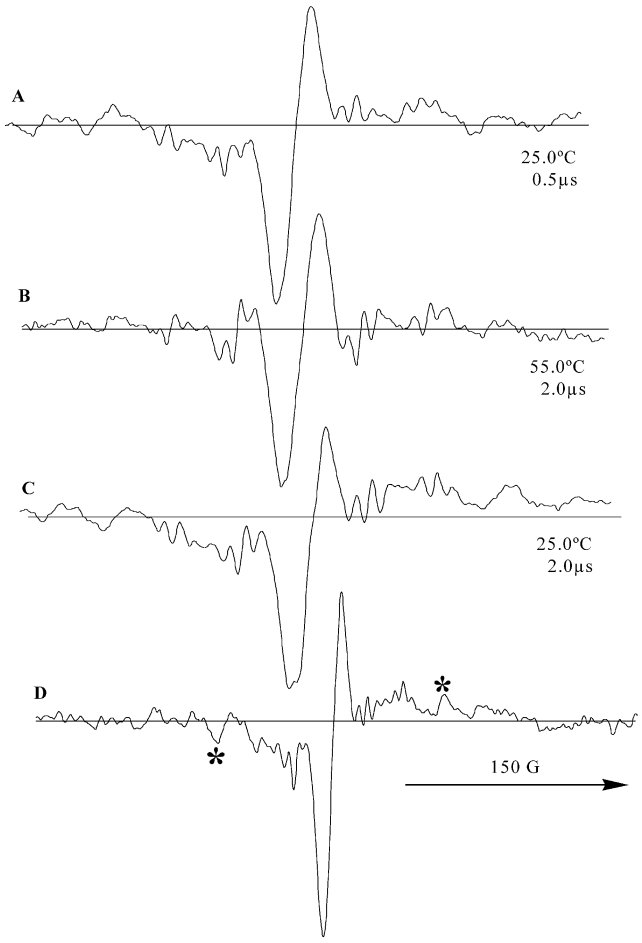



**Figure 2.** (A, B, and C) Temperature and time dependence of 6% (w/w) Brij-35/BP (1.6 mM) solution. Temperatures and delay times are shown to the right of the spectra and the magnetic field sweep width is 80 G. (D) Experimental TREPR spectrum of Brij-35/BP at 0.5 $\mu$s delay time and 25.0 °C. An asterisk denotes a radical from the interior alkyl chain.

surfactants reported earlier from our laboratory which exhibited SCRP/RPM pattern superposition.[9]

Figure 2A shows experimental TREPR spectra, taken at two different temperatures and delay times, of an aqueous Brij-35 solution (6 wt %) with 1.6 mM BP. The observed hyperfine splitting patterns are clearly similar to those observed in Figure 1 for PEG solutions and this is good evidence that the structure of the surfactant chain radical is the same as that shown in Scheme 2. The room temperature spectrum of Brij-35 clearly displays characteristics of SCRP polarization, most notably the sharp APS in the central line of the spectrum. There is also RPM polarization superimposed on this SCRP pattern. This is most clearly manifested in the PEG radical signals which are mostly low field E, high field A. As the temperature is increased, the SCRP pattern becomes more intense as shown in Figure 2B where the PEG radicals exhibit E/A doublets rising above and falling below the baseline. This is the classic signature of SCRPs undergoing weak exchange and fast motion. Stronger SCRP polarization is observed at later delay times even at room temperature (Figure 2C). Comparison of this spectrum with that in Figure 2A shows that absorptive high field lines of the PEG radical have clearly moved toward the baseline and exhibit more APS structure. Figure 2D shows a wider sweep width for the Brij-35/BP system, and an asterisk is placed on two transitions we have assigned to alkyl radicals from the core.

The alkyl core radical signals are much weaker than those from the PEG-based radicals from the shell. There are several possible reasons for this. First, the benzophenone parent compound may be located at the PEG/alkyl layer interface. Also, the H-atom abstraction rate may be different for the two radical-forming reactions. Finally, the magnitude of the SCRP polarization may be different for the two sets of radical pairs. Although we do not have the capability to directly relate TREPR signal intensities to radical concentrations, it is likely that they are proportional in this case. For example, signal intensities from radicals created by BP abstract in neat PEG are similar to those created in neat alkyl solutions.[7] To the best of our ability to discern given the signal-to-noise ratio, the SCRP to RPM ratio appears to be about the same for the two radical pairs, indicating that the polarization mechanism is identical for each set of radicals. The somewhat polar BP parent molecule prefers to reside near the PEG, and therefore, the differences in intensity are most likely due to different quantities of radicals being produced, i.e., different radical concentrations.

There are several noteworthy features of the spectra shown in Figure 2, the most striking of which is that the predominant surfactant radical is that from the hydrophilic PEG chains making up the shell structure. This means that there is relatively little photochemistry taking place in the core. The presence of a temperature-dependent RPM/SCRP polarization pattern allows us to conclude that the shells of Brij-35 micelles are viscous and still able to confine probe molecules such as BP. Additionally, because the SCRP becomes more intense at high temperatures and later delay times, the radical pair escape rates must be slow compared to SDS ($<10^5$ $s^{-1}$).[8] The micelles increase in size with temperature,[39] and this should also slow the escape process. The Brij micellar radical pairs show a temperature dependence very similar to those created from our photochemically active micelles reported previously.[9] For this reason, we can conclude that the radicals formed in Brij-type micelles have very similar diffusion coefficients as reported for the previous system. This is not surprising if one considers the radius of the Brij structures to include the shell and allow diffusion in both regions (or just in the shell), providing a nearly identical boundary condition to that in the earlier study.

Triton X-100 also forms core−shell type micelles in aqueous solution. However, literature reports are disparate with regard to conclusions about their shape and size.[40−42] The most reliable data suggests that at room temperature the structures are disk shaped, with a core major semiaxis radius of roughly 35 Å (minor axis 10 Å) for the core and the major semiaxis is approximately 50 Å (minor axis 30 Å) for the shell. There is a consensus that Triton-based surfactants are less fluid than Brij or PEG itself.[42]

Figure 3A shows the room temperature TREPR spectrum obtained during photolysis of BP (1.6 mM) solubilized in a 6% (w/w) aqueous solution of Triton X-100. Clearly, the TM is dominant in this spectrum which is to be expected if the BP is experiencing higher microviscosity than in Brij-35. At longer delay times (Figure 3B), no SCRP polarization is observed; however, the high field PEG radical transitions appear to become overall more net emissive. This is probably to be due to $S-T^-$ mixing in the SCRP, which is often observed at long delay times in highly viscous media.[43] It is interesting to note that no APS features are present at any delay time for this system and that the overall signal intensity is much weaker (by an order of magnitude) than in the Brij or PEG solutions.

Figure 3C shows the Triton X-100 system at 55°C. Within the limits of the baseline noise, we are unable to detect the APS

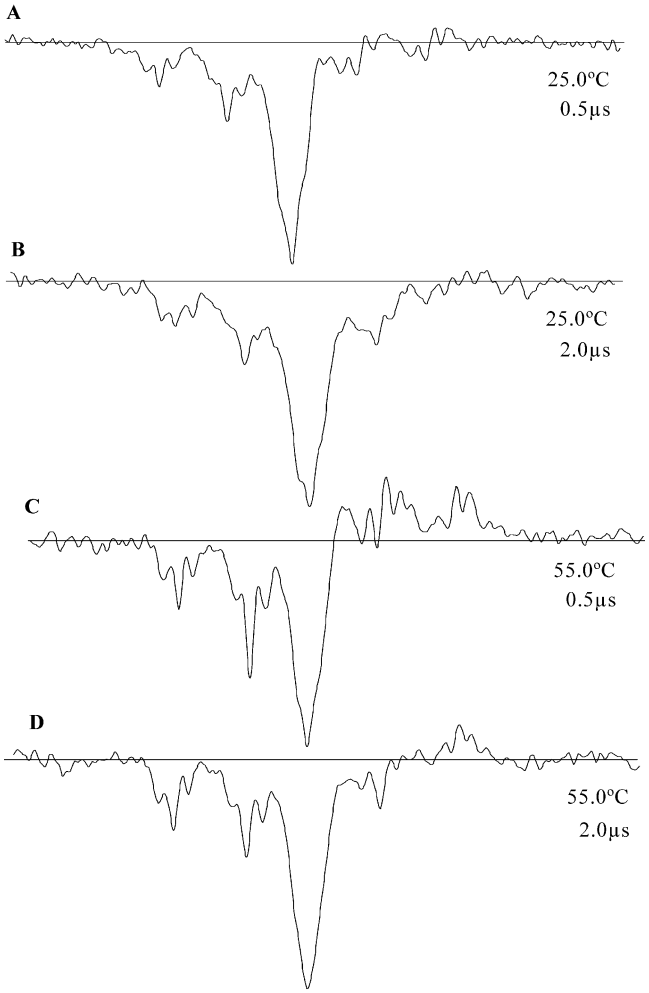



**Figure 3.** Experimental TREPR spectra of the temperature and time dependence of a 6% (w/w) solution of Triton X-100 in water with 1.6 mM BP. Temperatures and delay times are reported to the right of the spectra. Magnetic field sweep width is 80 G for all spectra.

pattern in this spectrum. There is a larger ratio of RPM to TM polarization compared to the room-temperature spectrum shown in Figure 1A, and this again fits accepted CIDEP viscosity dependencies for both mechanisms.[10] Similar to that observed for the room-temperature spectra, more net emission is seen at later delay times, and we also attribute this to $S-T^-$ mixing. In summary, for the BP/Triton X-100 system, we can conclude that the primary photochemical reaction is H-atom abstraction from the PEG shell chains by triplet BP and that the microviscosity of the Triton X-100 shell is much higher than that for Brij-35. Because $S-T^-$ mixing is occurring, it is likely that escape processes in Triton X-100 shells are also relatively slow.

Photoexcitation of a 6% (w/w) solution of CrEL with 1.6 mM BP gave no TREPR signal to the limit of our detection. This was not an expected result as the ensuing free radicals from H-atom abstraction from CrEL should have the same general structure as those giving rise to the spectra in Figures 1-3. There is no reason to expect that the photochemistry would be different in this structurally similar surfactant. One possible explanation is that the allylic alcohol in the surfactant chain (Scheme 2) has undergone a small amount of elimination, leading to diene formation on the chains which could quench the BP triplet state. In fact, CrEL is a slightly yellowish material, and UV/vis confirms a tail of absorbance extending well into the near UV, which supports this explanation. No purification methods for CrEL have been reported to date.

## Conclusions

The most important finding in this work is that free radicals produced photochemically in Brij and Triton PEG based micelles are found to exist primarily in the more hydrophilic PEG shell rather than the hydrophobic alkyl chain interior. Escape rates from these micelles appear to be slow ($<10^5$ $s^{-1}$). These results imply that probe molecules dissolved in such assemblies may interact more favorably with the PEG moieties and reside closer to the aqueous phase than previously believed. This paper also represents the first TREPR observation (in Brij) of SCRPs in any nonionic surfactant. Triton X-100 micelles appear to have a higher microviscosity in the PEG shell than in Brij micelles, and this is in line with previous characterization data, which tend to describe Triton micelles as "less fluid."[42] Future work will include TREPR experiments in both Brij and Triton micelles with different shell sizes (e.g., Brij-58, Triton X-165) and a variation of the polarity of the probe molecule to see if it can be forced to spend more time near the hydrocarbon chain interior. Product analyses and the development of a method for the purification of CrEL will also be pursued. Finally, a rigorous simulation program will be developed for these micelles to extract quantitative diffusion data, in particular for the Brij structures.

**Acknowledgment.** We thank the National Science Foundation for continued strong support of our program through Grant # CHE-0213516.

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