The Photodimerization of a Cinnamoyl Moiety Derivative in Dilute Solution Based on the Intramolecular Chain Interaction of Gemini Surfactant

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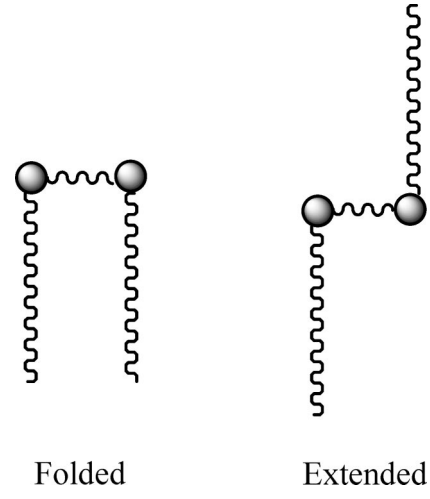
A Gemini surfactant, sodium *N*,*N*′-di(4-*n*-butyloxy cinnamoly)-L-cystine, containing a cinnamoyl moiety in the alkyl chains and disulfide bond in the spacer was designed and synthesized. The incorporation of a cinnamoyl moiety into the alkyl chains of Gemini surfactant makes it easy to probe the conformational information of the amphiphile molecule. The UV/vis absorption spectra and steady-state fluorescence were investigated at a concentration far below the critical micelle concentration (cmc). Both blue-shift of absorption and red-shift of fluorescence emission spectra indicate the existence of intramolecular interaction between the two alkyl chains in Gemini surfactant in the singly dispersed state. Results based on the breakdown of the disulfide bond by dithiotheritol (DTT) further confirmed the conclusion. Moreover, the characteristic of intramolecular chain interaction in Gemini surfactant improves the topochemical geometrical requirements of cinnamoyl moiety and increases the local concentration of reactant in dilute solution. Utilizing the incorporation of cinnamoyl moiety into the alkyl chains of Gemini surfactant, the cinnamoyl moiety upon irradiation undergoes dimerization in dilute aqueous solution with high yield of 78%.

1. Introduction

The photodimerization of cinnamic acid and its derivatives, which is an important process for modification of polymers,[1,2] liquid crystal displays,[3,4] and total synthesis of natural products,[5,6] has been a continued interest since its initial reports, especially in confined and well-ordered media.[7–12] Results based on the photolysis of these acids in crystals lead to the conclusion that the two reactive C═C bonds are within the topochemically stipulated distance (<4.2 Å) and parallel.[13–15] In contrast to the solid state, the photodimerization of cinnamates derivates is inefficient in dilute solution due to the difficulty of controlling the geometrical requirements. Usually, the main reason is the occurrence of trans−cis isomerization.[16,17] Many efforts have been made to improve the efficiency of dimerization in dilute solution. Lewis et al. reported a significant increase in photodimerization efficiency (dimerization yield: 90%) through the use of Lewis acid catalysis such as BF_3 and $SnCl_4$. In fact, the high yields of photodimerization were obtained at a concentration of 0.2 M; however, only photoisomerization occurred in dilute solution.[18,19] Bassani et al. made use of hydrogen-bonded tape-like structure to improve the photodimerization efficiency of cinnamates in dilute solution with a yield of 45%.[20] Consequently, it is still necessary to develop a method for improving the photodimerization efficiency of a cinnamoyl moiety in dilute solution.

Gemini surfactants have attracted much interest because of their superior properties in comparison with those of conventional surfactants.[21,22] Many previous studies have been done on exploiting their surface properties, aggregation behavior, and methods to control the transition of their self-assemblies.[23–29] With the structure of monomeric surfactants connected by a spacer group, Gemini surfactant has two limiting arrangements at the singly dispersed state: a folded and an extended conformation (Scheme 1). Such conformation should affect the morphology of their aggregates, since the type and structure of the self-assembly system depend on their geometrical parameters,[30] which are determined from the conformational structure. The association between the alkyl chains of a Gemini surfactant may lead to a change of the packing parameter. Furthermore, the association between the two alkyl chains of Gemini surfactant will increase the cmc, since the free energy of transfer of Gemini surfactant from the aqueous phase to the micelles was reduced.[31,32] Therefore, the research on the conformation of Gemini surfactant in solution is very important to understand their aggregation behavior. In fact, the conformation of Gemini surfactant at a concentration below the critical micelle concentration (cmc) has received much attention. The values of the

SCHEME 1: Limiting Conformation of Gemini Surfactant in a Singly Dispersed State



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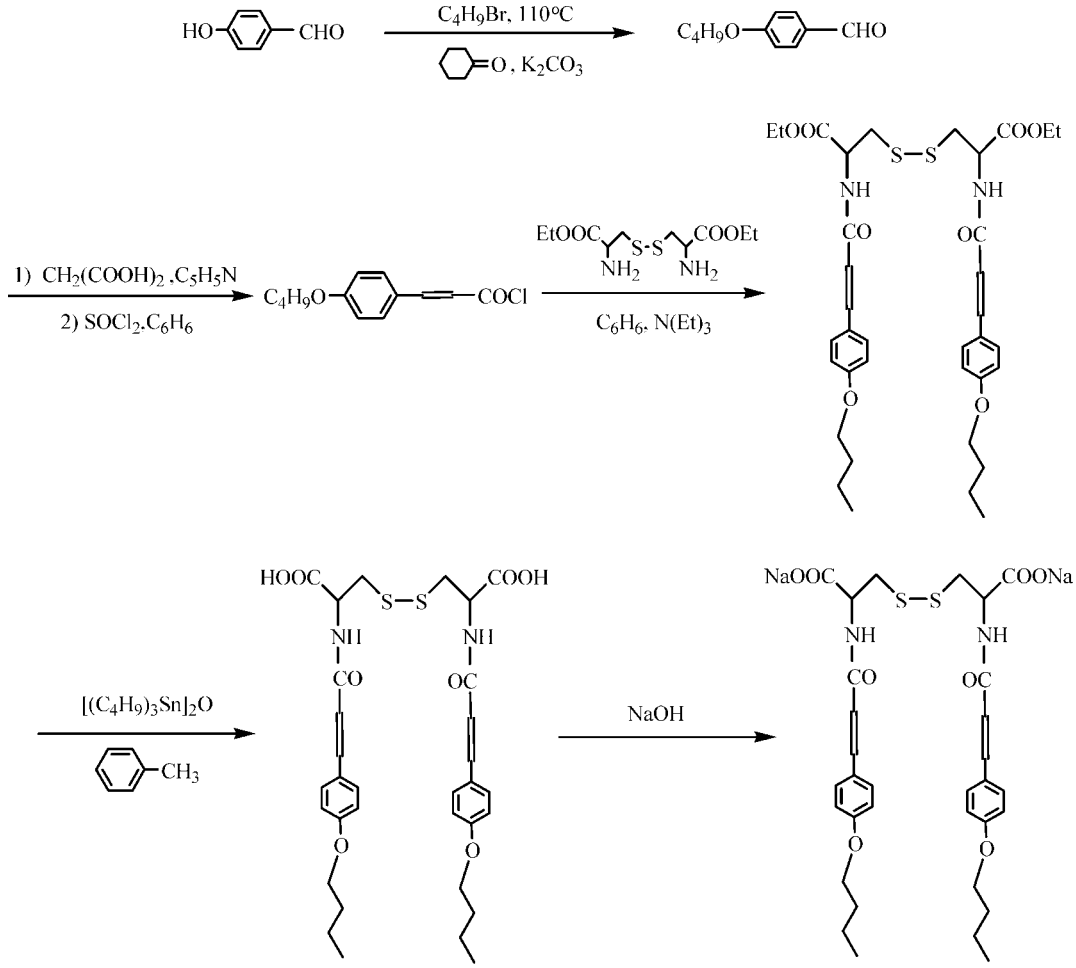
SCHEME 2: Synthesis of SDBCC



apparent molar volumes and enthalpy of dilution suggested that the two alkyl chains in the Gemini surfactant molecule might be intramolecularly associated when the surfactant in the singly dispersed state.[33] However, subsequent volumetric and calorimetric studies of closely related cationic Gemini surfactants showed no evidence of intramolecular association of the alkyl chains in the submicellar range.[34,35] Thus, it is necessary to make systematical studies on molecular conformations in this kind of surfactant system.

It is of current interest to study chromophore-containing amphiphiles in terms of their spectral features,[36–43] since the spectra of the chromophore can reflect the circumstances caused by physical and chemical environmental changes. However, the research on chromophore introduced to the alkyl chains of Gemini surfactant is still rare. Thus, in the present paper, a functional Gemini surfactant, sodium *N*,*N*′-di(4-*n*-butyloxy cinnamoly)-L-cystine (SDBCC), was designed and synthesized. In this Gemini surfactant, two alkyl chains containing cinnamoyl moieties were linked by disulfide bond. First, the incorporation of chromophore into the alkyl chains makes it convenient to probe the conformational information of Gemini surfactant. The disulfide bond introduced to the spacer of Gemini surfactant can be reduced to a thiol group by dithiotheritol (DTT), [44–48] which can be used to exploit the influence of molecular structure. Furthermore, understanding the spectra of the cinnamoyl moiety in dilute solution makes it possible to study the photodimerization of cinnamoyl moiety. Utilizing the characteristic of intramolecular chain interaction in Gemini surfactant, the incorporated cinnamoyl moiety upon irradiation undergoes dimerization with a yield of 78% in dilute solution of this Gemini surfactant.

2. Experimental Section

2.1. Materials. Bis[tributyltin(V)] (96%) and DTT (99%) were purchased from Aldrich Company. Chloroform, methylene dichloride, ethanol, methanol were chromatogram grade and purchased from Tianjin Siyou Biomedicinal Company. Dimethyl sulfoxide (DMSO) was from Merck Company. L-Cystine, 4-hydroxybenzalde, butyl bromide, and all other reagents were A.R. grade and purchased from Beijing Chemical Company. Water was distilled twice from $KMnO_4$-containing deionized water to remove traces of organic compounds. 4-(*n*-Butyloxy)-benzaldehyde[49] and L-cystine diethylester[50] were synthesized using experimental procedures described in the literature.

2.2. Synthesis. The compound SDBCC was synthesized according to Scheme 2[51] and characterized by ^{1}H NMR and elemental analysis.

4-(n-Butyloxy)cinnamic Acid. Three drops of piperidine were added to the solution containing of 4-(*n*-butyloxy)benzaldehyde (3.56 g, 0.02 mol), malonic acid (4.17 g, 0.04 mol) and pyridine (30 mL). The mixture was refluxed for 4 h. The resulting solution was poured into a mixture of 50 mL of hydrochloric acid (36.5%) and 100 g of ice and stirred until crystallization was complete. The precipitate was filtered and recrystallized four times from acetic acid in 52% yield. ^{1}H NMR ($CDCl_3$/tetramethylsilane (TMS), δ): 0.99 (t, CH_3, 3H), 1.50 (m, CH_2, 2H), 1.80 (m, CH_2, 2H), 4.00 (t, CH_2, 2H), 6.31, 7.74 (d, CH═CH, 2H), 6.91, 7.49 (d, C_6H_4, 4H).

N,N′-Di(4-n-butyloxycinnamoly)-L-cystinediethylester. A solution of 4-(*n*-butyloxy)cinnamic acid (4.84 g, 0.022 mol) and thionyl chloride (4.17 g, 0.035 mol) was heated for 4 h at 60 °C. The excess thionyl chloride was removed under reduced pressure. The primrose yellow residue was used for further reaction without purification. To a solution of 4-(*n*-butyloxy)-cinnamic acid chloride (0.022 mol) and triethylamine (4.2 mL) in benzene (50 mL), L-cystine diethylester was added gradually, and the mixture was stirred for 8 h at room temperature. The reaction suspension was filtered and concentrated. Then, dilute hydrochloric acid (5%, 20 mL) was added to the resulting mixture, and it was extracted with chloroform (3 × 40 mL). The combined organic layers were washed by $KHCO_3$ (10% aq, 3 × 10 mL) and dried over $MgSO_4$. Part of the solvent was removed under reduced pressure. The resulting chloroform solution was added to cyclohexane (150 mL). The crude product was recrystallized twice from chloroform/ethyl ether to yield the product as a white solid (2.97 g, 38.6%). ^{1}H NMR ($CDCl_3$/TMS, δ): 0.99 (t, CH_3, 3H), 1.31 (t, CH_3, 3H), 1.48 (m, CH_2, 2H), 1.76 (m, CH_2, 2H), 3.17, 3.39 (q, CH_2, 2H), 3.93 (t, CH_2, 2H), 4.26 (q, CH_2, 2H), 5.05 (m, CH, 1H), 6.44, 7.65 (d, CH═CH, 2H), 6.79, 7.42 (d, C_6H_4, 4H), 6.90 (d, NH, 1H).

N,N′-Di(4-n-butyloxy cinnamoly)-L-cystine. A solution of *N*,*N*′-di(4-*n*-butyloxy cinnamoly)-L-cystine diethylester (1.4 g, 0.002 mol) and bis[tributyltin(V)] oxide (14.90 g, 0.025 mol) was refluxed for 30 h at 130 °C. The solvent then removed under reduced pressure, and the residue was dissolved in ethyl acetate (50 mL). The ethyl acetate solution was washed with 10% $KHCO_3$ (3 × 10 mL). The combined aqueous phase was acidified to pH = 2 with 5% hydrochloric acid, and extracted with ethyl acetate (3 × 30 mL). The organic phase were combined, dried over Na_2SO_4, and evaporated. To the residue, acetone (10 mL) was added, and the suspension was refluxed. After cooling, the crude product was separated by filtration. Recrystallization from ethanol/water (9/1, V/V) gave 0.062 g (yield: 4.81%) of *N*,*N*′-di(4-*n*-butyloxycinnamoly)-L-cystine. ^{1}H NMR (d_6-DMSO/TMS, δ): 0.91(t, CH_3, 3H), 1.43 (m, CH_2, 2H), 1.70 (m, CH_2, 2H), 3.01, 3.22 (q, CH_2, 2H), 3.98 (t, CH_2, 2H), 4.65 (m, CH, 1H), 6.54, 7.37(d, CH═CH, 2H), 6.92, 7.47 (d, C_6H_4, 4H), 8.43 (d, NH, 1H), 12.98 (br, COOH, 1H). Anal. Calc. for $C_{32}H_{40}N_2S_2O_8$: C, 59.60%; H, 6.25%; N, 4.22%; Found: C, 59.36%; H, 6.24%; N, 4.34%.

Sodium N,N′-Di(4-n-butyloxy cinnamoly)-L-cystine (SDBCC). SDBCC was prepared by neutralizing *N*,*N*′-di(4-*n*-butyloxycinnamoly)-L-cystine with equivalent molar NaOH in ethanol, then the solvent was removed under reduced pressure. ^{1}H NMR (d_6-DMSO/TMS, δ) (see Figure S1 in Supporting Information): 0.73 (t, CH_3, 3H), 1.18 (m, CH_2, 2H), 1.44 (m, CH_2, 2H), 2.97, 3.23 (q, CH_2, 2H), 3.58 (t, CH_2, 2H), 4.63 (q, CH, 1H), 6.39, 7.33 (d, CH═CH, 2H), 6.54, 7.24 (d, C_6H_4, 4H). Anal. Calc. for $C_{32}H_{38}N_2S_2O_8\ Na_2$: C, 55.80%; H, 5.56%; N, 4.07%; Found: C, 56.14%; H, 5.42%; N, 3.95%.

2.3. Methods. ***Sample Preparation.*** Stock solutions of SDBCC in 10 mM borax buffer (pH = 9.2) or organic solvent were prepared by weighting the appropriate mass of solid surfactant and then diluted by adding corresponding solvent. All measurements were conducted at 30.0 ± 0.5 °C.

Surface Tension Measurement. The surface tension of the surfactant solutions was measured by the drop volume method. Three measurements were performed for each sample, and the mean γ ($mN \cdot m^{-1}$) was recorded. The values of the cmc can be determined from the break points in the γ−log C curves.

Spectra Measurements. Optical absorption spectra were recorded using a Perkin-Elmer lambda 35 spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Hitachi F-4500 spectrofluorometer.

Photoreaction of Cinnamoyl Moiety. Solutions containing cinnamoyl moiety were irradiated using a high-pressure Hg lamp system of 100 W. After 1 day or more to reach the photostationary state, the resulting irradiated solutions were analyzed by UV/vis spectrometer.

3. Results and Discussion

3.1. Intramolecular Interaction between the Two Alkyl Chains of Gemini Surfactant. The UV/vis absorption spectrum of SDBCC in chloroform at a concentration of 2.5×10^{-5} M is shown in Figure 1a. It can be seen that the absorption spectrum has a maximal absorbance at 315 nm, which is the contribution of the cinnamate unit.[52,53] The cinnamate unit is generally expected to have a $\pi-\pi^*$ transition with weak charge-transfer character in the ground-state and considerably stronger charge separation in the excited state.[54] Thus, a positive solvatochromic effect is anticipated. However, the solution of 2.5×10^{-5} M SDBCC in borax buffer had a maximal absorption at 290 nm as shown in Figure 1b. So this apparent blue-shift cannot be attributed to a change of the medium polarity but reflected the exciton interaction between chromophores. According to the results of McRae and Kasha,[55] it is recognized that a blue shift means parallel stacking of chromophores, with the transition dipoles of the cinnamate units in a parallel fashion. This parallel stacking of chromophores in Gemini surfactant can also be reflected in the chromophore fluorescence emission spectra.[56] As seen from Figure 2, the fluorescence intensity had a maximal emission at 381 nm in chloroform, whereas in borax buffer, the intensity of the band is further red-shifted to 401 nm. As mentioned above, the absorption of SDBCC in chloroform is very similar to that for a monomer of the cinnamate unit. However, in borax buffer, the two chromophores are stacked parallel. Therefore, the maximal emission wavelength at 381 nm is assigned to the monomer emission of the cinnamate unit, and the maximal emission wavelength at 401 nm may be attributed to a folded excimer-like state.

It is worth noting that the cmc of SDBCC in borax solution is 1.4×10^{-3} M (see Figure S2 in Supporting Information). In the present case, the concentration of SDBCC is only 2.5×10^{-5} M, which is far below its cmc, and the SDBCC molecules are in the singly dispersed state. Thus, intermolecular chromophore interaction is impossible, indicating that the parallel packing of the chromophores should be attributed to the two chromophores in one molecule. Combining all the UV/vis and fluorescence results, the existence of intramolecular interaction between the two alkyl chains of Gemini surfactant can be confirmed.

To further confirm the intramolecular interaction between the two alkyl chains of Gemini surfactant, experiments were performed by using DTT to reduce disulfide bond to thiol group, which makes SDBCC transform to a single-chained amphiphile as illustrated in Scheme 3. It should be noted that the reduction of disulfide bond by DTT is not complete, especially in dilute solution. Figure 3 shows the UV/vis absorption spectra of SDBCC in borax buffer after the addition of DTT. As expected, an obvious maximal absorbance red-shift form 290 to 307 nm with DTT addition was observed, indicating that the interaction between the chromophore is weakened.

3.2. Role of the Hydrophobic Interaction. The hydrophobic interaction is an important driving force for the intramolecular interaction between the alkyl chains of Gemini surfactant. The hydrophobic interaction can be modified by the solvent polar-

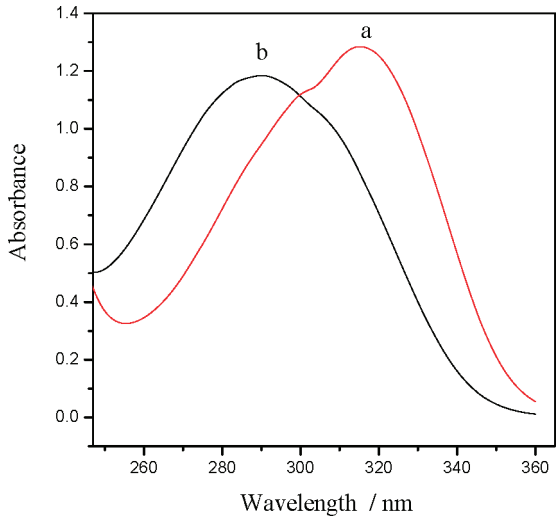


Figure 1. UV/vis spectra of 2.5 × 10^{-5} M SDBCC at 30 °C in (a) chloroform and (b) borax buffer.

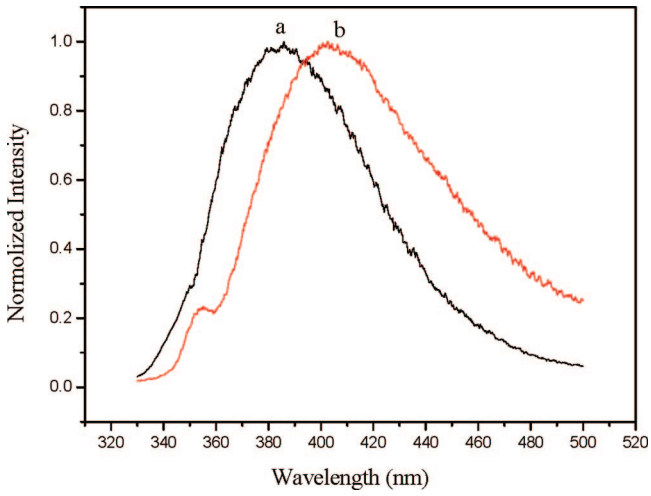
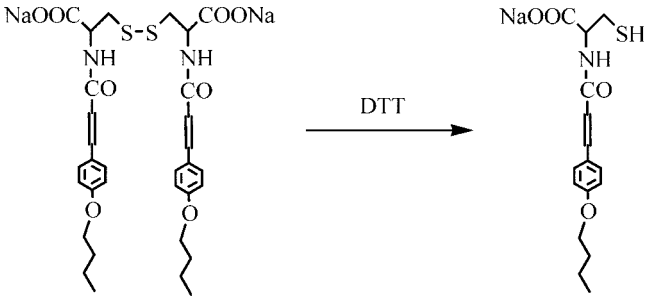


Figure 2. Fluorescence emission spectra of 2.5 × 10^{-5} M SDBCC (λ_{ex} = 320 nm) at 30 °C in (a) chloroform and (b) borax buffer.

SCHEME 3: Reaction Formula of Reduce SDBCC by DTT



ity.[57] Namely, this interaction will be reinforced with the solvent polarity increasing, as observed in chloroform and borax buffer. The intramolecular interaction is very weak in chloroform, and the chromphores are probably quite far apart, so the absorption spectrum of the cinnamate units in SDBCC is almost the same as the monomer in intensity. However, in borax buffer, a blue-shifted absorption may be attributed to H-dimer formation. To further illustrate the influence of solvent polarity, Figure 4 shows the absorption spectra of SDBCC in CH_2Cl_2, CH_3OH, and DMSO. It can be seen that the absorption spectrum of SDBCC in CH_2Cl_2 showed a maximal absorption at 315 nm as observed

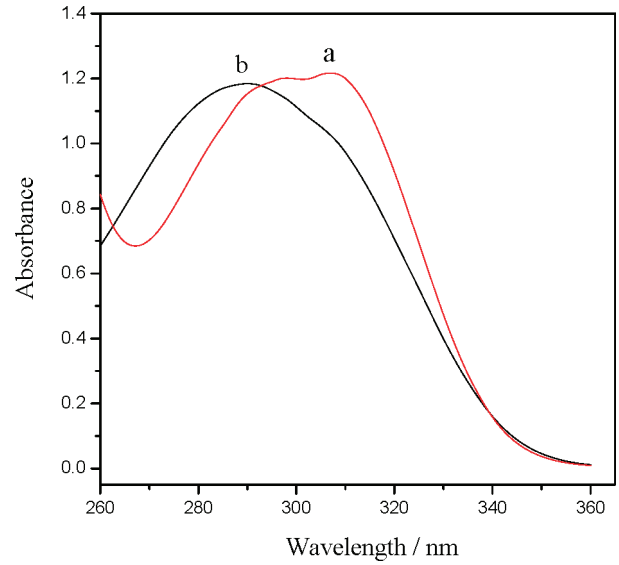


Figure 3. UV/vis spectra of 2.5 × 10^{-5} M SDBCC in borax buffer at 30 °C (a) after and (b) before 2.5 × 10^{-3} M DTT addition.

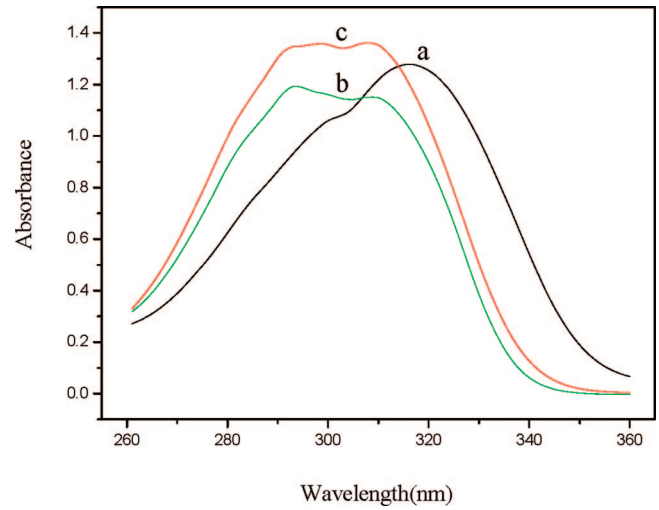


Figure 4. UV/vis spectra of 2.5 × 10^{-5} M SDBCC at 30 °C in (a) methylene dichloride, (b) methanol, and (c) DMSO.

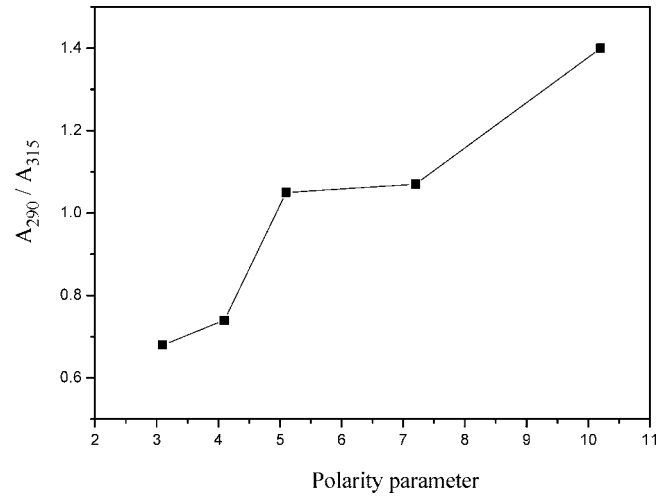


Figure 5. Absorbance at 290 nm versus absorbance at 315 nm as a function of polarity parameter.

in $CHCl_3$, which is the contribution of cinnamate monomer unit. However, the absorption spectra of SDBCC in CH_3OH and DMSO showed a superposition of monomer and H-dimer. The

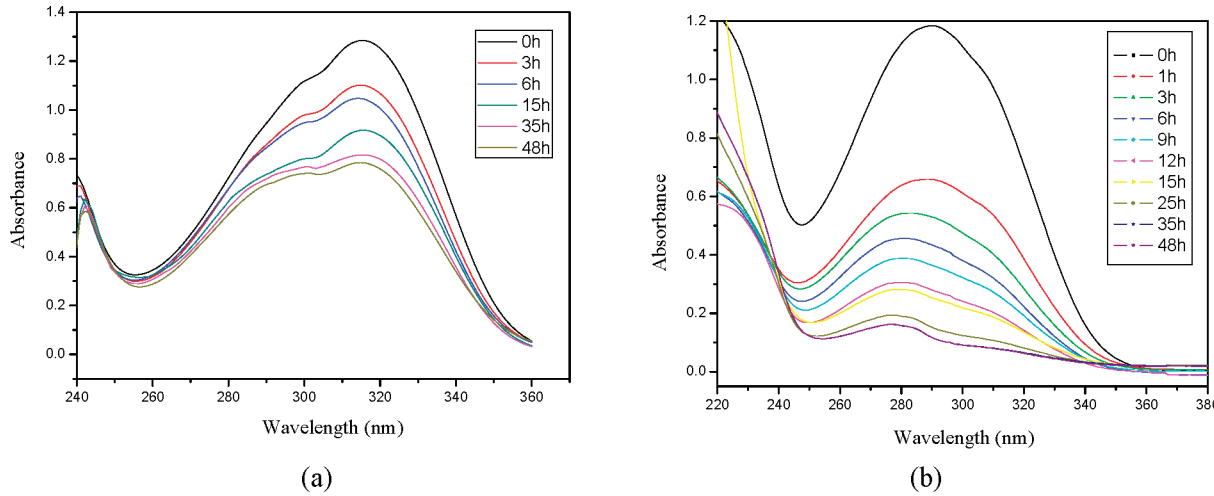


Figure 6. UV/vis spectra change of 2.5 × 10^{-5} M SDBCC upon irradiation at 30 °C in (a) chloroform and (b) borax buffer.

change of the absorption ratio of A_{290}/A_{315} as a function of polarity parameter [58–60] was shown in Figure 5. The increase in A_{290}/A_{315} with polarity parameter indicates that the association of alkyl chains is enhanced with the solvent polarity increasing.

3.3. The Photodimerization of the Cinnamoyl Moiety in Dilute Solution. As mentioned above, there is intramolecular interaction between the two alkyl chains in the singly dispersed state due to the characteristic of Gemini surfactant molecular structure. Thus, the incorporation of the cinnamoyl moiety into the alkyl chains of Gemini surfactant would improve the geometrical requirements and increase the local concentration of the reactant.

The photodimerization of the cinnamoyl moiety was studied in dilute solution. Figure 6 displays the UV/vis absorption spectra of SDBCC in chloroform and borax buffer upon UV light irradiation at different times. It can be seen that the intensity of the absorption band apparently decreases with an increase in irradiation time. Finally at 48 h, the spectra showed no obvious changes. The change of UV/vis absorption spectra is a convenient method to investigate the photoreaction of cinnamoyl moiety.[61,62] It allows an estimation of photoproduct distribution. Using absorbance at the maximal wavelength and an isosbestic point of the UV/vis spectra, the fraction of photoproducts can be calculated according to the following equations:

$$f_{\text{trans-isomer}} = A^{\text{t}}_{\text{max}}/A^{0}_{\text{max}} \quad (1)$$

$$f_{\text{dimmer}} = 1 - A^{\text{t}}_{\text{iso}}/A^{0}_{\text{iso}} \quad (2)$$

$$f_{\text{cis-isomer}} = A^{\text{t}}_{\text{max}}/A^{0}_{\text{max}} - A^{\text{t}}_{\text{iso}}/A^{0}_{\text{iso}} \quad (3)$$

where $A^{\text{t}}_{\text{max}}$, $A^{\text{t}}_{\text{iso}}$ are the absorbances during photoreaction at the maximal wavelength and a wavelength of an isosbestic point, and A^{0}_{max}, A^{0}_{iso} are the corresponding absorbances before irradiation.

The photoproduct distributions in chloroform and borax solution are summarized in Figure 7. In chloroform solution, the decrease in the fraction of trans-isomer is due to the predominant formation of cis-isomer formed by photoisomerization. However, in borax solution, the photodimerization takes place more predominantly. It is worth noting that the 78% photodimerization yield in borax solution is prominently higher than 10% yield in chloroform upon 48 h of irradiation. Comparing these two systems, the main difference is the conformation of SDBCC molecular. The above results and discussions illustrate the existence of intramolecular interaction between the alkyl chains of Gemini surfactant in dilute borax solution. Thus, the incorporation of a cinnamoyl moiety into the alkyl chains of Gemini surfactant effectively improves the

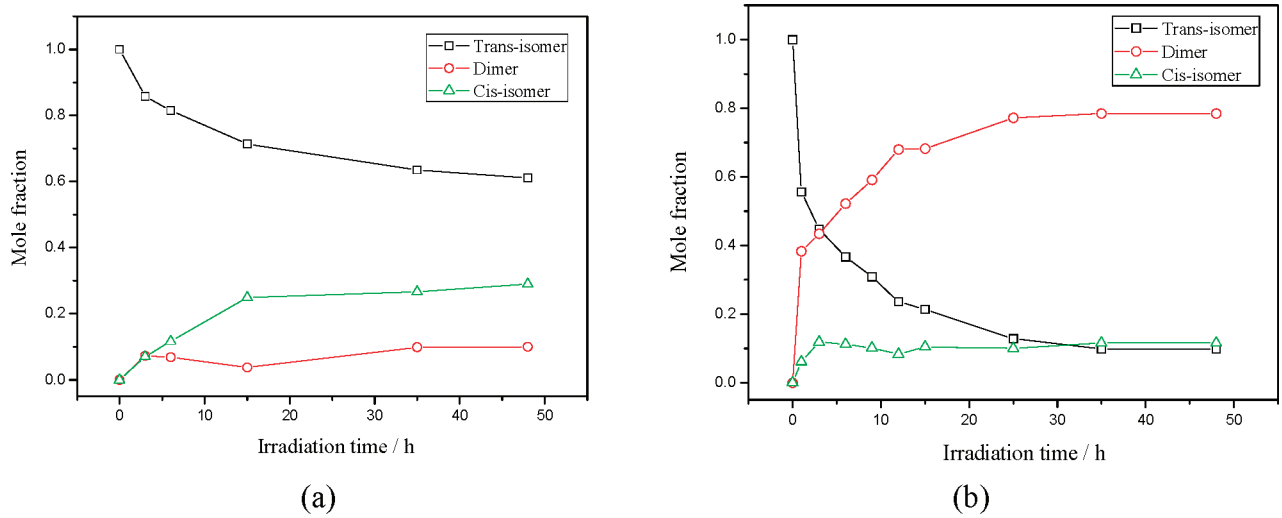


Figure 7. Fractions of trans- and cis-isomers and dimers as a function of irradiation time in (a) chloroform and (b) borax buffer.

geometrical requirements and increases the local concentration of the reactant, thereby enhancing the efficiency of photodimerization.

4. Conclusion

The spectra response of chromophore in the alkyl chains of Gemini surfactant were investigated at a concentration far below the cmc. The existence of intramolecular interaction between the alkyl chains of Gemini surfactant was demonstrated by both the blue-shift absorption and red-shift fluorescence emission spectra. Utilizing this intermolecular interaction, the cinnamoyl moiety incorporated into the alkyl chains of Gemini surfactant upon irradiation undergoes dimerization in dilute borax solution with a yield of 78%. We hope that this work may advance the understanding on the state of Gemini surfactant in solution and promote the development of a method for improving the photodimerization efficiency of a cinnamoyl moiety in dilute solution.

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Supporting Information Available: ^{1}H NMR spectrum and the surface tension curve of SDBCC. This material is available free of charge via the Internet at http://pubs.acs.org.

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