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Gemini Amphiphiles Regulated Photopolymerization of Diacetylene Acid in Organized Molecular Films

Ling Zhong, Tifeng Jiao, and Minghua Liu*

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Colloid and Interface Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100190, People's Republic of China

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In this paper, we have investigated the photopolymerization of an amphiphilic diacetylene, 10,12-pentacosadiynoic acid (PCDA), in organized molecular films in the presence of a series of gemini amphiphiles with different spacer lengths. It has been found that, when gemini amphiphiles were mixed with the diacetylene, the film-forming properties were greatly improved and the photopolymerization could be regulated by the gemini amphiphiles. Miscibility and Fourier transform infrared spectroscopy (FT-IR) investigations revealed that the polymerization of PCDA in a mixed film was regulated by the mixing ratio and spacer length of the gemini amphiphiles. Although a slight amount of gemini amphiphile did not make the PCDA polymerize into blue films, the increment of the gemini amphiphile with the short spacer length in the mixed film caused the formation of a red film, and the intensity of red phase to blue phase can be modulated by changing the mixing ratios. When gemini amphiphiles with longer spacer lengths were mixed, blue films were predominantly obtained in all mixing ratios. A mechanism including the interaction between the headgroup of the gemini amphiphiles and the diacetylene and the regulation of the spacer was proposed.

Introduction

Photopolymerization of diacetylene derivatives has been attracting great interest mainly from two aspects. One is its topochemical reaction feature. Under UV irradiation, well-aligned diacetylene can be polymerized into a conjugated polymer and shows "red" or "blue" phases; this process is very sensitive to the subtle molecular arrangement and the environment of the diacetylene[1,2] The other is the functionality of the formed polydiacetylene (PDA) polymers, which have excellent electrical and optical properties.[3–6] The conjugated PDA polymer can experience colorimetric transition from blue to red phase under external stimulus such as temperature,[7] mechanical stress,[8] chemical solvents, and pH changes.[9,10] This property has been widely used as an important kind of chemical sensor. There have been many reports on PDA colorimetric sensors for toxins,[11] cations,[12] antibody-epitope recognition,[13] cyclo-dextrin,[14] lipopolysaccharide,[15] *E. coli*,[16] and influenza virus.[17,18]

As for the topochemical polymerization, it was proved that only with the proper alignment of the molecules can the topochemical reaction proceed. Thus, how to control the molecular arrangement of the diacetylene derivative to regulate the photopolymerization becomes a key point in research. Amphiphilic diacetylene, when assembled into organized molecular nanostructures such as Langmuir–Blodgett films or vesicles,[7,18–23] is found to easily undergo photopolymerization. In those amphiphilic diacetylenes, the design of the amphiphilic molecules with certain molecular lengths and headgroups is of considerable importance in controlling the photopolymerization of PDA film. Besides, interaction of the amphiphilic diacetylene derivatives with other molecules through hydrogen bonds, van der Waals interaction, or metal ion coordination can alter the polymerization of the PDA. For example, we have shown that by Langmuir method the addition of metal ions in the suphase can change the polymerization of the PDA. When Cu(II) ion

was used as the subphase, the formed monolayer showed chirality and the polymerization afforded only red film. When Zn(II) ion was employed, a colorimetric transition could be realized.[24] In this paper, we have shown that, using a series of gemini amphiphiles, the polymerization of 10,12-pentacosadiyno-ic acid (PCDA) in organized molecular films can be regulated.

A gemini amphiphile, as an interesting type of amphiphile, can be regarded as an entity formed from two traditional amphiphiles covalently linked by a spacer. Due to the unique structure, gemini amphiphiles have been investigated in many aspects and many interesting properties have been revealed.[25–27] Our group has also revealed that, with the gemini amphiphiles involved in interfacial assemblies, dye aggregation,[28,29] DNA condensation,[30] and fluorescence of POM[31,32] can be controlled not only by the molecular structure of the gemini amphiphiles but also by the spacers. Furthermore, our previous work has also shown that films composed of gemini amphiphiles exhibited excellent stability because the two headgroups of gemini amphiphiles can anchor the solid plates much stronger than conventional amphiphiles.[33] In this work, we have mixed an amphiphilic diacetylene derivative with a series of gemini amphiphiles having various lengths of hydrophobic spacers and investigated their photopolymerization in organized molecular films. We have found that the photopolymerization of the PCDA as well as the red or blue phase can be regulated by the miscibility of PCDA with the gemini amphiphiles. Furthermore, with similar miscibility, the spacer length of the gemini amphiphile has also a great effect on the red or blue phase of the film. So far, many works have been reported on the photopolymerization of the diacetylene by changing their headgroups or alkyl chains to regulate their packing,[18–23] and herein we showed a simple and effective way of regulating the polymerization by mixing the gemini amphiphile with various spacer lengths.

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* Corresponding author. E-mail: liumh@iccas.ac.cn.

CHART 1: Molecular Structures of G*n* and PCDA Used in This Work
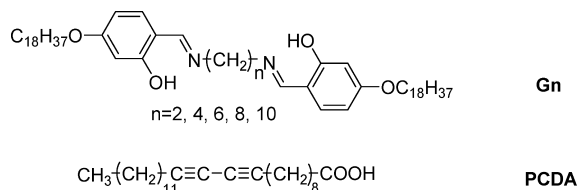
The photopolymerization and their mixing properties were investigated by surface pressure−area isotherms, UV−vis spectroscopy, and Fourier transform infrared (FT-IR) spectroscopy.

Experimental Section

Materials. Gemini-type Schiff base amphiphiles G*n* ($n = 2$, 4, 6, 8, 10) were prepared as described before,[34] and the structures are shown in Chart 1. Monomer diacetylene acid 10,12-pentacosadiynoic acid (abbreviated as PCDA) was purchased from Lancaster Synthesis and purified by dissolving in chloroform and filtrating to remove polymerized monomers before use. Solvents used in this work were obtained from Beijing Chemicals and distilled before use. Ultrapure deionized water (Millipore-Q, 18 MΩ·cm) was used as the subphase.

Procedures. PCDA was mixed with G*n* in chloroform solution with different molar ratios, and typical ratios of 2:1, 1:1, 1:2, 1:3, and 1:4 were used. The total mole concentration for all solution is 1 mM. The Langmuir films on pure water subphase were performed on a KSV minitrough (KSV Instruments, Helsinki, Finland). The monolayer was formed by carefully spreading the chloroform solution of PCDA/G*n* mixture on pure water subphase. After waiting 30 min for the evaporation of chloroform, the monolayers were compressed with a speed of 7.5 cm²/min. The surface pressure was monitored by an electronic microbalance with platinum as a pressure sensor. Subphase temperature was maintained at 20.0 ± 0.2 °C, using a circulating water bath. For UV−vis and FT-IR measurements, monolayers were first compressed to a certain pressure, and then transferred onto solid substrate (quartz or CaF₂) by a horizontal lifting method. All the experiments were performed in the dark. After the mixed monolayers were transferred onto solid plates, the films were subjected to UV irradiation with a 25 W UV lamp at a distance of 20 cm. In order to monitor the polymerization process, the samples were irradiated for different time intervals and their UV−vis spectra were recorded by a JASCO UV-550 spectrophotometer. FT-IR spectra were obtained by a JASCO FT/IR-660 plus spectro-photometer with a resolution of 4 cm⁻¹.

Results

Miscibility of the Mixed Films. In order to understand the interaction between PCDA molecules and the gemini am-phiphiles, surface pressure−area isotherms of the mixed mono-layers were investigated. Here, we take G2 as an example to show the features of mixed monolayers. Figure 1 shows the π−A isotherms of the mixed monolayers of PCDA with G2 at different molar ratios. The data for PCDA/G4, PCDA/G6, PCDA/G8, and PCDA/G10 are shown in the Supporting Information (Figure S1). For the pure PCDA molecular film, the limiting area per molecule is 0.28 nm²/molecule with a transition pressure at around 15 mN/m, which is in agreement with the literature value.[16] In the case of pure G2, a phase transition point can be seen at around 25 mN/m, and the extrapolated molecular area is 0.52 nm²/molecule. For isotherms
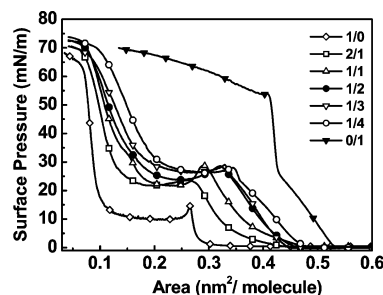
Figure 1. Surface pressure−area isotherms of PCDA/G2 at mixing molar ratios of 1/0 (−◇−), 2/1 (−□−), 1/1 (−△−), 1/2 (−●−), 1/3 (−▽−), 1/4 (−○−), and 0/1 (−▼−).

of the mixed monolayers at various ratios, a transition point is always observed for each monolayer and these isotherms all fall between isotherms of the two pure samples. The transition points of mixed monolayers can be used to identify the miscibility of two components. For completely immiscible components, the isotherms of mixed monolayers will exhibit two different transition points, which correspond to the pure components. Thus, from this aspect, complete immiscibility of PCDA and G*n* can be ruled out.

On the other hand, molecular average area can act as another criterion to examine the miscibility. The miscibility of two components can be analyzed from the excess area (A^E) of mixed monolayers at the air−liquid interface. The excess area can be obtained by comparing the molecular area (A_{12}) of a mixed monolayer consisting of components 1 and 2 with that of an ideal mixed monolayer (A_{id}):

$$A^E = A_{12} - A_{id} = A_{12} - (x_1A_1 + x_2A_2) \qquad (1)$$

where x_1 and x_2 are the mole fractions of components 1 and 2 in the mixed monolayer and A_1 and A_2 represent the molecular areas of the pure monolayers, respectively. For two components that can be miscible, the interaction between like molecules is the same as that with unlike molecules. In the case of complete immiscibility, interaction between like molecules is much stronger than that betweeen unlike molecules. In the two cases, the excess area is zero. However, such situations are rare and nonzero values are usually observed. In addition, the value of excess molecular area also reflects the interaction between the two components. If a negative value of the A^E is obtained, more attractive interactions between the two components exist and the film will be more compact. By contrast, a positive value means that the two components have a strong repulsion and the film will be more expanded.[35]

In our experiments, we measured the π−A isotherms of the mixed monolayers of PCDA and all the gemini amphiphiles and obtained the plot of the excess molecular area against mole fraction of G*n* in Figure 2 for all combinations. The limiting molecular area of the mixed monolayers increased with increas-ing G*n* component. However, the increment was not linear, indicating the deviation from the ideal mixture of the two components. As shown in Figure 2 for limiting molecular area, the A^E is negative for all mixed monolayers, indicating attractive interactions between PCDA and the geminis. This may be caused by the electrostatic interaction between acid (PCDA) and base (Schiff base headgroups), which will be discussed later. Moreover, of all the mixed monolayers, PCDA/G2 shows the minimum derivation for ideal miscibility, while PCDA/G10 shows the maximum derivation. PCDA/G4, PCDA/G6, and

Photopolymerization of Amphiphilic Diacetylene

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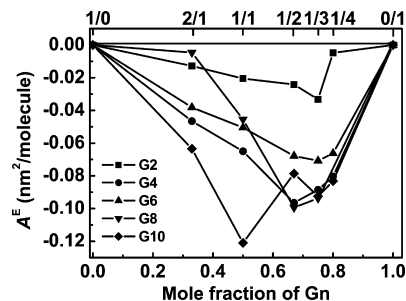
Figure 2. Excess molecular area as a function of mole fraction of G2 (−■−), G4 (−●−), G6 (−▲−), G8 (−▼−), and G10 (−◆−). The top scale represents the PCDA/G*n* molar ratio.
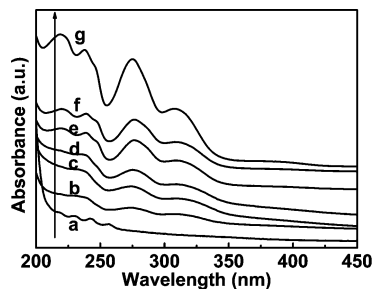

Figure 3. UV−vis spectra of PCDA/G4 films prepared at 20 mN/m at mixing ratios of 1/0 (pure PCDA, a), 2/1 (b), 1/1 (c), 1/2 (d), 1/3 (e), 1/4 (f), and 0/1 (pure G4, g).

PCDA/G8 fall between PCDA/G2 and PCDA/G10. This indicates that the miscibility between PCDA and geminis depends on the spacer length of the gemini.

Photopolymerization of the Mixed Film. PCDA/G*n* mixed monolayers on pure water subphase were then transferred onto quartz substrates at a certain surface pressure for UV−vis measurement, as shown in Figure 3. For the films from pure PCDA (molar ratio of 1/0), three weak absorption bands appeared at 230, 242, and 256 nm (Figure 3a). Because the series of geminis have similar spectral features, we take G4 as an example. Pure G4 shows absorption at 220, 238, 246, 276, and 308 nm (mixing ratio of 0/1). Compared with the two components, the absorption of PCDA/G4 mixed films is closer to G4, while the PCDA absorption bands can be hardly distinguished due to the strong absorbance of G4 at the same region. On the other hand, as the ratio of G4 increases (from curve a to curve g), the intensity of absorption bands of G4 increases, and when the mixing ratio is lowered to 1/3 (Figure 3e), split peaks at 246 and 276 nm can still be clearly observed.

The photopolymerization of PCDA occurred when the transferred films were exposed to UV light, and UV−vis spectroscopy was used to monitor the reaction. It is well-known that pure diacetylene monomers are transparent in the visible region, and after polymerization the formed PDA exhibited two different structures with absorption maxima centered around 540 and 640 nm, the so-called red and blue forms. In the pure PCDA films in our work, the polymerized PDA showed the absorption maximum at 635 nm. It was found that upon irradiation the intensity of the absorption band at 635 nm increased with the irradiation time and the reaction completed within 15 min (Supporting Information, Figure S2). No significant changes occurred when the irradiation time was elongated. Thus we selected 20 min for the irradiation of all the films.

Figure 4 shows the UV−vis spectra of PCDA/G2, PCDA/G4, and PCDA/G8 mixed films at different ratios after photopolymerization. (The spectra of PCDA/G6 and PCDA/G10 films are shown in Figure S3 in the Supporting Information.) Two
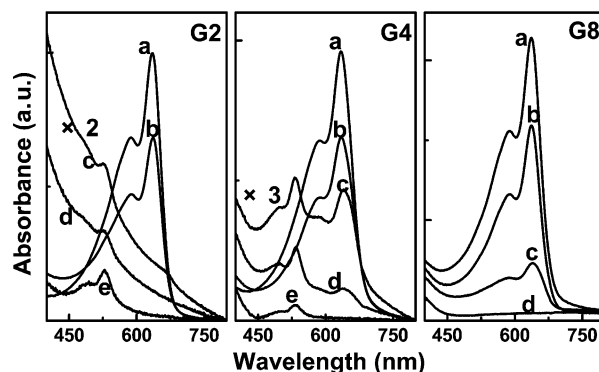
Figure 4. UV−vis spectra of PCDA/G2, PCDA/G4, and PCDA/G8 mixed films at mixing ratios of 2/1 (a), 1/1 (b), 1/2 (c), 1/3 (d), and 1/4 (e). The UV−vis spectra of G2 and G4 at ratios 1/2, 1/3, and 1/4 were amplified 2- and 3-fold, respectively.

TABLE 1: Peak Positions of Poly(diacetylene) in Mixed Films at Various Ratios after Photopolymerization for 20 min

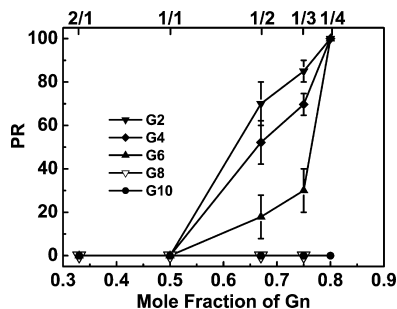|	PCDA/G*n* (molar ratio)							
			1/2		1/3		1/4	
G*n*	2/1	1/1	blue	red	blue	red	blue	red
G2	636	637		528		528		528
G4	638	638	638	532	642	534		534
G6	637	636	637	535	640	535		533
G8	637	636	640					
G10	637	636	634		634		635	

interesting features were observed for the polymerization in these mixed films. First, for the series of gemini amphiphiles, when the mole fraction of PCDA is high (2/1 and 1/1), strong absorption bands appeared around 637 nm and the so-called blue form films were predominantly detected in all the mixed films upon polymerization. However, when the mixing ratio of PCDA to G*n* is lower than 1/1, the polymerization of PCDA in mixed films is quite different among the series of gemini amphiphiles. For PCDA/G2, when the mixing ratio is 1/2, a strong absorption band appears at 528 nm after photopolymerization, which is assigned to the red phase. Despite no obvious absorption band of the blue form, the absorbance increases sharply from 700 to 550 nm, indicating that blue phase may also exist in the films. When the mixing ratio further decreases to 1/3 and 1/4, the intensity of the red phase decreases gradually, and the films only show red phase at the mixing ratio of 1/4. All the peak positions of poly(diacetylene) at different mixing ratios are shown in Table 1. Different from PCDA/G2 film, the mixed films of PCDA/G4 and PCDA/G6 show both blue and red forms at the ratios of 1/2 and 1/3. When the ratio is up to 1/4, the red form is also the only form in the mixed films. On the other hand, in the PCDA/G8 and PCDA/G10 mixed films, only blue form can be found at various ratios. Interestingly, the PCDA/G8 mixed films cannot be photopolymerized when the ratio of PCDA/G8 is lower than 1/3.

To calculate the proportion of red phase, "percent of red" (abbreviated as PR) is defined as

$$PR = A_{Red}/[A_{Red} + A_{Blue}] \times 100\% \qquad (2)$$

where A_{Red} represents red phase absorbance (around 530 nm) in UV−vis spectra, and A_{Blue} represents the blue phase (around 640 nm). The plot is shown in Figure 5.

Figure 5. Plot of percent of red in mixed films after polymerization for 20 min versus mole fraction of geminis: G2 ($-\blacktriangledown-$), G4 ($-\blacklozenge-$), G6 ($-\blacktriangle-$), G8 ($-\triangledown-$), and G10 ($-\bullet-$). The top scale represents the PCDA/Gn molar ratio.
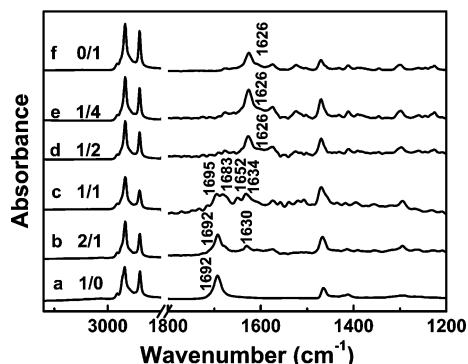
Figure 6. FT-IR spectra of PCDA/G4 mixed films at ratios of 1/0 (pure PCDA) (a), 2/1 (b), 1/1 (c), 1/2 (d), 1/4 (e) and 0/1 (pure G4) (f) before polymerization.

From the plot in Figure 5, the following conclusion can be deduced. As the mole fraction of Gn increases, red phase emerges in place of blue phase. As the spacer length of Gn increases, the appearance of red form needs a higher mole fraction of Gn.

FT-IR Spectra. In order to get further insight into the interaction between the two components, FT-IR spectra of the mixed films were recorded at various ratios. Herein we also take PCDA/G4 as an example, as shown in Figure 6. Pure PCDA films (Figure 6a) show characteristic absorption at 2920, 2849, and 1692 cm^{-1}, which can be assigned to asymmetric and symmetric vibrations of CH_2 and carbonyl C=O in H-bond.[22,24] When PCDA was mixed with G4 at the ratio of 2/1, C=O absorption also appeared at 1692 cm^{-1}, and a weak shoulder peak appeared around 1680 cm^{-1}. Besides that, a new peak appeared at 1630 cm^{-1}, which can be assigned to the C=N group of G4. As the molar ratio of G4 increased to 50% (mixing ratio 1/1), there appeared two absorptions at 1695 and 1683

cm^{-1}. The carbonyl C=O absorption at higher wavelength indicates that the H-bond was partly destroyed by interacting with G4. The absorption at lower wavelength can be assigned to species of carboxylic anions. In addition, besides 1634 cm^{-1}, there is also an absorption band at 1652 cm^{-1}, which can be assigned to C=NH$^+$. When G4 was increased further (mixing ratio of 1/2 and 1/4), C=N absorption band appeared at lower wavelength of 1626 cm^{-1}, the same as that in pure G4 sample (Figure 6f). The absorption band of C=NH$^+$ decreased in intensity and even disappeared at the ratio of 1/4, indicating deprotonation of Schiff base. Thus it can be speculated that the Schiff base in gemini amphiphiles can interact with carboxyl groups in PCDA by acid and base reactions. When the fraction of gemini amphiphile is small, most of the carboxyl groups exist in the form of H-bonded one, and Schiff base groups of Gn can be protonated. As the addition of gemini amphiphile increases, the H-bond between neighboring PCDA molecules may be partly destroyed.

Discussion

From the results above, it is clear that the polymerization, blue form, or red form of the polymerized species can be regulated by the gemini amphiphiles, in which both the mixing ratio and the spacer lengths of the gemini amphiphiles played important roles. The miscibility study revealed an essentially attractive interaction between the two components and deviation from the ideal additivity increased with the spacer length of the gemini. FT-IR spectra indicated the presence of an ionic interaction between the headgroups of gemini amphiphile and PCDA. Thus, all the experimental results can be discussed as shown in Scheme 1.

When PCDA was mixed with the gemini amphiphiles, an ionic interaction between the headgroup of the geminis and the carboxylic acid group occurred as verified from the FT-IR spectra. It is well-known that the color of the resulted poly(diacetylene), red or blue form, has much relevance to the packing of monomer diacetylene. Pure PCDA formed H-bonds in organized films. In this case, the H-bond between the headgroups as well as the hydrophobic interaction between the alkyl chains leads to a regular packing of diacetylene, which meets the requirement for the formation of blue phase. When gemini amphiphiles was added, they will interact with the headgroup of the diacetylene as well as the hydrophobic chains, which will possibly alter the molecular arrangement of diacetylene as well as the photoreaction. As a result, when the fraction of geminis was small, the H-bonds were still maintained among most of the PCDA molecules and the blue form was predominantly formed in PCDA/Gn mixed films. As the fraction of Gn increased, such an ionic interaction became stronger, leading

SCHEME 1: Illustration of Molecular Packing in Mixed PCDA/Gn Film^a
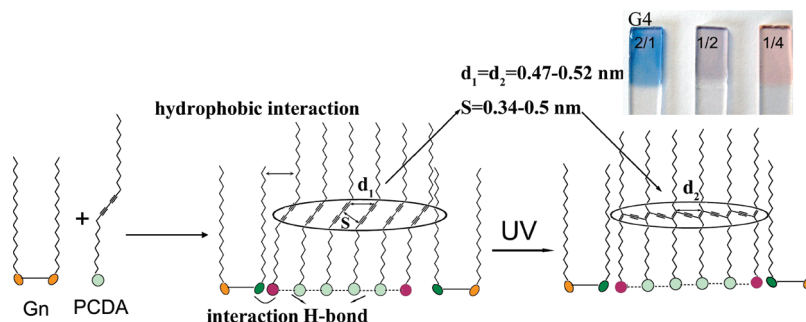
^{a} The inset shows the color of the photopolymerized PCDA/G4 films with different ratios.

to the packing changes of diacetylene molecules and the red form chiefly emerged. Thus, we observed the red film in the PCDA/G2, PCDA/G4, and PCDA/G6 mixed films when the molar ratio of these gemini amphiphiles increased. However, in PCDA/G8 and PCDA/G10 films, no red films were found even when the molar ratios of G8 and G10 increased to a large extent. Therefore, besides the interaction between the headgroups, the spacer length is also an important factor that affects the polymerization of PCDA.

The ionic interaction between the headgroups can cause a large deviation of the molecular packing from the H-bonded one in pure PCDA molecular films. When the gemini amphiphiles were used, the neighboring ionic interaction could be weakened by the flexible spacer. With increasing spacer length, the flexibility of the spacer increased. The longer spacer can obviously decrease such ionic interaction and keep the H-bonded packing of diacetylene. Therefore, we mainly observed the blue film when G8 and G10 were mixed. There have been several reports on the effect of the alkyl chain length within the diacetylene unit.[36−38] It is reported that the packing of the long alkyl chain, which is along the direction of the diacetylene unit, is advantageous for the polymerization into blue film. It seems that the alkyl spacer in the gemini amphiphile, which is in a perpendicular direction to the diacetylene unit, has a similar regulation effect. It is interesting that photopolymerization of PCDA could not proceed in the PCDA/G8 mixed film when the molar ratio of PCDA/G8 was lower than 1/3. Previously, we have found that the alkyl spacer could change its conformation and the properties of the complex gemini films showed a turning point at a certain spacer length.[30−32] It seems that in the present mixed films of PCDA with Gn such a turning point appeared at C8.

From our work and other reports, the Langmuir−Blodgett film of PCDA is not very stable in aqueous solution and is easily peeled off from the plate, which would limit the application of diacetylene film as a chemical sensor. On the other hand, the film of a gemini amphiphile shows excellent stability due to the fact that the two headgroups anchor on the supporting plates. When PCDA is mixed with the gemini amphiphile, we have also found that the film is very stable on the support and their further functionalization is underway.

Conclusion

When gemini amphiphiles were mixed with PCDA in organized molecular films, the photopolymerization of PCDA could be regulated by the gemini amphiphiles from two aspects. One is the mixing ratio, and the other is the spacer length of the gemini amphiphiles. When less geminis were mixed in the film, blue film was obtained, while the red film was obtained upon increasing the mixing ratio of geminis. Gemini amphiphiles with longer spacers favored the PCDA to be polymerized into blue film, while those with short spacers preferred the formation of red phase. It was suggested that the ionic interaction between the headgroups of geminis and diacetylene played an important role in causing such differences. The strong ionic interaction deviated the packing of PCDA molecules from the one with their carboxylic acid groups H-bonded and tended to form red film when the spacer length was short, while a longer spacer in the gemini can weaken the ionic interaction and keep the film packing in favor of the blue film. The present work provides an efficient way of regulating the photopolymerization of diacetylene through simple mixing with gemini amphiphiles.

Supporting Information Available: Surface pressure−area isotherms of mixed films of PCDA/G4, PCDA/G6, PCDA/G8, and PCDA/G10 at various ratios of 1/0, 2/1, 1/1, 1/2, 1/3, 1/4, and 0/1. The absorbance of the polymerized film as a function of the irradiation time. UV−vis spectra of PCDA/G6 and PCDA/G10 mixed films with ratios of 2/1, 1/1, 1/2, 1/3, and 1/4. This information is available free of charge via the Internet at http://pubs.acs.org.

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