7540 *Macromolecules* **2010**, *43*, 7540–7548
DOI: 10.1021/ma101264k

Macromolecules
ARTICLE

Tuning Down of Color Transition Temperature of Thermochromically Reversible Bisdiynamide Polydiacetylenes

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Received June 7, 2010; Revised Manuscript Received July 29, 2010

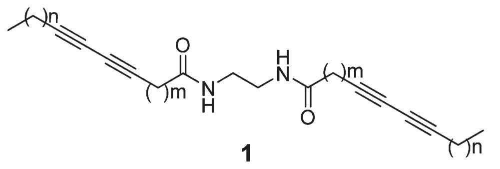
ABSTRACT: A series of bisdiynamide lipids containing various lengths of methylene spacer (m = 2, 3 and 4) between the diynes and the diamide headgroup and number of methylene units (n = 6 and 9) in their hydrophobic tails are synthesized. All six lipids synthesized can be dispersed in water and photopolymerized by UV irradiation to give the corresponding polydiacetylene (PDA) sols. The color transitions from blue to red during heating–cooling cycles of the PDA sols are photographically recorded and monitored by UV–vis absorption spectroscopy. The bisdiynamide PDAs exhibit excellent thermochromic reversibility and the color transition temperature can be tuned between ca. 25–55 °C by the variation of m and n values. Temperature indicators can be obtained by applying a screen printing ink formulated from the bisdiynamide monomer on plastic substrates followed by UV irradiation to generate desired patterns of thermochromically reversible PDAs.

Introduction

Polydiacetylenes (PDAs) are ene–yne π-conjugated polymers possessing unique chromic properties that can be developed into practical colorimetric transducers in biological[1] and chemical[2] sensors. A PDA is generally obtained from a topopolymerization of a diacetylene monomer under UV or γ-ray irradiation. Various forms of PDAs such as bulk crystals,[3] monolayer,[4] multilayer films,[5] and composites[6] have been prepared and studied. Most interestingly, their π-conjugated backbone can be disturbed by various external stimuli to cause changes in its electronic absorption and color. The colorimetric transition caused by the external stimuli such as heat (thermochromism),[7] solvent (solvatochromism),[8] mechanical stress (mechanochromism)[9] and ligand–receptor interaction,[10] are often detectable by naked eye.

Thermochromism is probably one of the earliest known properties of PDAs and most widely studied for its mechanism. Thermochromic reversibility of PDAs have been achieved by increasing the attractive intramolecular interaction among their side-chains.[7a–c,11] In our continuing attempt to develop PDA-based sensors, we have recently found that thermochromically reversible PDAs can be obtained from the diamide derivatives of 10,12-pentacosadiynoic acid (PCDA).[7i] These diamide PDAs and all other thermochromically reversible PDAs reported to date possess color transition temperature higher than that of poly(PCDA) which is above 65 °C. Reducing the color transition temperature of the PDAs without severe distress of their thermochromic reversibility is mechanistically challenging. Furthermore, the thermochromically reversible materials with color transition temperatures near or below ambient temperature are of commercial interest as temperature indicators for various consumer products such as foods and beverages.

The reduction of the aliphatic chain length of the diacetylene monomers has been reported to decrease the thermal stability of thermochromically irreversible PDAs attributed to the weakening of cohesive hydrophobic interaction.[11c] We figured that the shortening of the aliphatic chain length may also be used as a strategy for tuning down the color transition temperature of thermochromically reversible PDAs. Report herein is the synthesis and thermochromic properties of bisdiynamide monomers **1** with varied length of the methylene spacer between the diyne and amide headgroup (m) and the number of methylene groups within its tail (n) which form thermochromically reversible PDAs with color transition temperature near or below ambient temperature.



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Results and Discussion

1. Synthesis of Diacetylene Monomers. The synthesis of the diamide diacetylene (**1**) began with the copper-catalyzed cross coupling reaction (Scheme 1) between an iodoalkyne (**2** or **3**) and an alkynoic acid (**4**–**6**) under a modified Cadiot–Chodkiewicz condition[12] to afford the diynoic acids (**7**–**12**) in moderate to good yields (49–75%). The competitive homocoupling of the iodoalkyne sometimes lessened the diynoic acid yield. Subsequent treatment of the diynoic acids with 0.5 equiv of ethylenediamine in the presence of N, N'-dicyclohexylcarbodiimide (DCC) coupling reagent afforded the desired bisdiynamide monomers (**1a**–**1f**) as white solids in good yields (68–78%). These bisdiynamides were

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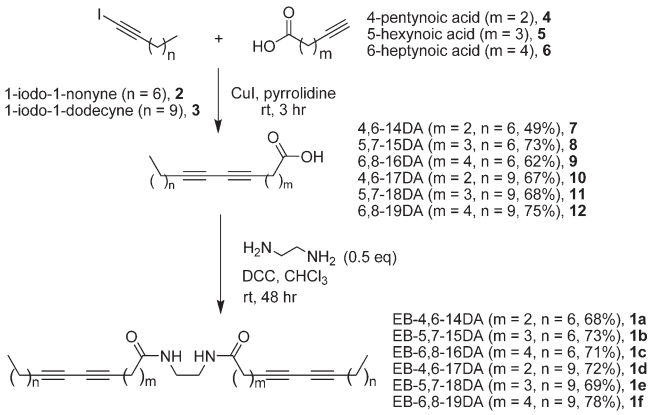
readily isolated from dicyclohexyl urethane (DCU) byproduct and the monoamide side-product by crystallization in methanol.

2. Preparation of PDA Sols. The phospholipid-liked monomers **1a−f**, containing two hydrophobic tails, were well dispersed in Milli-Q water under sonication at 80−85 °C to form either transparent or semitransparent sols (see Supporting Information S15, first row) suggesting a good formation of lipid assembly. Notworthingly, the corresponding fatty acid-liked monomers, containing only one hydrophobic tail, i.e. diynoic acids and monoamide diacetylenes with $m = 2, 3$ and $n = 6, 9$, formed large aggregate and precipitate under the same preparative condition. Upon UV-irradiation (254 nm, 900 μw/cm^2) in an ice bath, the diacetylene sols rapidly turned intense blue or purple color within 5 min, signifying an efficient topopolymerization of the monomer assemblies to form the ene−yne conjugated PDAs. The blue PDA sols showed a characteristic absorption band with two maxima near 640 and 580 nm corresponding to the $\pi-\pi^*$ electronic transition with double bond vibronic coupling. In addition, the blue PDA sols of EB-4,6-17DA and EB-4,6-14DA also showed an extra peak at unusually long wavelength near 700 nm. The origin of this low energy absorption remains mysterious to us.[7i]

After the temperature of the polymerized sols was allowed to warm up to 20 °C, the appearance of the PDA sols were photographically recorded (see Supporting Information S15, second row). Notably, the PDA sols obtained from EB-4,6-14DA, EB-4,6-17DA, EB-5,7-18DA and EB-6,8-19DA (**1a**, **1d**, **1e**, and **1f**) appeared as a blue color while the PDA

Scheme 1. Synthesis of Diacetylene Lipid Monomers



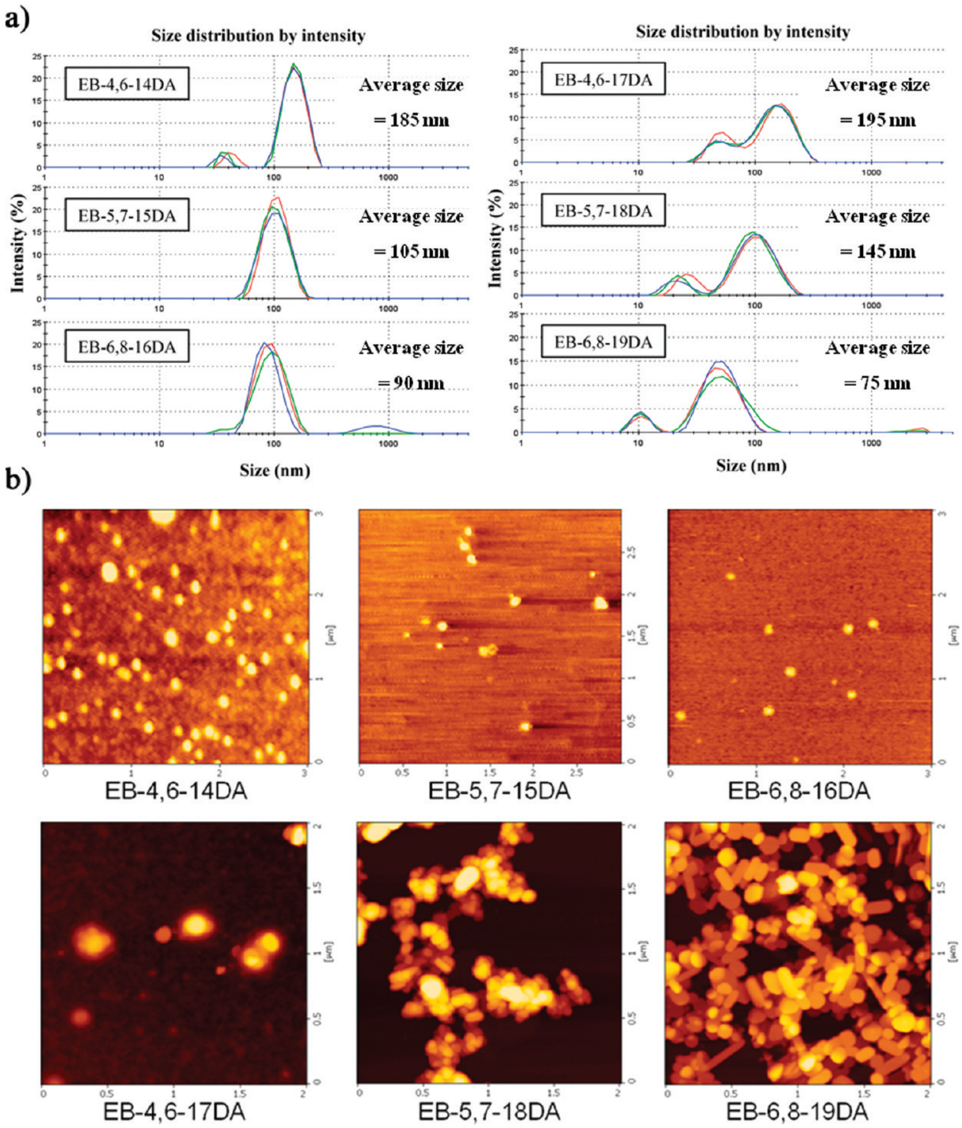


Figure 1. (a) Size distribution obtained from dynamic light scattering (b) AFM images of poly(bisdiynamide).

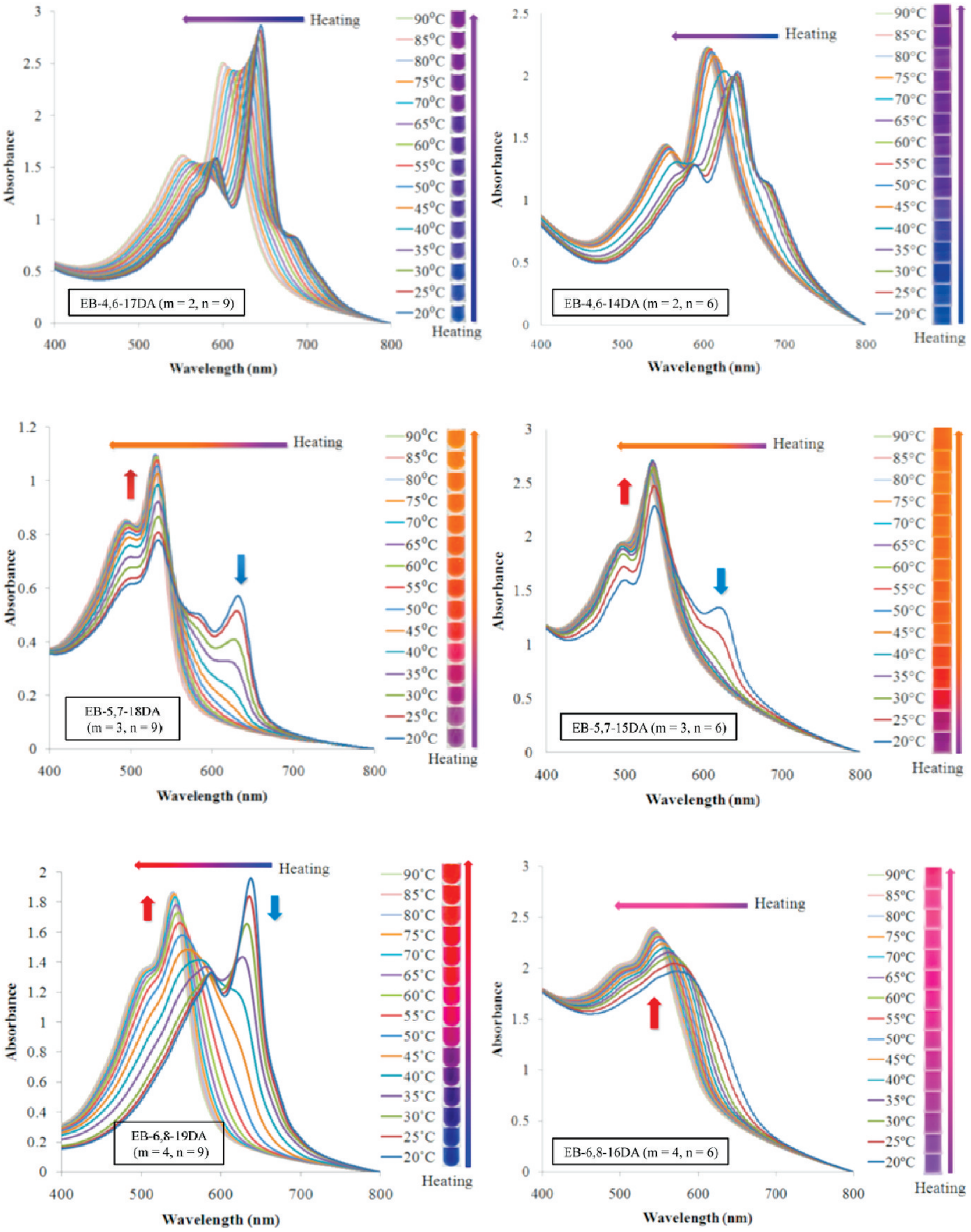


Figure 2. Electronic absorption spectra of bisdiynamide PDA sols upon stepwise heating from 20 to 90 °C along with the color appearance of the sols recorded by photography.

sols obtained from EB-5,7-15DA and EB-6,8-16DA (**1b** and **1c**) appeared as a purple color at room temperature. The results suggested that both the numbers of the *m* and *n* values played subtle roles in governing the thermochromic sensitivity of this PDA series which will be elaborated in the subsequent section.

The sizes and shapes of the lipid assembled particles within the PDA sols were characterized by dynamic light scattering (DLS) technique and atomic force microscopy (AFM). The DLS size distribution revealed the average hydrodynamic diameter of the particles in the range of 75−195 nm (Figure 1a). The PDA sol obtained from EB-6,8-19DA showed the smallest particle size of 75 nm while the largest size of 195 nm was observed for the sol obtained from EB-4,6-17DA indicating that the particle size tended to increase with the decreasing m value. The AFM image of the dry sample of poly(EB-4,6-17DA) sol showed mainly spherical structures while those of poly(EB-5,7-18DA) and poly(EB-6,8-19DA) sols illustrated mixtures of spherical and rod-like structures (Figure 1b) that is in good agreement with the decreasing packing parameter (ρ) of the lipids.

3. Thermochromic Properties of PDA Sols. The thermochromic transition of the successfully prepared PDA sols was monitored from 20 to 90 °C using photography and electronic absorption spectroscopy. From the results shown in Figure 2, both the numbers of the *m* and *n* values in the bisdiynamide lipid structures cast effects on the color transition temperature. By fixing the *m* value, the reduction of the *n* value decreased the color transition temperatures:

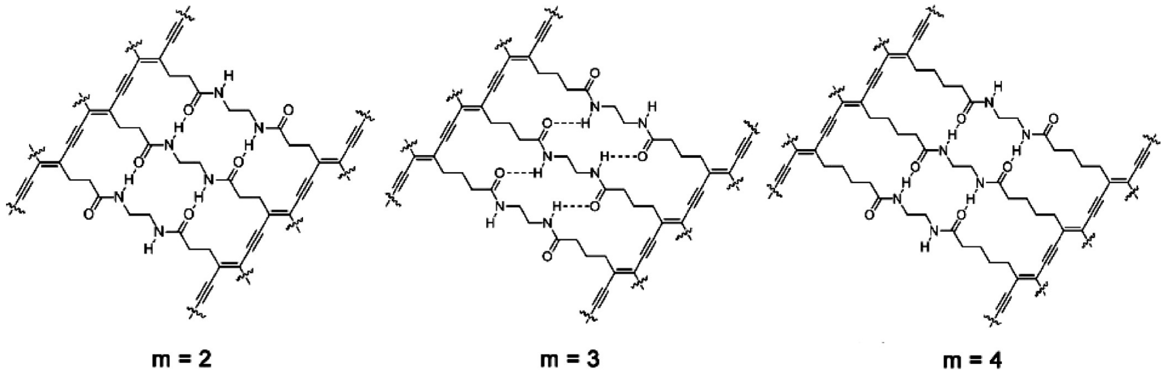


Figure 3. Hypothetical packing of the diamide side-chains of the PDAs with $m = 2$, 3 and 4.

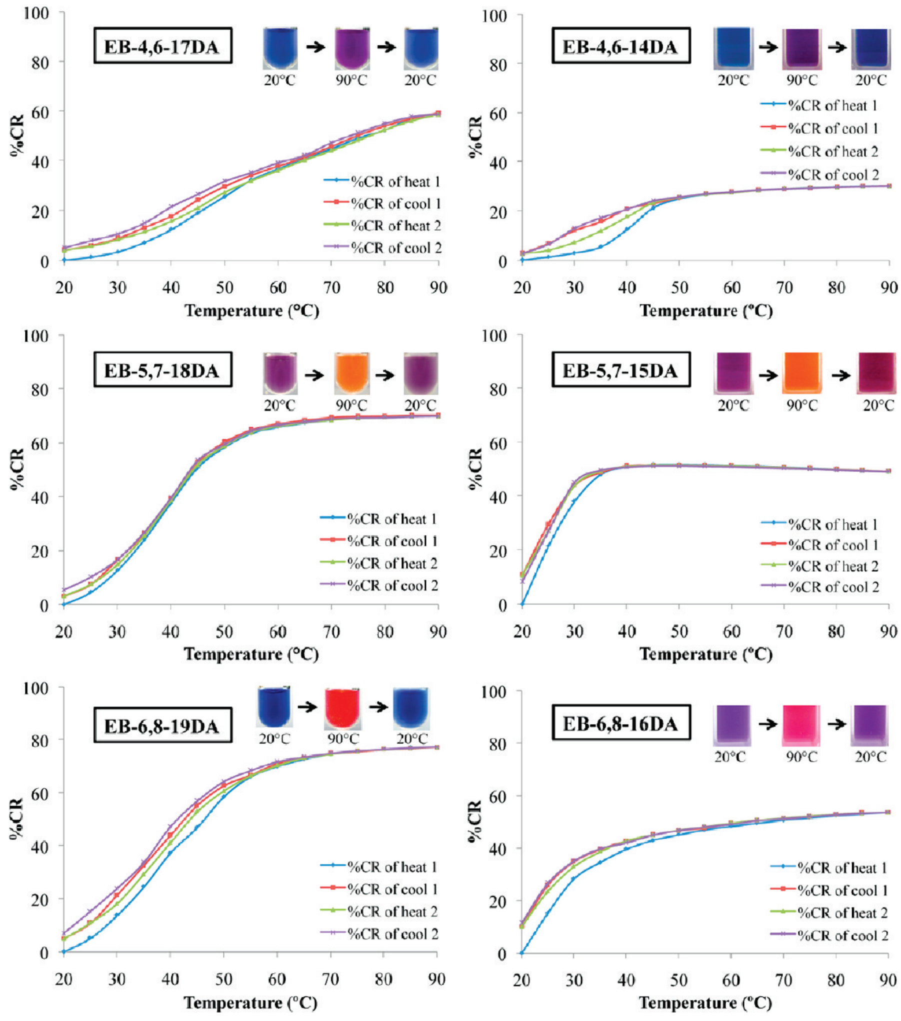


Figure 4. The colorimetric responses (% CR) of bisdiynamide PDA sols during two cycles of stepwise heating/cooling processes. The inset color photographs show the appearance of the sols at initial temperature of 20 °C, after being heated to 90 °C, and after lowering the temperature back to 20 °C.

poly(EB-5,7-18DA) > poly(EB-5,7-15DA) and poly(EB-6,8-19DA) > poly(EB-6,8-16DA). Considering PDAs with the same n value, the effect of m value was more complicated. For instance, poly(EB-4,6-17DA) and poly(EB-4,6-14DA) which has $m = 2$ are unusually thermally stable and did not turn red at 90 °C. In fact, in solid state these PDAs did not turn red even at 150 °C (data is not shown). In contrast, the PDAs with $m = 3$ such as poly(EB-5,7-18DA) and poly(EB-5,7-15DA) are rather thermally sensitive exhibiting blue-red color transition temperature below the ambient temperature and those of PDAs with $m = 4$ were slightly higher (10−15 °C). The trend in thermal stability of the PDAs containing $m = 3$ and 4 may be attributed to either the length[11c] or odd/even effects.[13] However, these effects cannot account for the unexpectedly high thermal stability of poly(EB-4,6-17DA) and poly(EB-4,6-14DA). We hypothesize that, with $m = 2$, the diamide side-chains of the PDAs form extraordinary strong hydrogen bonding accommodated by the well positioned ene−yne backbone (Figure 3), but a clearer explanation on this issue will need further investigation.

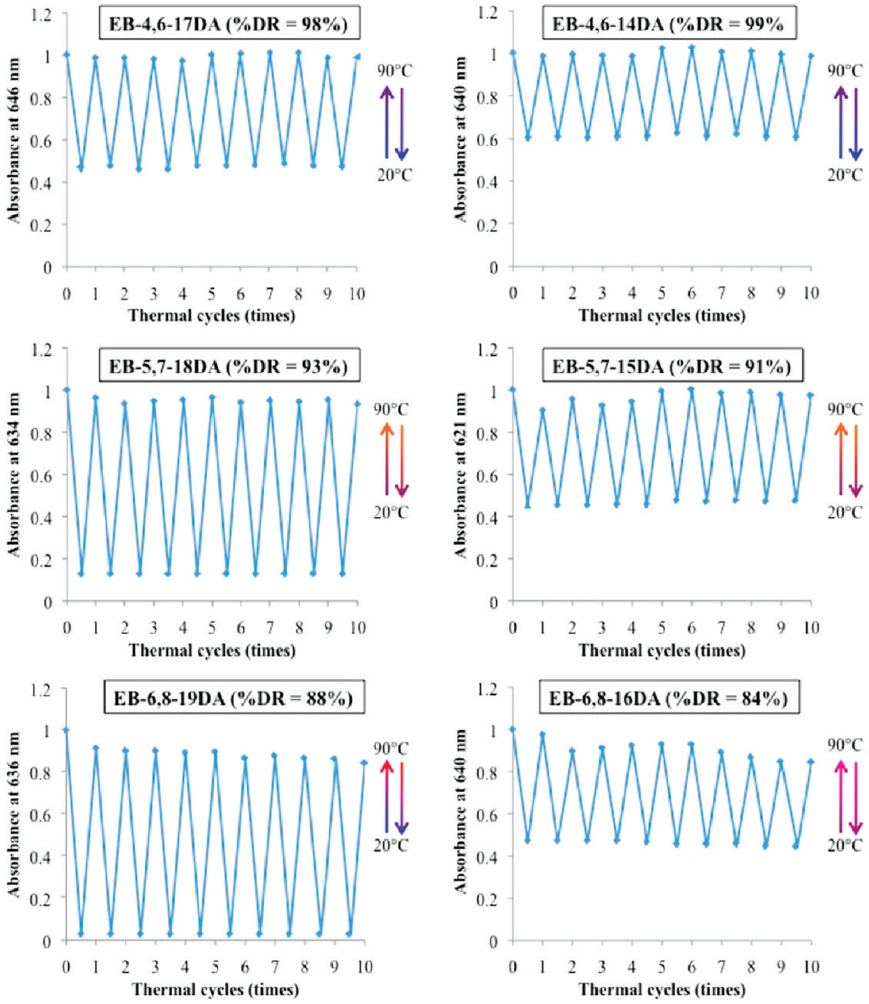


Figure 5. Normalized absorbance at the initial $\lambda_{\max}$ (A_λ) of the PDA sols at 20 and 90 °C in the heating/cooling cycles. The degree of reversibility (% DR) is the percentage ration of the average absorbance change in the second to tenth heating against the absobance change in the first heating.

From the results discussed above, the PDAs with color transition temperature near or below ambient temperature were successfully prepared and, to complete our research goal, the thermochromic reversibility of these PDAs was explored in the following section.

4. Thermochromic Reversibility of PDA Sols. To our delight, all the bisdiynamide PDAs were thermochromically reversible even the ones that showed relatively low color transition temperature such as EB-5,7-15DA, EB-5,7-18DA, EB-6,8-16DA and EB-6,8-19-DA (Figure 2, color photographic insets). Notably, PDAs obtained from these four monomers offer reversible thermochromic materials with significantly lower color transition temperature (25−55 °C) comparing to the bisdiynamide derivatives of PCDA (70−80 °C).[7i] The colorimetric response (% CR, see Experimental Section for calculation) of the PDA sols obtained from the first two cycles of stepwise heating/cooling processes, in the range of 20 to 90 °C, showed nearly complete reversibility (Figure 4). Despite complete reversibility after the first cycle, the % CR did not return to the initial zero value at the starting point. The discrepancies in % CR represent the degrees of unrecoverable backbone strain present in the as prepared PDAs, upon thermal annealing. Again, the fact that poly(EB-4,6-14DA) and poly(EB-4,6-17DA) showed the least discrepancy in % CR after the first heating/cooling cycle along with their barely visible color transition has confirmed the hypothetical presence of extraordinary strong force prevailing over the backbone strain in these PDAs. With $m = 2$, the side chain geometry (Figure 3) ene−yne backbone and the double hydrogen bonding of the diamide groups work collaboratively.

Quantitative evaluation of the thermochromic reversibility was performed by monitoring the absorbance of the PDA sols at their initial $\lambda_{\max}$ for 10 heating/cooling cycles. The plots in Figure 5 indicate that all bisdiynamide PDA sols possess excellent thermochromic reversibility up to at least 10 cycles. The degree of reversibility (% DR),[7i] of these PDA sols calculated (see Experimental Section for the calculation) for the first 10 cycles were higher than 84% and increased with the lessening m values but with the levitating n values. It is also interesting to note that the wider range of the absorbance change during the thermochromic process of the PDAs prepared from the monomers containing higher n value denotes the greater contrast in color change, desirable for practical application as a temperature indicator.

The bisdiynamide PDA sols were incubated at 95 ± 2 °C in an oil bath for evaluation of their long-term thermal stability. The incubated sols were sampled out at each time interval and allowed to cool to 20 °C. The electronic absorption spectra and photographs of the samples were recorded and presented in Figure S16. The color of poly(EB-4,6-17DA) remained blue but appeared much paler after 64 h

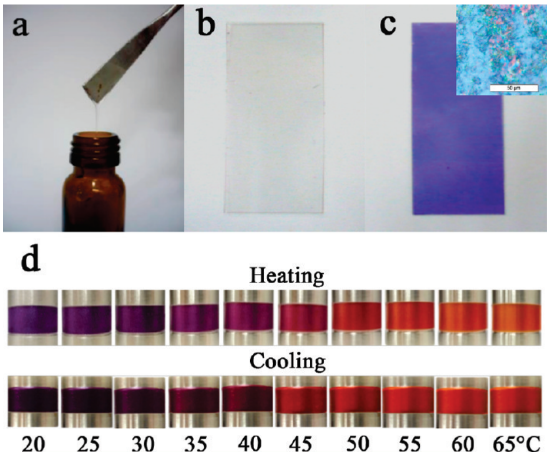


Figure 6. Preparation of thermochromic labels by screen printing process of a bisdiynamide monomer: (a) screen printing ink containing the bisdiynamide monomer, (b, c) screen printed transparency sheet before (b) and after (c) UV irradiation (insets are microscopic images under optical microscope), and (d) color transition of the thermochromic labels sleeving around a stainless ring.

of incubation due to serious precipitation. The intensity of the absorption band significantly decreased after 32 h of incubation (Figure S15 in Supporting Information). However, no significant change of the spectral shape was observed throughout the incubation period. The descent in the absorption is in association with the amount of precipitation observed. These results indicated that poly(EB-4,6-17DA) possesses exceptional chromic stability upon thermal stress despite undergoing extensive aggregation. The color appearance and the absorption spectra of poly(EB-5,7-18DA) and poly(EB-6,8-19DA) displayed obvious shift of color from blue to purple along with precipitation after 32 h of incubation. These bisdiynamide PDAs may be used as temperature indicators under conditions where there is no prolonged exposure to high temperature.

5. Fabrication of Thermochromic Labels. Although the colloidal liquid sol of PDAs is good for spectroscopic study due to its homogeneity and high polymerization yield, this form of PDAs is not practical for many applications requiring portability and long shelf life. Preparation of PDA thin films is a sensible solution for these limitations. A commercial transparent screen printing polymeric resin, composed of PVC and poly(vinyl acetate) as a major component was selected as a matrix for formulation of screen printing ink. (Figure 6a). The ink containing diacetylene monomer was applied on a transparency sheet by screen printing process (Figure 6b). The screen printed monomeric films was successfully polymerized by UV irradiation to generate the desired blue PDA pattern on the substrate (Figure 6c). The success of this method critically relies on the molecular self-assembly of the diacetylene lipids in the ink matrix that is necessary for topological polymerization of the diacetylene units. The microscopic images of the UV-irradiated film showed blue and purple micro dots corresponding to polydiacetylene aggregates dispersed within the white matrix (inset of Figure 6c). The blue PDA pattern was cut and used to form a sleeve aroud a stainless ring. The thermochromic transition of this PDA sleeve was photographically recorded in the temperature range of 20−65 °C (Figure 6d) that showed a blue-red color transtion temperature around 40−45 °C. The screen printing technique is thus proved to be useful for fabrication of a smart thermochromic label from our bisdiynamide monomers.

Conclusion

Tuning of color transition temperature of thermochromically reversible bisdiynamide series of polydiacetylenes (PDAs) can be achieved by systematic variation of the length of methylene spacer (*m*) between the diyne and the diamide headgroup as well as the number of methylene units (*n*) in the hydrophobic tail. While the decrease of *n* value enhances the thermal sensitivity resulting in lower color transition temperature, the effect of *m* value is not as straightforward. Not only the length and odd/even effects but also a magic number of $n = 2$ play important role in governing the thermal sensitivity of the PDAs. With appropriate *m* and *n* values, thermochromically reversible PDAs with color transition temperature near or below ambient temperature were obtained from the bisdiynamide monomers. Screen printing process can be conveniently used to fabricate the monomer into thermochromic labels that suggests potential applications in the field of smart labeling as a temperature indicator.

Experimental Section

Chemicals and Instruments. The starting acetylenic compounds were purchased from GFS Chemicals (USA). *N*,*N*′-dicyclohexylcarbodiimide (DCC), morpholine, pyrrolidine, iodine, ammonium chloride, sodium thiosulphate, sodium sulfate anhydrous, sodium carbonate were purchased from Fluka (Switzerland). Copper(I) iodide was purchased from Riedel-deHaën (Germany). Ethylenediamine was perchased from Aldrich (USA). Diethyl ether (reagent grade) was perchased from AnalaR (U.K.). Toluene (AR grade) was purchased from Fisher Scientific (U.K.). 1,1,1-Trichloromethane (AR grade) was purchased from Labscan (Thailand). All reagent grade compounds were used as purchased without further purification unless stated otherwise. For extraction and chromatography, solvents were commercial grade and they were distilled prior to use. Column chromatography was performed using Merck silica gel 60 (70−230 mesh). ^{1}H spectra were recorded on Varian Mercury 400 MHz NMR spectrometer (Varian, USA) using the residual solvent proton resonance of $CDCl_3$ at 7.26 ppm as the reference. Electronic absorption spectra were recorded on a temperature variable UV−visible spectrophotometer (Varian Cary 100 Bio). AFM images were taken on a SPA 400 atomic forced microscope (Seiko, Japan) Mass analysis was conducted with Quattro micromass^{TM} (Waters, France). The dynamic light scattering particle size measurements were performed on a Zetasizer Nano ZS (Malvern instruments, England). UV-irradiation was performed by UV light source (TUV 15W/G15 T18 lamp; Philips, Holland).

General Procedure for Synthesis of Iodoalkyne (2−3). A solution of morpholine (33.25 mL, 381.60 mmol) in toluene (300 mL) was treated with iodine (13.56 g, 53.42 mmol), shielded from light and stirred for an hour at 45 °C. A solution of 1-nonyne (6.26 mL, 38.15 mmol) in toluene (30 mL) was then added and the reaction mixture kept stirring at 45 °C for an hour. The reaction mixture was cooled to room temperature and filtered to remove the iodomorpholine salt. The filtrate was poured over a mixture of diethyl ether (200 mL) and saturated aqueous solution of $Na_2S_2O_3$ (100 mL) and shaken until the organic layer was colorless. The organic layer was separated, washed again with saturated aqueous solution of $Na_2S_2O_3$ (100 mL), dried over anhydrous Na_2SO_4, filtered, concentrated, and purified by column chromatography with hexane as an eluent to afford 1-Iodo-1-nonyne (**2**) as colorless oil (6.85 g, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.35 (t, $J = 7.1$ Hz, 2H; $ICCCH_2$), 1.50 (m, 2H; $ICCCH_2CH_2$), 1.35−1.25 (m, 8H; CH_2), 0.88 (t, $J = 6.7$ Hz, 3H; CH_3).

1-Iodo-1-dodecyne (**3**). This was synthesized according to the above general procedure from morpholine (33.25 mL, 381.60 mmol), iodine (13.56 g, 53.42 mmol) in 300 mL of toluene and solution of 1-dodecyne (8.16 mL, 38.17 mmol) in 30 mL of toluene, purified by column chromatography with hexane as colorless oil (8.76 g, 79%yield). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 2.35 (t, J = 7.1 Hz, 2H; $\mathrm{ICCC}H_2$), 1.50 (m, 2H; $\mathrm{ICCCH_2C}H_2$), 1.35−1.25 (m, 14H; $\mathrm{C}H_2$), 0.88 (t, J = 6.6 Hz, 3H; $\mathrm{C}H_3$).

General Procedure for Synthesis of Diynoic Acid Diacetylene Lipid Monomers (7−12). To a stirred solution of 4-pentynoic acid (**4**) (0.29 g, 3.0 mmol) and 1-iodo-1-nonyne (**2**) (0.90 g, 3.6 mmol) in pyrrolidine purum (≥98%) (1.24 mL, 15.0 mmol), copper(I) iodide was added. After that, the reaction mixture was stirred at room temperature for 3 h, a saturated aqueous solution of ammonium chloride (50 mL) was added and then extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over anhydrous $\mathrm{Na_2SO_4}$ and filtered, and solvent was removed by rotary evaporator. The crude product was purified by column chromatography with hexane:ethyl acetate (90:10 v/v) to yield 4,6-tetradecadiynoic acid (4,6-14DA) (**7**) as white solid (0.33 g, 49% yield); mp 61−63 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 2.59 (m, 4H; $\mathrm{COC}H_2$ and $\mathrm{COCH_2C}H_2$), 2.23 (t, J = 6.9 Hz, 2H; $\mathrm{CCC}H_2$), 1.50 (m, 2H; $\mathrm{CCCH_2C}H_2$), 1.36−1.25 (m, 8H; $\mathrm{C}H_2$), 0.87 (t, J = 6.6 Hz, 3H; $\mathrm{C}H_3$). Anal. Found: C, 76.23; H, 9.11 (Calcd for $\mathrm{C_{14}H_{20}O_2}$: C, 76.33; H, 9.15).

5,7-Pentadecadiynoic acid (*5,7-15DA*) (***8***). This was synthesized according to the above general procedure from 5-hexynoic acid (**5**) (0.34 mL, 3.0 mmol), 1-iodo-1-nonyne (**2**) (0.90 g, 3.6 mmol), and copper(I) iodide (0.01 g, 0.05 mmol) in pyrrolidine (1.24 mL, 15.0 mmol), purified by column chromatography with hexane:ethyl acetate (90:10 v/v) as white solid (0.41 g, 58% yield); mp 52−53 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 2.49 (t, J = 7.3 Hz, 2H; $\mathrm{COC}H_2$), 2.35 (t, J = 6.75 Hz, 2H; $\mathrm{COCH_2CH_2C}H_2$), 2.23 (t, J = 7.0 Hz, 2H; $\mathrm{CCC}H_2$), 1.84 (q, J = 7.1 Hz, 2H; $\mathrm{COCH_2C}H_2$), 1.50 (m, 2H; $\mathrm{CCCH_2C}H_2$), 1.36−1.25 (m, 8H; $\mathrm{CH_2}$), 0.87 (t, J = 6.6 Hz, 3H; $\mathrm{C}H_3$). Anal. Found: C, 76.49; H, 9.21 (Calcd for $\mathrm{C_{15}H_{22}O_2}$: C, 76.88; H, 9.46).

6,8-Hexadecadiynoic acid (*6,8-16DA*) (***9***). **9** was synthesized according to the above general procedure from 6-heptynoic acid (**6**) (0.38 mL, 3.0 mmol), 1-iodo-1-nonyne (**2**) (0.90 g, 3.6 mmol), and copper(I) iodide (0.01 g, 0.05 mmol) in pyrrolidine (1.24 mL, 15.0 mmol), purified by column chromatography with hexane:ethyl acetate (90:10 v/v) as white solid (0.42 g, 57% yield). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 2.37 (t, J = 7.4 Hz, 2H; $\mathrm{COC}H_2$), 2.28 (t, J = 7.0 Hz, 2H; $\mathrm{COCH_2CH_2CH_2C}H_2$), 2.23 (t, J = 7.1 Hz, 2H; $\mathrm{CCC}H_2$), 1.74 (m, 2H; $\mathrm{COCH_2C}H_2$), 1.58 (m, 2H; $\mathrm{COCH_2CH_2C}H_2$), 1.50 (m, 2H; $\mathrm{CCCH_2C}H_2$), 1.36−1.25 (m, 8H; $\mathrm{C}H_2$), 0.87 (t, J = 6.7 Hz, 3H; $\mathrm{C}H_3$).

4,6-Heptadecadiynoic acid (*4,6-17DA*) (***10***). **10** was synthesized according to above general procedure from 4-pentynoic acid (**4**) (0.29 g, 3.0 mmol), 1-iodo-1-dodecyne (**3**) (1.10 g, 3.6 mmol), and copper(I) iodide (0.01 g, 0.05 mmol) in pyrrolidine (1.24 mL, 15.0 mmol), purified by column chromatography with hexane:ethyl acetate (90:10 v/v) as white solid (0.58 g, 67% yield); mp 76−78 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 2.59 (m, 4H; $\mathrm{COC}H_2$ and $\mathrm{COCH_2C}H_2$), 2.24 (t, J = 6.9 Hz, 2H; $\mathrm{CCC}H_2$), 1.51 (m, 2H; $\mathrm{CCC}H_2$), 1.36−1.25 (m, 14H; $\mathrm{C}H_2$), 0.88 (t, J = 6.0 Hz, 3H; $\mathrm{C}H_3$) MS (ESI$^-$): $[\mathrm{M-H}]^-$ found, 261.30 (calcd for $\mathrm{C_{17}H_{26}O_2}$, 262.39).

5,7-Octadecadiynoic Acid (*5,7-18DA*) (***11***). **11** was synthesized according to the above general procedure from 5-hexynoic acid (**5**) (0.34 mL, 3.0 mmol), 1-iodo-1-dodecyne (**3**) (1.10 g, 3.6 mmol), and copper(I) iodide (0.01 g, 0.05 mmol) in pyrrolidine (1.24 mL, 15.0 mmol), purified by column chromatography with hexane:ethyl acetate (90:10 v/v) as white solid (0.46 g, 55% yield); mp 57−59 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 2.44 (t, J = 7.4 Hz, 2H; $\mathrm{COC}H_2$), 2.29 (t, J = 6.9 Hz, 2H; $\mathrm{COCH_2CH_2C}H_2$), 2.17 (t, J = 7.0 Hz, 2H; $\mathrm{CCC}H_2$), 1.78 (q, J = 7.1 Hz, 2H; $\mathrm{COCH_2C}H_2$), 1.45 (m, 2H; $\mathrm{CCCH_2C}H_2$), 1.30−1.19 (m, 14H; $\mathrm{C}H_2$), 0.81 (t, J = 6.8 Hz, 3H; $\mathrm{CH_3}$) MS (ESI$^-$): $[\mathrm{M-H}]^-$ found, 275.33 (calcd for $\mathrm{C_{18}H_{28}O_2}$, 276.41). Anal. Found: C, 78.22; H, 10.58 (Calcd for $\mathrm{C_{18}H_{28}O_2}$: C, 78.21; H, 10.21).

6,8-Nonadecadiynoic Acid (*6,8-19DA*) (***12***). 12 was synthesized according to the above general procedure from 6-heptynoic acid (**6**) (0.38 mL, 3.0 mmol), 1-iodo-1-dodecyne (**3**) (1.10 g, 3.6 mmol) and copper(I) iodide (0.01 g, 0.05 mmol) in pyrrolidine (1.24 mL, 15.0 mmol), purified by column chromatography with hexane:ethyl acetate (90:10 v/v) as white solid (0.57 g, 65% yield); mp 57−59 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 2.31 (t, J = 7.4 Hz, 2H; $\mathrm{COC}H_2$), 2.22 (t, J = 6.9 Hz, 2H; $\mathrm{COCH_2CH_2CH_2C}H_2$), 2.17 (t, J = 7.1 Hz, 2H; $\mathrm{CCC}H_2$), 1.68 (m, 2H; $\mathrm{COCH_2CH_2}$), 1.52 (m, 2H; $\mathrm{COCH_2CH_2C}H_2$), 1.43 (m, 2H; $\mathrm{CCCH_2C}H_2$), 1.30−1.28 (m, 14H; $\mathrm{C}H_2$), 0.81 (t, J = 6.8 Hz, 3H; $\mathrm{C}H_3$) MS (ESI$^-$): $[\mathrm{M-H}]^-$ found, 289.26 (calcd for $\mathrm{C_{19}H_{30}O_2}$, 290.44). Anal. Found: C, 78.71; H, 10.53 (Calcd for $\mathrm{C_{19}H_{30}O_2}$: C, 78.57; H, 10.41).

General Procedure for Synthesis of Bis(diynamide) (1a−1f). *N,N′*-Dicyclohexylcarbodiimide (0.46 g, 2.25 mmol) in chloroform (20 mL) was added into 4,6-tetradecadiynoic acid (**7**) (0.33 g, 1.5 mmol) in chloroform 20 mL and stirred for 1 h. Ethylenediamine (0.05 mL, 0.75 mmol) was then added dropwise into the reaction mixture and stirred for 48 h. The reaction mixture was concentrated under reduced pressure to yield the crude product as a light yellow solid. Recrystallization with methanol afforded *N,N′*-ethylenebistetradeca-4,6-diynamide (EB-4,6-14DA) (**1a**) as white solid (0.10 g, 59% yield). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 6.09 (br, 2H; $\mathrm{CON}H$), 3.35 (m, 4H; $\mathrm{CONHC}H_2$), 2.54 (t, J = 7.1 Hz, 4H; $\mathrm{COC}H_2$), 2.33 (t, J = 7.1 Hz, 4H; $\mathrm{COCH_2C}H_2$), 2.18 (t, J = 7.1 Hz, 4H; $\mathrm{CCC}H_2$), 1.44 (m, 4H; $\mathrm{CCCH_2C}H_2$), 1.30−1.20 (m, 16H; $\mathrm{C}H_2$), 0.81 (t, J = 7.0 Hz, 6H; $\mathrm{C}H_3$).

N,N′-Ethylenebispentadeca-5,7-diynamide (*EB-5,7-15DA*) (***1b***). **1b** was synthesized according to the above general procedure from *N,N′*-dicyclohexylcarbodiimide (0.83 g, 4.02 mmol), 5,7-pentadecadiynoic acid (0.63 g, 2.69 mmol) (**8**) and ethylenediamine (0.09 mL, 1.34 mmol) as a white solid (0.34 g, 51% yield); mp 148−150 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 6.13 (br, 2H; $\mathrm{CON}H$), 3.39 (m, 4H; $\mathrm{CONHC}H_2$), 2.32 (m, 8H; $\mathrm{COC}H_2$ and $\mathrm{COCH_2CH_2C}H_2$), 2.24 (t, J = 7.0 Hz, 4H; $\mathrm{CCC}H_2$), 1.85 (q, J = 6.9, 7.1 Hz, 4H; $\mathrm{COCH_2C}H_2$), 1.52 (m, 4H; $\mathrm{CCCH_2C}H_2$), 1.38−1.27 (m, 16H; $\mathrm{C}H_2$), 0.88 (t, J = 7.0 Hz, 6H; $\mathrm{C}H_3$).

N,N′-Ethylenebishexadeca-6,8-diynamide (*EB-6,8-16DA*) (***1c***). **1c** was synthesized according to the above general procedure from *N,N′*-dicyclohexylcarbodiimide (0.92 g, 4.47 mmol), 6,8-hexadecadiynoic acid (**9**) (0.74 g, 2.98 mmol), and ethylenediamine (0.1 mL, 1.49 mmol) as a white solid (0.42 g, 54% yield). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 6.16 (br, 2H; $\mathrm{CON}H$), 3.39 (m, 4H; $\mathrm{CONHC}H_2$), 2.24 (m, 12H; $\mathrm{COC}H_2$ $\mathrm{COCH_2CH_2CH_2C}H_2$ and $\mathrm{CCC}H_2$), 1.73 (m, 4H; $\mathrm{COCH_2C}H_2$), 1.53 (m, 8H; $\mathrm{COCH_2CH_2C}H_2$ and $\mathrm{CCCH_2C}H_2$), 1.37−1.27 (m, 16H; $\mathrm{C}H_2$), 0.88 (t, J = 6.7 Hz, 6H; $\mathrm{C}H_3$).

N,N′-Ethylenebisheptadeca-4,6-diynamide (*EB-4,6-17DA*) (***1d***). **1d** was synthesized according to the above general procedure from *N,N′*-dicyclohexylcarbodiimide (1.18 g, 5.72 mmol), 4,6-heptadecadiynoic acid (**10**) (1.00 g, 3.81 mmol) and ethylenediamine (0.13 mL, 1.91 mmol) as a white solid (0.57 g, 55% yield). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 6.16 (br, 2H; $\mathrm{CON}H$), 3.41 (m, 4H; $\mathrm{CONHC}H_2$), 2.60 (t, J = 7.1 Hz, 4H; $\mathrm{COC}H_2$), 2.39 (t, J = 7.1 Hz, 4H; $\mathrm{COCH_2C}H_2$), 2.23 (t, J = 7.0 Hz, 4H; $\mathrm{CCC}H_2$), 1.50 (m, 4H; $\mathrm{CCCH_2C}H_2$), 1.36−1.24 (m, 28H; $\mathrm{C}H_2$), 0.87 (t, J = 6.53 Hz, 6H; $\mathrm{C}H_3$) MS (ESI$^+$): $[\mathrm{M+H}]^+$ found, 549.69 (calcd for $\mathrm{C_{36}H_{56}N_2O_2}$, 548.84).

N,N′-Ethylenebisoctadeca-5,7-diynamide (*EB-5,7-18DA*) (***1e***). **1e** was synthesized according to above general procedure from *N,N′*-dicyclohexylcarbodiimide (1.12 g, 5.43 mmol), 5,7-octadecadiynoic acid (**11**) (1.00 g, 3.62 mmol) and ethylenediamine (0.12 mL, 1.81 mmol) as a white solid (0.56 g, 54% yield); mp 154−155 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 6.14 (br, 2H; $\mathrm{CON}H$), 3.38 (m, 4H; $\mathrm{CONHC}H_2$), 2.31 (m, 8H; $\mathrm{COC}H_2$ and $\mathrm{COCH_2CH_2C}H_2$), 2.24 (t, J = 7.0 Hz, 4H; $\mathrm{CCC}H_2$), 1.84 (q, J = 6.9, 6.9 Hz, 4H; $\mathrm{COCH_2C}H_2$), 1.51 (m, 4H; $\mathrm{CCCH_2C}H_2$), 1.36−1.25 (m, 28H; CH_2), 0.87 (t, J = 6.7 Hz, 6H; CH_3) MS (ESI$^+$): $[M + H]^+$ found, 577.76 (calcd for $C_{38}H_{60}N_2O_2$, 576.90). Anal. Found: C, 79.05; H, 9.76 (Calcd for $C_{38}H_{60}N_2O_2$: C, 79.11; H, 10.48).

N,N′-Ethylenebisnonadeca-6,8-diynamide (*EB-6,8-19DA*) (***1f***). **1f** was synthesized according to above general procedure from *N,N′*-dicyclohexylcarbodiimide (1.07 g, 5.16 mmol), 6,8-nonadecadiynoic acid (**12**) (1.01 g, 3.44 mmol) and ethylenediamine (0.12 mL, 1.72 mmol) as a white solid (0.48 g, 46% yield); mp 139−140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.17 (br, 2H; $CONH$), 3.39 (m, 4H; $CONHCH_2$), 2.24 (m, 12H; $COCH_2$- $COCH_2CH_2CH_2CH_2$ and $CCCH_2$), 1.73 (m, 4H; $COCH_2CH_2$), 1.52 (m, 8H; $COCH_2CH_2CH_2$ and $CCCH_2CH_2$), 1.36−1.25 (m, 28H; CH_2), 0.87 (t, J = 6.7 Hz, 6H; CH_3) MS (ESI$^+$): $[M + H]^+$ found, 605.77 (calcd for $C_{40}H_{64}N_2O_2$, 604.95)

Typical Method for the Preparation of Polydiacetylene Vesicles. Monomers were dissolved in chloroform (0.5 mL) in a test tube and the solvent was removed under reduced pressure. A volume of Milli-Q water was added to provide the lipid concentration of 1.0 mM. The suspensions were heated to 75−85 °C and sonicated in an ultrasonicating bath for 30−40 min forming a semitransparent or transparent vesicle solution. Then solution was kept at 4 °C for overnight. The vesicle solution was irradiated with UV light (254 nm) for 5 min at room temperature and filtered through a filter paper (no. 1) to give a clear intense blue-colored vesicle solution.

Study of Thermochromism. The color transition of the polymerized sols at various temperatures was observed by naked eye and photographed by a digital camera. The electronic absorption spectra of the sols were recorded by the temperature variable UV−visible spectrophotometer. The quantitative evaluation of the colorimetric response (% CR) was determined as the percentage of the change of the blue color fraction ($FB_0 - FB$) against the initial blue color fraction (FB_0) according to the following equation: $\% CR = 100 \times (FB_0 - FB)/FB_0$. FB is the blue fraction calculated from $A_{blue}/(A_{blue} + A_{red})$ where A_{blue} and A_{red} are the absorbance at the λ_{max} of the blue and the red forms of the polydiacetylenes, respectively. The degree of thermochromic reversibility (% DR) was determined from the percentage ratio of the average absorbance change from the second to the tenth heating (ΔA_{avg}) against the absorbance change in the first heating (ΔA_1) according to the following equation: $\% DR = 100 \times \Delta A_{avg}/\Delta A_1$. The absorbance change $\Delta A = A_{20\,°C} - A_{90\,°C}$ where the absorbances at the λ_{max} of the initial blue form are used for both temperatures.

Preparation of Polydiacetylene Films. Diacetylene monomer and screen ink base resin (GPV0906, Chaiyaboon brothers Co., LTD) was mixed into 10 mL vial. The diacetylene monomer used was 5−10% w/w compare with the resin weight. Screen ink was screened into commercial transparent sheet by using stencil. After screening, the film was kept in a refrigerator for 2−4 h. The film was polymerized by UV irradiation in an ice bath.

Acknowledgment. This study was financially supported by the grants from National Nanotechnology Center, National Science and Technology Development Agency (NANOTEC, NSTDA, Project NN-B-22-FN9-10-52-06) and the Thailand Research Fund (TRF). The work is part of the Project for Establishment of Comprehensive Center for Innovative Food, Health Products and Agriculture supported by the Thai government stimulus package 2 (TKK2555, SP2)". We would also like to thank Center for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, the 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund) and the Thailand Graduate Institute of Science and Technology (TGIST) for student scholarships.

Supporting Information Available: Figures showing ^{1}H NMR spectra of all synthesized compounds (**S1−S14**), photographs of the bisdiynamide sols (**S15**), and absorption spectra of the bisdiynamide sols upon thermal incubation (**S16**). This material is available free of charge via the Internet at http://pubs.acs.org.

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