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Notes

Thermochromic Polydiacetylene Supramolecules with Oligo(ethylene oxide) Headgroups for Tunable Colorimetric Response

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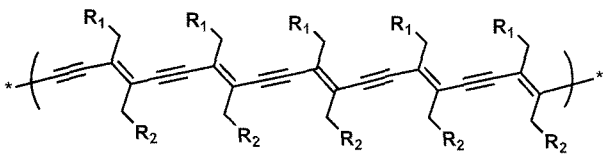
Introduction

Owing to the color (blue-to-red) and fluorescence (non-to-red) transitions that take place in response to environmental perturbations, polydiacetylenes (PDAs) have been extensively investigated as sensor matricies.[1-14] The backbone of the PDA is consists of alternating ene-yne structures.[15-28] PDAs are generally prepared by 254 nm UV- or γ-irradiation of self-assembled diacetylene (DA) supramolecules. Since no chemical initiators or catalysts are required for the polymerization process, the polymers are not contaminated with impurities and, consequently, purification steps are not required. PDAs generally have an intense blue color corresponding to maximum absorption wavelengths of *ca.* 640 nm when they are generated under optimized conditions. The extensively delocalized π-network in the PDA backbone is influenced by a variety of stimuli such as heat, pH, mechanical stress, solvent, and molecular recognition.[1-14] These environmental perturbations cause blue-to-red color transition of the PDAs.



Polydiacetylene (PDA)

The chemical mechanism for the blue-to-red color transition of the PDAs has attracted as much attention as its application to the design of polymeric chemosensors. A variety of experimental and theoretical techniques have been employed to gain an understanding of the mechanism of this unique colorimetric transition. Although the exact mechanism is not yet fully understood, observations have been made that suggest that the release of side-chain strain taking place upon stimulation causes rotation about the C-C bonds in PDA backbone.[17] This conformational change perturbs the conjugated π-orbital array and leads to a change in the chromophore responsible for the electronic transition. Theoretical calculation demonstrates that significant changes in the degree of π-conjugation in PDAs would be caused by even small amounts of C-C bond rotation.[29]

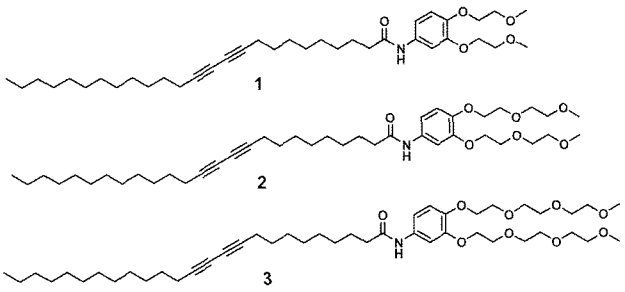


Figure 1. Structures of DA monomers investigated in this study.

In our earlier studies,[30-35] we observed that colorimetric response of the PDAs could be readily manipulated by modification of headgroup interactions. Thus, we were able to control both the thermochromic temperature and the colorimetric reversibility of the PDA supramolecules by changing headgroup structures. In the present investigation, we report a new approach for the design of colorimetrically tunable PDA supramolecules. Instead of manipulating headgroup hydrogen bonding and aromatic interactions, the tunable colorimetric response was achieved by changing size of the headgroups in PDAs. The three DA monomers having different headgroup sizes, shown in Figure 1, were selected for the purpose of making colorimetrically tunable polymers. Hydrophilic ethylene oxide groups were used to make the DA monomers **1-3** amphiphilic which is desirable for the formation of stable DA vesicles in aqueous solution. It is expected that PDA derived from the DA monomer **3** which have the longest headgroups induces color transition at lowest temperature due to the bulky headgroup.

Experimental

Synthesis of 1,2-Bis(2-methoxyethoxy)-4-nitrobenzene (8). To a mixture containing 4-nitrocatechol (0.37 g, 2.40 mmol) and K_2CO_3 (1.30 g, 9.40 mmol) in MeCN was added 2-methoxyethyl 4-methylbenzenesulfonate (1.40 g, 6.00 mmol).

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The resulting mixture was stirred at reflux for 18 h, filtered, and the filtrate was concentrated *in vacuo* giving a residue which was subjected to silica gel column chromatography (ethyl acetate : hexane = 2 : 3) to yield 286 mg (44%) of the desired product **8**. Compounds **9** and **10** were prepared by employing similar procedures.

Compond **8**: m.p 35-36 °C ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.24 (s, 6H), 3.79 (m, 4H), 4.22 (m, 4H), 6.96 (d, 1H), 7.80 (s, 1H), 7.90 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 154.3, 148.3, 141.4, 117.9, 111.7, 108.9, 71.1, 71.0, 69.4, 69.3, 59.8, 59.7; IR (NaCl, cm^{-1}) 2885-2875, 2360,1587, 1517, 1340, 1276, 1106, 744.

Compound **9**: ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.20 (s, 6H), 3.59 (m, 4H), 3.75 (m, 4H), 3.91 (m, 4H), 4.25 (m, 4H), 6.96 (d, 1H), 7.80 (s, 1H), 7.87 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 154.3, 148.3, 141.4, 117.9, 111.7, 108.9, 71.8, 70.9, 70.8, 69.4, 69.3, 69.0, 68.9, 59.0; IR (NaCl, cm^{-1}) 2885-2875, 1587, 1517, 1340, 1276, 1106, 744.

Compound **10:** ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.40 (s, 6H), 3.60-3.80 (m, 16H), 3.84 (m, 4H), 4.20 (m, 4H), 6.95 (d, 1H), 7.80 (s, 1H), 7.84 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 154.7, 148.7, 141.7, 118.2, 112.2, 109.2, 72.2, 71.2, 70.9, 70.8, 69.7, 69.6, 69.4, 69.2, 59.3; IR (NaCl, cm^{-1}) 2885-2875,1739, 1587, 1517, 1340, 1276, 1106, 744.

Synthesis of 3,4-Bis(2-methoxyethoxy) benzeneamine (11). Activated Pd/C (0.11 g, 1.00 mmol) was added to a solution of 1,2-bis(2-methoxyethoxy)-4-nitrobenzene (**8**) (0.22 g, 0.80 mmol) in 27 mL of MeOH. The resulting mixture was stirred at room temperature for 1.5 h under a H_2 atmosphere. The mixture was filtered and the filtrate was concentrated *in vacuo* to yield 142 mg (74%) of the amine derivative **11**. Compounds **12** and **13** were prepared by employing similar procedures.

Compound **11**: ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.42 (s, 6H), 3.60-3.80 (m, 4H), 4.00-4.20 (m, 4H), 6.22(d, 1H), 6.35 (s, 1H), 6.80 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 150.5, 141.9, 141.8, 118.5, 107.8, 103.5, 71.5, 71.2, 70.4, 68.7, 59.3, 59.2; IR (NaCl, cm^{-1}) 3276, 3016, 2969, 2780-2730, 1735, 1512, 1365, 1216.

Compound **12**: ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.40 (s, 6H), 3.56 (m, 4H), 3.72 (m, 4H), 3.83 (m, 4H), 4.12 (m, 4H), 6.22 (d, 1H), 6.35 (s, 1H), 6.79 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 150.7, 142.1, 142.0, 118.5, 107.9, 103.5, 72.4, 71.2, 71.0, 70.7, 70.4, 70.2, 69.0, 59.5; IR (NaCl, cm^{-1}) 3488, 3394, 3295, 3093-3014, 2877, 2775, 1820-1775, 1675, 1560, 1511, 1413, 1228, 1116.

Compound **13**: ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.40 (s, 6H), 3.56 (m, 8H), 3.60-3.78 (m, 8H), 3.84 (m, 4H), 4.20 (m, 4H), 6.22 (d, 1H), 6.35 (s, 1H), 7.80 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 150.4, 141.9, 141.7, 118.3, 107.6, 103.4, 72.0, 70.9, 70.8, 70.7, 70.4, 70.1, 69.8, 68.7, 59.2, 59.1; IR (NaCl, cm^{-1}) 3567, 3392, 3303, 3012, 2877, 2780, 1780-1758, 1670, 1550, 1513, 1419, 1226, 1108.

Synthesis of *N*-(3,4-Bis(2-methoxyethoxy)phenyl) pentacosa-10,12-diynamide (1). To a prepurged (N_2 gas) solution of 0.20 g (0.85 mmol) of 3,4-bis(2-methoxyethoxy) benzenamine (**11**) and 0.17 mL (1.20 mmol) of triethylamine in THF was added dropwsie a THF solution containing 0.16 g (0.4 mmol) of 10,12-pentacosadiynoyl chloride (PCDA-Cl). The resulting solution was stirred for 2.5 h at room temperature. After adding ample amount of ethyl acetate, the organic layer was washed with water, dried over $MgSO_4$, and concentrated *in vacuo* giving a residue which was subjected to silica gel column chromatography (hexane : ethyl acetate = 1.5 : 1) to yield 230 mg (96%) of the desired DA monomer **1**. The DA monomers **2** and **3** were prepared by employing similar procedures.

Diacetylene **1**: m.p 72-74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 0.88 (t, 3H), 1.20-1.80 (m, 32H), 2.20-2.40 (m, 6H), 3.45 (s, 6H), 3.79 (m, 4H), 4.18 (m, 4H), 6.85 (s, 2H), 7.02 (s, 1H), 7.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 171.5, 149.1, 145.6, 132.7, 115.6, 112.7, 108.0, 71.3, 71.1, 69.5, 65.4, 65.3, 59.3, 37.8, 32.1, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.3, 29.2, 29.0, 29.0, 28.9, 28.5, 28.4, 25.7, 22.8, 19.4, 19.3, 14.3; IR (NaCl, cm^{-1}) 3290-3280, 2856-2846, 1658, 1604, 1517, 1450, 1425, 1371, 1261, 1232, 1197, 1132, 1035, 962, 862, 804, 786, 721.

Diacetylene **2**: m.p 54-56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 0.88, (t, 3H), 1.20-1.80 (m, 32H) 2.20-2.40 (m, 6H), 3.41 (s, 6H), 3.60 (m, 4H), 3.75 (m, 4H), 3.84 (m, 4H), 4.18 (m, 4H), 6.84 (m, 2H), 7.16 (s, 1H), 7.37 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 171.4, 149.3, 145.5, 132.6, 115.6, 112.6, 107.6, 72.2, 70.2, 70.9, 70.8, 70.0, 69.9, 69.6, 68.9, 65.5, 65.4, 59.3, 59.2, 37.8, 32.1, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 29.4, 29.3, 29.1, 29.0, 28.9, 28.6, 28.5; IR (NaCl, cm^{-1}) 3290-3280, 2856-2846, 1658, 1604, 1517, 1450, 1425, 1371, 1261, 1232, 1197, 1132, 1035, 962, 862, 804, 786, 721.

Diacetylene **3**: m.p 43-44 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 0.88 (t, 3H), 1.20-1.80 (m, 32H), 2.20-2.40 (m, 6H), 3.40 (s, 6H), 3.60-3.80 (m, 16H), 3.84 (m, 4H), 4.20 (m, 4H), 6.89 (d, 1H), 7.02 (d, 1H), 7.22 (s, 1H), 7.37 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 171.5, 149.1, 145.6, 132.7, 115.6, 112.7, 108.0, 72.0, 70.9, 70.8, 70.8, 70.7, 70.6, 70.5, 65.4, 65.3, 59.2, 59.1, 37.7, 33.9, 32.0, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.5, 28.4, 25.7, 22.8, 19.3, 19.3, 14.3; IR (NaCl, cm^{-1}) 3585-3357, 3232, 2900-2856, 1955, 1614, 1517, 1456, 1351, 1295, 1250-1236, 1058-1025, 848.

Preparation of DA Suspensions. The DA monomer was dissolved in a minimum amount of DMF (ca. 100 mL) and portions of the resulting DA solution was added dropwise into heated deionized water at 80 °C and vortexed. After completion of the addition, the resulting mixture was then heated at 80 °C for 5 min and probe-sonicated for 15 min. After filtration through a cotton filter, the filtrate was cooled at 4 °C for overnight for stabilization.

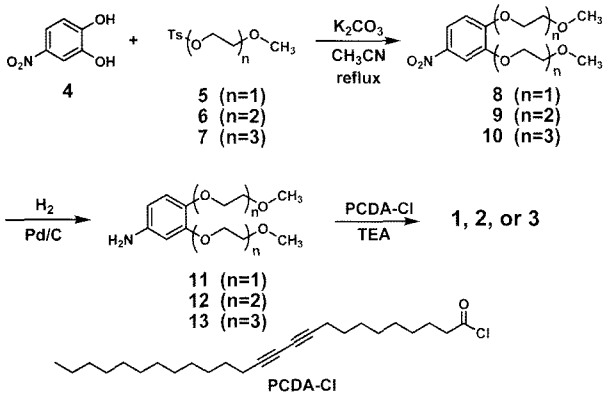
Results and Discussion

Preparation of DA Monomers. The DA monomers used in this study were readily prepared. Synthetic procedures employed for the preparation of DA monomers **1-3** are shown in Scheme I. The nitrocatechol **4** was treated with tosylated ethylene oxides **5-7** to yield the substituted nitrobenzene intermediates **8-10**. Hydrogenation of the intermediates **8-10** gave the desired substituted aminobenzenes **11-13** which were coupled with PCDA-Cl to provide the DA monomers **1-3**.

Preparation of PDA Suspension. Routine procedures were used to transform the DA lipid monomers **1-3** to polydiacetylenes in aqueous solution (see experimental section for detailed condition). A suspension of DA monomer (final concentration of 1 mM) prepared from dropping method in water was heated at 80 °C for 5 min. Following probe-sonication for 15 min, the monomer suspension was filtered with a cotton filter to remove solid aggregates. Cooling overnight afforded a molecularly-ordered DA suspension which was confirmed by the efficient formation of a blue-colored PDA upon 254 nm UV irradiation. All DA lipid monomers **1-3** were found to undergo polymerization to form stable, blue-colored PDAs.

Thermochromism. Having prepared the PDA-embedded PVA films, we next investigated their thermally stimulated colorimetric responses. Accordingly, the PDA suspensions derived from the DA monomers **1-3** were placed on a temperature-controlled hot plate and the color change was monitored while the temperature was gradually increased.

Visible absorption spectra (Figure 2) and photographs (Figure 3) of PDA suspensions during the heating process are displayed in Figures 2 and 3. The visible absorption spectra show that the colorimetric response of the PDA supramolecules is highly dependent on the DA monomers used. Thus, PDAs derived from **1** are least sensitive and those made of **3** are the most sensitive. The photographs shown in Figure 3 are also supportive of this observation.



Scheme I. Synthetic procedures employed for the preparation of DA monomers **1-3**.

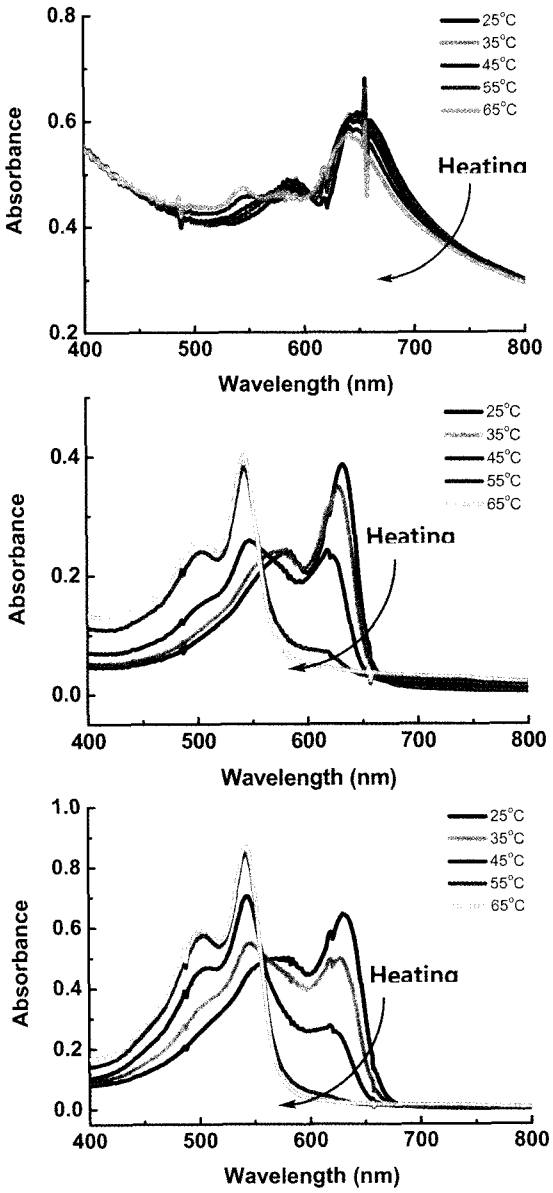


Figure 2. Visible spectra of PDA supramolecules prepared with DA monomers **1-3** during the heating process.

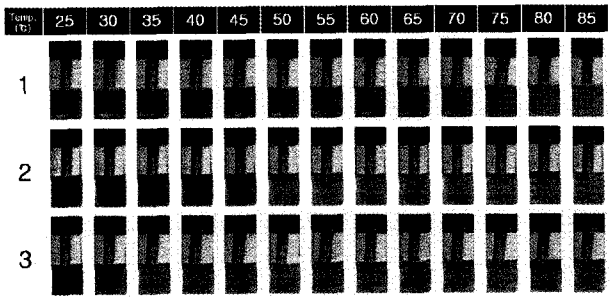


Figure 3. Photographs of PDA supramolecules prepared with DA monomers **1-3** during the heating process. Inside the vial is a probe thermometer.

Thus, PDAs derived from **1** become purple at 75 °C and eventually change to red above 85 °C. The PDA suspension obtained from DA monomer **2** has initiation of an apparent color transition at 40 °C and becomes red above 55 °C. The PDA derived from the DA monomer **3** is found to show most sensitive colorimetric response. Thus, a blue-to-purple color transition was observed at 30 °C and became red above 40 °C.

The results described above clearly support that the size of headgroup affects the colorimetric response of the PDA supramolecules. Thus, the PDA supramolecules having longer ethylene oxide headgroups initiate color transition at lower temperature.

Conclusions

In this effort, we have prepared PDA suspensions derived from oligoethylene oxide-containing DA monomers and investigated their colorimetric responses to thermal stimulation. Depending on the DA monomers employed, the PDA supramolecules displayed different initial color changing temperatures. In general, DA monomers having larger headgroups result in the generation of colorimetrically less stable PDA supramolecules. The results described in the current investigation should provide useful information about the design of colorimetrically tunable PDA supramolecules.

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