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Low Temperature Thermochromic Polydiacetylenes: Design, Colorimetric Properties, and Nanofiber Formation

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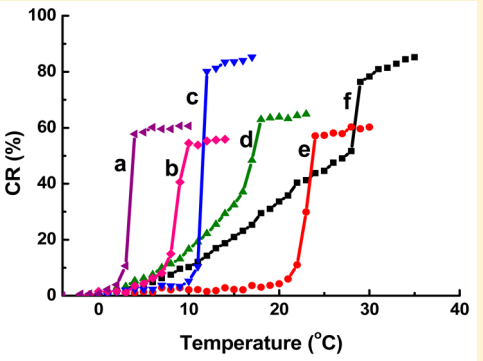
Supporting Information

ABSTRACT: Owing to their stimulus responsive color changing properties, polydiacetylenes (PDAs) have been extensively investigated as colorimetric sensors. Thermochromic properties of PDAs have been the central focus of a number of investigations that were aimed not only at gaining a fundamental understanding of the physical basis of the color change but also at developing practical applications as temperature sensors. The thermochromic transition temperature of a PDA polymer is closely related to the melting point of the corresponding diacetylene (DA) monomer. In addition, the majority of PDAs described to date undergo a blue-to-red color change above room temperature because PDAs are generally derived from DA monomers that have melting points above room temperature. In the current study, we developed a series of low temperature colorimetric PDAs that were designed based on the reasoning that removal of the sources for strong headgroup interactions would lower the melting points of the corresponding DA monomers. This strategy was used to design and fabrication of PDA sensors that display color transitions in the range of 5−30 °C. Moreover, the thermochromic transition temperatures of the PDAs were found to decrease by ca. 10 °C when the alkyl chain length in the DA monomer is truncated by two methylene units. The results of FTIR and Raman spectroscopic analyses suggest that the PDA alkyl chain adopts an *all-trans* conformation in the blue-phase and some *gauche* forms exist in the alkyl chain in the red-phase PDA. Finally, the new PDAs are stable up to 300 °C, and their processable nature enables them to be fabricated in nanofiber forms by employing an anodized aluminum oxide (AAO) membrane as a template.



INTRODUCTION

Polydiacetylenes (PDAs)[1−11] are a family of supramolecular conjugated polymers that have received great attention because they display stimulus-responsive color (generally blue-to-red) and fluorescence (non-to-red) changes. A wide range of chemical/biochemical (e.g., solvents,[12−20] ions,[21,22] surfactants,[23−27] biomolecules,[28−36] explosives[37]) and physical (e.g., temperature,[38−45] mechanical strain,[46−48] magnetic field,[49] electric current[50−52]) stimuli promote colorimetric and fluorometric transitions of properly designed PDAs. Colorimetrically responsive PDAs also respond to water when they contain hygroscopic elements in headgroups[53] or when they are embedded in a hydrogel matrix.[54]

Thermochromic properties of PDAs have been the central focus of a number of investigations since the time of the discovery of these conjugated polymers. This effort has not only provided a fundamental understanding of the physical basis for thermochromism but also led to practical applications of PDAs as temperature sensors. The majority of thermochromic PDAs reported to date have colorimetric transition temperatures above room temperature (typically >40 °C). This property is a consequence of the fact that the transition temperatures of PDAs are closely related to the melting points of the corresponding diacetylene (DA) monomers, which for the most part are solids at room temperature because they contain moieties that enable intermolecular hydrogen bonding as well as arene−arene and electrostatic interactions.

Low temperature thermochromic PDAs have potential utility as temperature sensors for goods that require refrigeration or freezing. In this type of application, a colorimetrically irreversible sensor is more desirable because it would indicate when goods have been exposed to an environment above room temperature any time during the storage period. We[55] and others[56] have already described low temperature thermochromic PDAs derived from isocyanate containing and aliphatic DA monomers. In the current study, we designed and prepared a new series of PDAs that undergo a blue-to-red color transition in the temperature range between 5 and 30 °C. The PDAs are prepared by polymerization reactions of DA monomers that contain methyl or methoxyethyl ester groups. These DAs were found to be liquids below 30 °C, and they solidify in a freezer at −5 °C. UV irradiation of the solid DAs results in generation of

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the corresponding blue PDAs, which undergo colorimetric transition at temperatures close to the melting points of the respective monomers. The results of FTIR and Raman spectroscopic analyses suggest that alkyl chains in the blue-phase of these PDAs adopt *all-trans* conformations, whereas some *gauche* conformations exist in the red-phase. In addition, the soluble and thermally stable (up to 300 °C) nature of PDAs enables them to be used in a straightforward approach for the preparation of PDA nanofibers, which employs an anodized aluminum oxide (AAO) membrane as a template. The results of these studies reveal important information about strategies needed to design DA monomers that will generate PDAs that have desired thermochromic properties and provide a mechanistic basis for the color changing phenomenon and fiber formation of low temperature thermochromic PDAs.

EXPERIMENTAL SECTION

Materials and Instruments. 1-Ethyl-3-(3-(dimethylamino)-propyl)carbodiimide (EDC) was purchased from TCI Chemicals (Japan). 2-Methoxyethanol and anhydrous solvents were obtained from Sigma-Aldrich (USA). 10,12-Pentcosadiynoic acid (PCDA), 10,12-tricosadiynoic acid (TCDA), and 8,10-heneicosadiynoic acid (HCDA) were purchased from GFS-Chemicals (USA). ^{1}H NMR spectra were recorded on a Varian Unitylnova (300 MHz) spectrometer, and ^{13}C NMR spectra were recorded on a Varian Premium COMPACT NMR Magnet System (150 MHz) spectrometer using $CDCl_3$ as solvent. DSC spectra were obtained on a DSC2010 (TA Instruments, Inc.). IR spectra were recorded on a MAGNa-IR E.S.P (Thermo Fisher Scientific, Inc.). The absorption spectra were examined on an USB2000 miniature fiber-optic spectrometer (Ocean Optics). Raman spectra were collected by direct illumination of laser radiation (785 nm, Invictus, Kaiser Optical Inc.). Optical and fluorescence images of the samples were obtained using an Olympus (BX51 W/DP70) microscope. Scanning electron microscope (SEM) images were obtained using a JEOL (JSM-6330F) FE-SEM at an accelerating voltage of 15 kV. A homemade Peltier device was used to investigate the thermochromism of the polydiacetylene at low temperatures. Molecular weight of the polymer was estimated with a Waters 717plus autosampler which is equipped with a refractive index detector (Waters 2415) and four series columns (Styragel, HR 5, 50K−4M; Styragel, HR 4, 5K−600 K; Styragel, HR 2, 500−20K; Styragel, HR 0.5, 0−1K; columns are packed with 5 μm particles and the size of the column is 7.8 mm × 300 mm). In GPC measurements, chloroform was used as the eluent at a flow rate of 1 mL/min. GPC samples were taken at 0.2 wt % concentration and filtered with a 0.2 μm hydrophobic PTFE filter (Advantec Syringe Filters) to remove aggregates.

Representative Procedure for Preparation of Diacetylene Monomers. A tetrahydrofuran (THF) solution containing 10,12-pentacosadiynoic acid (PCDA) (500 mg, 1.33 mmol), 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide (510 mg, 2.67 mmol), 2-methoxyethanol (1.05 mL, 13.35 mmol), and 4-(dimethylamino)-pyridine (20 mg) was stirred for 18 h at room temperature. The mixture was concentrated *in vacuo*, and the residue was dissolved in hexane. The hexane solution was washed with saturated NaCl(aq), and the organic layer was dried over $MgSO_4$, concentrated to give an oil that was subjected to a silica gel column chromatography (hexane:ethyl acetate (20:1 v/v)) to afford 2-methoxyethyl pentacosa-10,12-diynoate (PCDA-EGME) (495 mg, 86%); mp 24.01 °C. IR (NaCl) ν_{max} (cm^{-1}): 2925, 2854, 1737, 1464, 1377, 1348, 1240, 1176, 1130, 1097, 1035, 931, 865, 723. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.23 (2H, m), 3.56 (2H, m), 3.40 (3H, s), 2.34 (2H, t, J = 7 Hz), 2.24 (4H, t, J = 7 Hz), 1.62 (2H, q, J = 7 Hz), 1.56−1.46 (4H, m), 1.41−1.26 (26H, m), 0.88 (3H, t, J = 7 Hz), 0.88 (3H, t, J = 7 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.0, 77.7, 77.6, 70.7, 65.4, 65.3, 63.4, 59.1, 34.3, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.2, 29.2, 29.2, 29.0, 29.0, 28.9, 28.5, 28.4, 25.0, 22.8, 19.3, 19.3, 14.3. HRMS m/z 432.3607 (calcd $C_{28}H_{48}O_3$, 432.3603). Other diacetylene monomers were prepared by employing a similar strategy.

2-Methoxyethyl Tricosa-10,12-diynoate (TCDA-EGME). 510 mg, 88%; mp 15.45 °C. IR (NaCl) ν_{max} (cm^{-1}): 2927, 2854, 1737, 1463, 1376, 1240, 1178, 1130, 1099, 1035, 931, 863, 723. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.22 (2H, m), 3.59 (2H, m), 3.39 (3H, s), 2.34 (2H, t, J = 7 Hz), 2.24 (4H, t, J = 7 Hz), 1.62 (2H, q, J = 7 Hz), 1.53−1.46 (4H, m), 1.40−1.26 (22H, m), 0.88 (3H, t, J = 7 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.0, 77.7, 77.6, 70.7, 65.4, 65.3, 63.4, 59.1, 34.3, 32.0, 31.7, 29.7, 29.6, 29.4, 29.2, 29.2, 29.2, 29.0, 29.0, 28.9, 28.5, 28.4, 25.0, 22.8, 22.8, 19.3, 19.3, 14.3. HRMS m/z 404.3293 (calcd $C_{26}H_{44}O_3$, 404.3290).

2-Methoxyethyl Heneicosa-8,10-diynoate (HCDA-EGME). 472 mg, 80%; mp 4.86 °C. IR (NaCl) ν_{max} (cm^{-1}): 2926, 2854, 1737, 1462, 1377, 1348, 1252, 1200, 1175, 1130, 1092, 1038, 988, 864, 723. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.23 (2H, m), 3.59 (2H, m), 3.40 (3H, s), 2.35 (2H, t, J = 7 Hz), 2.24 (4H, t, J = 7 Hz), 1.61 (2H, q, J = 7 Hz), 1.56−1.49 (4H, m), 1.41−1.26 (18H, m), 0.88 (3H, t, J = 7 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.9, 77.8, 70.6, 65.5, 65.3, 63.5, 59.1, 34.2, 32.0, 29.7, 29.6, 29.4, 29.2, 29.0, 28.7, 28.6, 28.5, 28.2, 24.9, 22.8, 19.3, 19.3, 14.3. HRMS m/z 376.2976 (calcd $C_{24}H_{40}O_3$, 376.2977).

Methyl Pentacosa-10,12-diynoate (PCDA-Me). 470 mg, 91%; mp 29.00 °C. IR (NaCl) ν_{max} (cm^{-1}): 2924, 2854, 1741, 1464, 1435, 1362, 1323, 1238, 1196, 1171, 1099, 1016, 881, 854, 723. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (3H, s), 2.30 (2H, t, J = 7 Hz), 2.24 (4H, t, J = 7 Hz), 1.61 (2H, q, J = 7 Hz), 1.55−1.46 (4H, m), 1.39−1.25 (26H, m), 0.88 (3H, t, J = 7 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.4, 77.7, 77.6, 65.4, 65.3, 51.6, 34.2, 32.1, 31.7, 29.8, 29.8, 29.7, 29.6, 29.5, 29.2, 29.2, 29.2, 29.0, 29.0, 28.9, 28.5, 28.4, 25.0, 22.8, 22.8, 19.3, 19.3, 14.3. HRMS m/z 388.3344 (calcd $C_{26}H_{44}O_2$, 388.3341).

Methyl Tricosa-10,12-diynoate (TCDA-Me). 1.56 g, 75%; mp 20.61 °C. IR (NaCl) ν_{max} (cm^{-1}): 2924, 2854, 1741, 1466, 1434, 1360, 1323, 1238, 1196, 1170, 1099, 1016, 879, 856, 723. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (3H, s), 2.30 (2H, t, J = 7 Hz), 2.24 (4H, t, J = 7 Hz), 1.61 (2H, q, J = 7 Hz), 1.54−1.47 (4H, m), 1.39−1.26 (22H, m), 0.88 (3H, t, J = 7 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.4, 77.7, 77.6, 65.4, 65.3, 51.6, 34.2, 32.0, 31.7, 29.7, 29.6, 29.4, 29.2, 29.2, 29.0, 29.0, 28.9, 28.5, 28.4, 25.0, 22.8, 22.8, 19.3, 19.3, 14.3. HRMS m/z 360.3026 (calcd $C_{24}H_{40}O_2$, 360.3028).

Methyl Heneicosa-8,10-diynoate (HCDA-Me). 510 mg, 88%; mp 9.76 °C. IR (NaCl) ν_{max} (cm^{-1}): 2925, 2854,1741, 1463, 1435, 1365, 1323, 1252, 1201, 1167, 1093, 1076, 1016, 877, 842, 723. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (3H, s), 2.31 (2H, t, J = 7 Hz), 2.25 (4H, t, J = 7 Hz), 1.63 (2H, q, J = 7 Hz), 1.56−1.26 (22H, m), 0.88 (3H, t, J = 7 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.3, 77.8, 77.4, 65.5, 65.3, 51.6, 34.1, 32.0, 29.7, 29.6, 29.4, 29.2, 29.0, 28.7, 28.6, 28.5, 28.2, 24.9, 22.8, 19.3, 19.3, 14.3. HRMS m/z 332.2716.

Representative Procedure for Preparation of Polydiacetylenes. PCDA-EGME (640 mg) was placed on a Peltier device and the surface temperature was lowered to −5 °C. After UV irradiation (254 nm, 1 mW/cm^2) for 1 h at −5 °C, unreacted monomer (331 mg) was recovered by using a cotton-filled syringe filter with hot ethyl acetate. The residual red precipitate was triturated with hot chloroform, and the organic solvent was concentrated *in vacuo* to afford poly(PCDA-EGME) (267 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.22 (2H, t, J = 4.4 Hz), 3.59 (2H, t, J = 4.6 Hz), 3.38 (3H, s), 2.47 (2H, br), 2.34 (3H, t, J = 7.3 Hz), 1.61 (7H, br), 1.42−1.18 (27H, m), 0.88 (3H, t, J = 6.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.7, 70.5, 63.2, 58.9, 34.2, 31.9, 29.8, 29.7, 29.6, 29.4, 29.3, 29.2 28.7 24.9, 22.7, 14.1. Other polydiacetylenes were prepared by employing a similar strategy.

Poly(TCDA-EGME). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.22 (2H, t, J = 4.4 Hz), 3.59 (2H, t, J = 4.6 Hz), 3.38 (3H, s), 2.47 (2H, br), 2.34 (3H, t, J = 7.3 Hz), 1.56 (7H, br), 1.40−1.18 (23H, m), 0.88 (3H, t, J = 6.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.8, 70.5, 63.2, 58.9, 34.2, 31.9, 29.7,29.6, 29.4, 29.3, 29.2 28.7, 24.9, 22.7, 14.1.

Poly(HCDA-EGME). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.22 (2H, t, J = 4.4 Hz), 3.59 (2H, t, J = 4.6 Hz), 3.38 (3H, s), 2.47 (2H, br), 2.34 (3H, t, J = 7.1 Hz), 1.61 (7H, br), 1.40−1.18 (20H, m), 0.88 (3H, t, J

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= 6.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.6, 70.5, 63.2, 59.0, 34.1, 32.0, 29.8, 29.7, 29.4, 29.3, 29.2, 28.9, 28.7, 28.5, 24.9, 22.7, 14.1.

Poly(PCDA-Me). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (3H, s), 2.47 (2H, br), 2.29 (3H, t, J = 7.6 Hz), 1.61 (6H, br), 1.40−1.26 (28H, m), 0.88 (3H, t, J = 7.0 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.2, 51.4, 34.1, 31.9, 29.8. 29.7, 29.6, 29.4, 29.3, 25.0, 22.7, 13.1.

Poly(TCDA-Me). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (3H, s), 2.48 (1H, br), 2.30 (3H, t, J = 7.6 Hz), 1.61 (6H, br), 1.39−1.24 (24H, m), 0.88 (3H, t, J = 7.0 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.2, 51.4, 34.1, 31.9, 29.8, 29.7, 29.6, 29.4, 29.3, 24.9, 22.7, 14.1.

Poly(HCDA-Me). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (3H, s), 2.47 (1H, br), 2.30 (3H, t, J = 7.1 Hz), 1.63 (6H, br), 1.39−1.24 (18H, m), 0.88 (3H, t, J = 6.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.1, 51.4, 34.1, 31.9, 29.8, 29.7, 29.4, 29.3, 29.2, 28.8, 24.9, 22.7, 14.1.

Preparation of Polydiacetylene Nanofiber. Poly(PCDA-EGME) powder was coated on the surface of an anodized aluminum oxide (AAO) (pore diameter: ca. 200 nm; thickness: 60 μm) membrane, and the membrane was placed on a hot plate at 150 °C. The red poly(PCDA-EGME) powder turned yellow as the polymer melts, and yellow polymer penetrates into the porous membrane. The PDA embedded AAO membrane was cooled to room temperature, and the residual PDA on the membrane surface was removed by using a razor blade. Incubation of the PDA embedded AAO membrane in aqueous KOH solution (20 wt %) results in dissolution of the membrane. The PDA nanofibers were collected by centrifugation and washed with DI water.

RESULTS AND DISCUSSION

Preparation and Properties of Diacetylene Monomers. In line with the general trend observed for long alkyl chain diacetylenic acids, 10,12-pentcosadiynoic acid (PCDA, mp: 62−63 °C), 10,12-tricosadiynoic acid (TCDA, mp: 54−56 °C), and 8,10-heneicosadiynoic acid (HCDA, mp: 51−52 °C) are solids at room temperature. Again following the general rule of thumb that the temperature needed to promote thermochromism of a PDA is close to the melting point of the corresponding DA monomer, the color changes of PDAs derived from PCDA, TCDA, and HCDA were observed to be initiated at around 65, 55, and 52 °C, respectively.

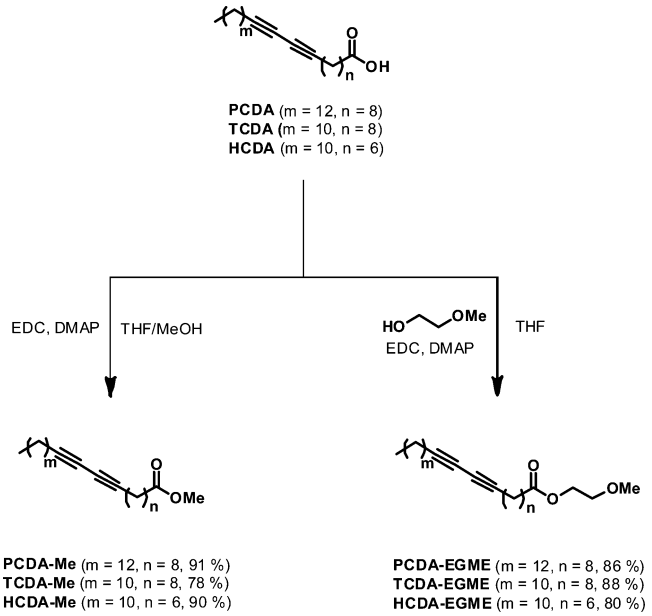
Conversion of a carboxylic acid group to an ester moiety removes the source for intermolecular hydrogen bonding, and as a result, it causes the melting temperature of a substance to decrease. Based on this trend, six ester group containing DA monomers were prepared from the corresponding carboxylic acids (Scheme 1). Three DA monomers PCDA-Me, TCDA-Me, and HCDA-Me were obtained using standard esterification reactions of diacetylenic acids with MeOH in the presence of 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide (EDC) and (dimethylamino)pyridine (DMAP). Ester containing DA monomers PCDA-EGME, TCDA-EGME, and HCDA-EGME were prepared by employing a similar strategy.

One of the advantageous features of PDAs that is not shared by other conjugated polymers is their ability to contain alkyl chains that are readily modified in order to manipulate colorimetric transition properties. In general, PDAs having shorter alkyl chains are colorimetrically more sensitive to environmental stimuli. Thus, PDAs arising by polymerization of the monomers displayed in Scheme 1 are also expected to have variable thermochromic transition temperatures.

In Figure 1 are shown normalized differential scanning calorimetry (DSC) thermograms for six DA monomers. Analysis of these thermograms shows that the maximum heat flow is in the following order: PCDA-Me (29.0 °C), PCDA-EGME (24.0 °C), TCDA-Me (20.6 °C), TCDA-EGME (15.5 °C), HCDA-Me (9.8 °C), and HCDA-EGME (4.9 °C) (see also Figure S1, Supporting Information). DSC analyses provide information about the thermal properties of the DA monomers. For example, owing to the structural flexibility of methoxyethyl moiety, members of the EGME family of PDAs have lower melting temperatures (4.9−5.2 °C) than the methyl ester family. Second, the melting points of DA esters was found to decrease ca. 8.5 °C (Me family: 8.39 °C; EGME family: 8.56 °C) as the number of methylene groups between the diacetylene and terminal methyl group (m value) decreases. In addition, a decrease in the number of methylene groups between the diacetylene and ester groups (n value) of the DA monomers causes an approximate 10.7 °C decreases in melting point (Me family: 10.85 °C; EGME family: 10.59 °C). The observed relationship between melting point and chain length suggests that the carbon chains of the DA monomers play an important role in governing intermolecular interactions.

Because they are liquid at room temperature, structural analysis of the DA monomers by using X-ray diffraction (XRD) and transmission electron microscopy (TEM) is difficult. Much

Scheme 1. Preparation of Diacetylene Monomers Used for Preparation of Low Temperature Thermochromic Polydiacetylenes



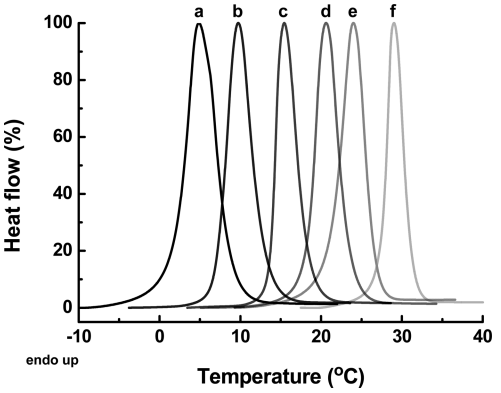


Figure 1. Nomalized DSC thermograms of DA monomers monitored in endothermic regions: HCDA-EGME (a), HCDA-Me (b), TCDA-EGME (c), TCDA-Me (d), PCDA-EGME (e), and PCDA-Me (f). The heating rate is 10 °C/min.

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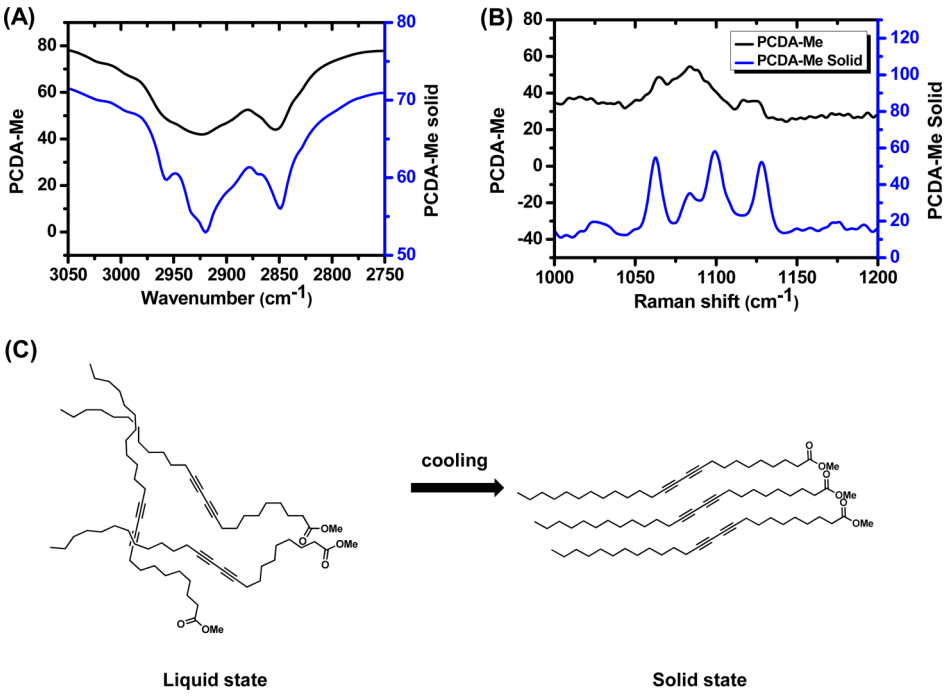

Figure 2. (A, B) Infrared (A) and Raman (B) spectra of liquid (black line) and solid (blue line) state diacetylene monomer PCDA-Me. (C) Schematic representation of PCDA-Me molecules in liquid (left) and solid (right) states.

information exists in the literature about how the conformations of hydrocarbons having long alkyl chains in the solid state can be determined by FTIR and Raman spectroscopic methods.[57−62] As a result, the CH_2 stretching regions (3050−2750 cm^{-1}) in FTIR spectra of the liquid and solid states PCDA-Me (Figure 2A, see also Figure S2 for other DA monomers) were analyzed. The C−H stretching region in the FTIR spectrum of PCDA-Me in the liquid state contains two broad bands corresponding to asymmetric stretching at 2924−2927 cm^{-1} and C−H symmetric stretching at 2854−2856 cm^{-1}. The FTIR spectrum of solid state PCDA-Me was obtained by placing the liquid monomer on a NaCl plate followed by cooling to below the melting temperature by using a Peltier device. The C−H stretching region in the spectrum of solid PCDA-Me contained bands in the same region as that of the liquid state of DA monomer except that they split into groups with 3−5 bands in the asymmetric stretching region and 2−3 sharp peaks in the symmetric stretching region. A similar peak splitting phenomenon was observed in the C−H wagging and rocking vibration regions of the FTIR spectra of PCDA-Me. The broad bands in the spectrum of the liquid state DA correspond to overlapping vibration bands associated with various C−C and C−H bond conformations. However, at low temperature the solid DA monomer will likely exist in a single conformation, and as a result, the FTIR spectrum will contain well-defined bands (Figure 2A).[59]

In order to gain more information about the molecular structure, Raman spectra were recorded for both liquid and solid states of the DA monomers. It is known that the Raman bands in the region of 1150−1000 cm^{-1} provide useful information about the conformational preferences of long alkyl chains of hydrocarbons and, in particular, that the presence of a broad band at 1089 cm^{-1} indicates the existence of some *gauche* conformations in liquid state.[57] In addition, Raman spectra of solid state hydrocarbons contain two bands at approximately 1065 and 1129 cm^{-1}. Inspection of the Raman spectrum of liquid PCDA-Me in the C−C stretching region (Figure 2B, see also Figure S3 for other DA monomers) contains major broad bands in the 1075−1084 cm^{-1} region. In contrast, three major bands at around 1063, 1100, and 1127 cm^{-1} are present in the spectrum of solid PCDA-Me. This Raman spectroscopic data along with those accumulated for the five other DA monomers in both liquid and solid states suggest that these substances exist in *all-trans* conformations in the solid state, and they have random coil structures with some *gauche* conformations when they are in the liquid state (Figure 2C).

Preparation and Thermochromic Properties of Polydiacetylenes. In order to investigate the feasibility of photopolymerization of the DA monomers and the thermochromic properties of the resulting PDAs, each monomer was immobilized on filter paper. The monomer-wetted paper was placed on a homemade Peltier device, and the surface temperature of the device was lowered to below the melting point of the monomer. Solidification of the monomer was readily observed by using the naked eye. Irradiation of the solid sample with a hand-held laboratory UV lamp (254 nm, 1 mW/cm^2) leads to formation of a blue PDA. Polymers derived from six DA monomers were soluble in chloroform, and the molecular weight of the polymers was dependent on the headgroup structures. For instance, the polymer derived from PCDA-Me had a weight-average molecular weight (M_w) of 208 000 with a polydispersity (PD) of 2.93. Similarly, poly(TCDA-Me) and poly(HCDA-Me) displayed M_w of 210 000 (PD: 1.98) and 160 000 (PD: 3.16), respectively. Interestingly, polymers derived from EGME containing DAs showed lower M_w values compared to those obtained with Me derivatives. Thus, poly(PCDA-EGME) and poly(TCDA-EGME) had molecular weights of 50 000 (PD:2.25) and 89 000 (PD: 2.53), respectively. The molecular weight of the polymer derived from HCDA-EGME was not obtained owing to the precipitation of the polymer in the column during the GPC analysis.

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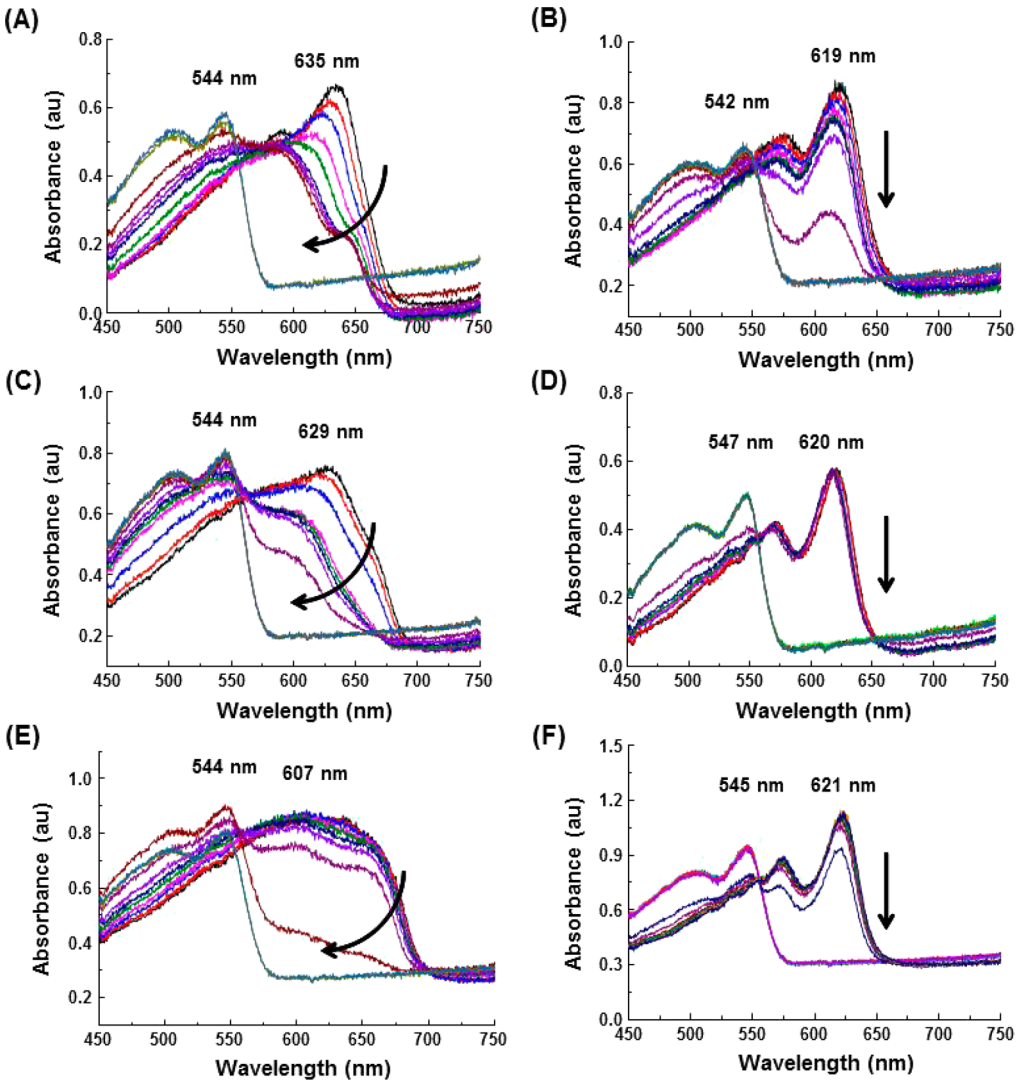

Figure 3. Absorption spectra of PDAs derived from PCDA-Me (A), PCDA-EGME (B), TCDA-Me (C), TCDA-EGME (D), HCDA-Me (E), and HCDA-EGME (F) upon heating.

Real-time spectroscopic monitoring of color change undergone by the PDAs as the temperature increases was carried out using a fiber-optic absorption spectrometer over the following temperature ranges: PCDA-Me (0−30 °C), PCDA-EGME (0−26 °C), TCDA-Me, (−2−22 °C), TCDA-EGME (0−18 °C), HCDA-Me (−2−11 °C), HCDA-EGME (−4−10 °C). As can be seen in Figure 3, the absorption maximum (635−607 nm) of the blue phase PDA shifts to lower wavelength (547−542 nm) upon gradual heating.

Plots of colorimetric responses (CR) of thermochromic PDAs as a function of temperature often provides useful information about the thermochromic properties of the polymer.[3] CR, a relative evaluation of color changes, is defined as CR = $(PB_0 - PB_f)/PB_0 \times 100\%$, where PB is the percentage of absorbance of blue before (PB_0) and after (PB_f) the thermochromic transition as given by PB = $A_{blue}/(A_{blue} + A_{red}) \times 100\%$. In Figure 4 are displayed plots of CR values of the PDAs as a function of temperature in the range of −5−30 °C. The plots show that each PDA has characteristic temperature range over which the CR values sharply increase. The temperature regions are as follows: PCDA-Me (28−29 °C), PCDA-EGME (21−24 °C), TCDA-Me (15−18 °C), TCDA-EGME (10−12 °C), HCDA-Me (7−10 °C), and HCDA-EGME (2−5 °C). Interestingly, the temperature at which the PDA undergoes a sharp colorimetric transition was found to be related closely to the melting point of the corresponding monomer. In general, PDAs derived from Me ester containing

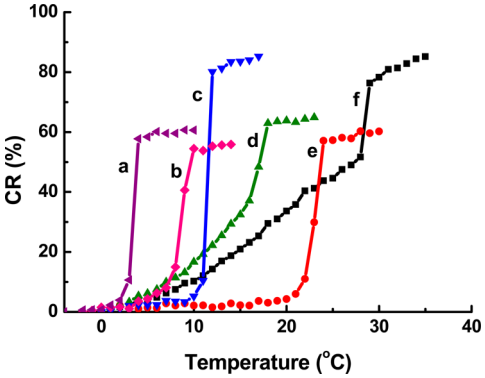

Figure 4. Plots of colorimetric response (CR) values of PDAs derived from HCDA-EGME (a), HCDA-Me (b), TCDA-EGME (c), TCDA-Me (d), PCDA-EGME (e), and PCDA-Me (f) as a function of temperature.

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DA monomers display a gradual increase of CR before the sharp transition takes place while the PDAs derived from EGME containing DA monomers undergo abrupt colorimetric transitions without an preliminary gradual increases.

Changes occurring in the molecular structures of PDAs during the blue-to-red color transition caused by a temperature increase were indirectly demonstrated by using Raman spectroscopy. In the Raman spectra of both the blue phase of the PDAs (Figure S4), bands associated with ene−yne groups in the conjugated backbone appear at ca. 1450 (C═C) and ca. 2080 cm^{-1} (C≡C), respectively. The Raman bands for the ene−yne groups in the red phase PDAs created by heating are shifted to higher frequencies (ca. 1520 and ca. 2120 cm^{-1}, respectively). This spectral change is promoted by the thermally induced conformational distortion of PDA backbone.

In a similar manner, Raman bands in the C−C stretching region give useful information about the molecular structure of aliphatic alkyl chains in the PDA backbone.[57] The blue-phase PDA prepared by UV irradiation of solid PCDA-Me contains a strong band at 1081 cm^{-1} and two weak bands at 1107 and 1128 cm^{-1} (Figure 5). The three bands are associated with alkyl chains containing *all-trans* conformations. However, upon heating to 40 °C these bands disappear being replaced by one major band at lower frequency (1070 cm^{-1}). The results suggest that the major *all-trans* C−C conformation of the alkyl chain is altered during the color transition, becoming at least partially *gauche*. In addition, when a red-PDA sample is subjected to a cooling, the three characteristic bands associated with of the *all-trans* alkyl chains of the blue phase are not restored, and the red phase PDA band at 1070 cm^{-1} remains unchanged (Figure S5). These spectroscopic features indicate that the original conformation of the blue phase PDA is not restored by cooling of the thermally stimulated PDA.

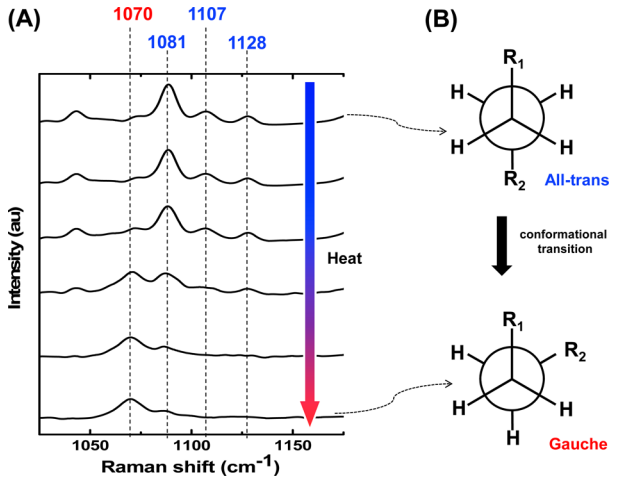
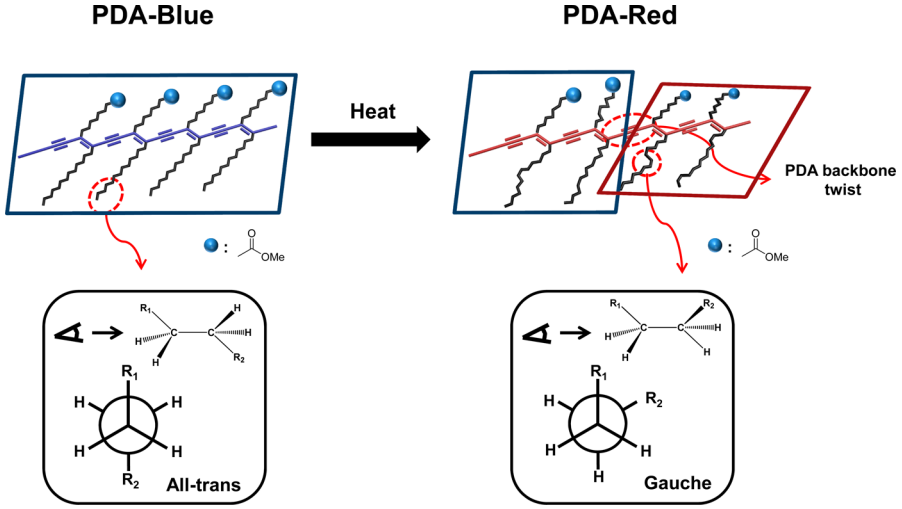


Figure 5. (A) C−C stretching region of Raman spectra used to monitor the blue-to-red color transition of poly(PCDA-Me) upon gradual heating from 10 to 40 °C. (B) Single bond conformational change of a long alky chain attached to PDA backbone upon heating.

The mechanism for operation of the low temperature color transition PDAs described above is interesting. The close relationship that exists between the DA melting point and the colorimetric transition temperature of the PDA indicates that conformational changes in the macromolecule play a significant role in thermochromism. Evidence gained from Raman spectroscopic studies support the proposal that the conformations of alkyl chains in the PDAs change from *all-trans* in the solid state (monomer) and in the blue-phase PDA (polymer) to some *gauche* above the monomer melting and PDA color transition temperatures. Thus, it appears that thermally induced conformational changes of alkyl chains cause distortion of the conjugated p-orbital array in the PDA (Scheme 2).

Fabrication of Polydiacetylene Nanofiber. Recently, generation of PDA nanofibers using nanoporous inorganic templates has been reported, and the method enables fabrication of nanofibers with controlled diameters and lengths.[63] PDA nanofibers were prepared from polymerization of monomeric diacetylenes that are encased within templates. However, owing to difficulties associated with UV penetration, only monomers on the template surface undergo polymerization. In order to circumvent this limitation, we have developed a technique for nanofiber construction that utilizes a soluble PDA instead of the monomer as the starting material. Inspection of the TGA curves displayed in Figure 6 shows that poly(PCDA-Me) and poly(PCDA-EGME) have nearly identical thermal stabilities and that decomposition of both begins at around 300 °C. In DSC curves, endothermic peaks of poly(PCDA-Me) are observed at 133.7 and 149.9 °C, while

Scheme 2. Proposed Mechanism for the Blue-to-Red Color Transition of a Low Temperature Thermochromic Polydiacetylene



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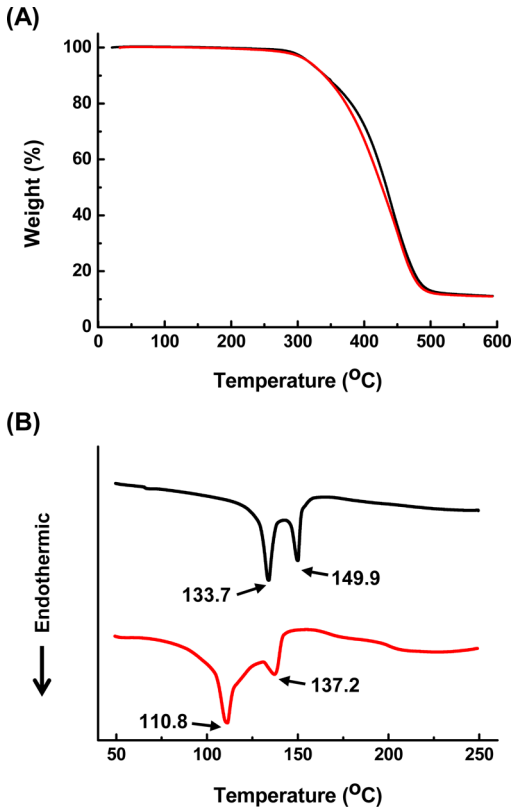

Figure 6. TGA (A) and DSC (B) of PDAs derived from PCDA-Me (black line) and PCDA-EGME (red line). The heating rate is 10 °C/min.

poly(PCDA-EGME) displays endothermic peaks at 110.8 and 137.2 °C. The data obtained from TGA and DSC analyses suggest that the two polymers should be able to be processed in their liquid states at reasonably high temperatures.

Anodized aluminum oxide (AAO) membrane was chosen as a template to prepare poly(PCDA-EGME) nanofibers using the new procedure we have devised. At 150 °C, a film of poly(PCDA-EGME) melts on the surface of the AAO template accompanied by a red-to-yellow color transition. After cooling to room temperature, a red PDA filled AAO membrane is obtained. The residual PDA film on the AAO template surface was removed by scratching with a knife, and the PDA nanofiber is generated by etching the AAO template with aqueous NaOH and collected by using centrifugation. In Figure 7 are shown optical, fluorescence, and SEM images of the poly(PCDA-EGME) nanofibers formed in this manner. Inspection of the optical microscopic image (Figure 7A) demonstrates that bundles of PDA fibers are generated. In addition, because the red phase PDAs are fluorescent, red-emitting fibers are clearly visible in the fluorescence microscopic image (Figure 7B). Importantly, analysis of the SEM image (Figure 7E) indicates that the diameter of the PDA fibers (ca. 300 nm) is similar to the pore diameter of the template AAO membrane (Figure 7F). Furthermore, although some short PDA fibers are produced, the length of the majority of the fibers is similar to that of the AAO membrane. Finally, the surface of the PDA nanofiber is relatively smooth and absent of any porous structures (Figure 7E). The simple and straightforward method described above should be applicable to the preparation of PDA nanofibers having controlled dimensions.

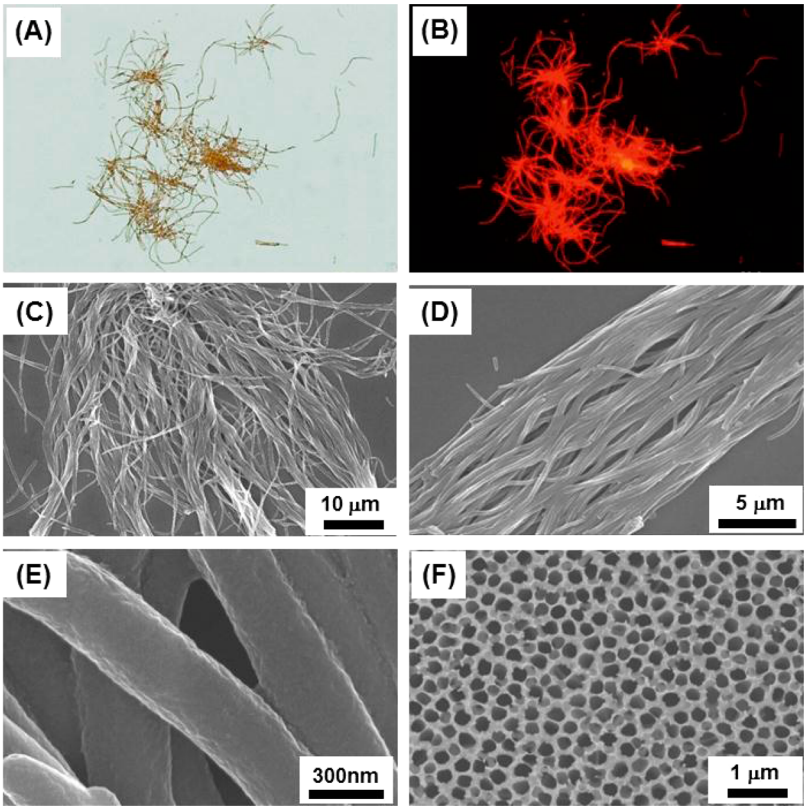

Figure 7. Optical (A), fluorescence (B), and SEM images (C–E) of poly(PCDA-EGME) nanofibers obtained using the AAO templating method. (F) SEM image of top view of an AAO membrane.

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CONCLUSION

Several low temperature thermochromic PDAs, derived from methyl and methoxyethyl ester containing DA monomers, were designed and prepared. Removal of the source of intermolecular interactions between head groups leads to a significant decrease in the melting point of the DA monomer, an effect that is directly reflected in the colorimetric transition temperature of the corresponding PDA. As a result, we were able to prepare PDAs that display thermochromic transition temperature in the range of 5−30 °C. FT-IR and Raman spectroscopic analyses provided useful information about the conformations of alkyl groups in blue and red phase PDAs. Specifically, the results show that *all-trans* conformations of the alkyl groups, which exit in the blue-phase, are converted to some *gauche* forms in the red-phase. In addition, the thermochromic transition temperature of the PDAs was found to decrease ca. 10 °C when the alkyl chain length decreases by two methylene units. Lastly, the high thermal stability of the PDAs enables them to be employed to generate nanofibers using anodized aluminum oxide (AAO) as a template. It is believed that the strategy described above, which is based on weak headgroup interactions in both DA monomer and resulting PDA polymer, should be generally applicable to the design of new low temperature thermochromic and processable PDAs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b02683.

DSC thermograms for six DA monomers, FTIR and Raman spectra in specific regions for monomers and polymers, and ^{1}H NMR and ^{13}C NMR spectra for the monomers (PDF)

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Notes

The authors declare no competing financial interest.

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