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Reversible thermochromism in self-layered hydrogen-bonded polydiacetylene assembly

Zhongzhe Yuan, Chan-Woo Lee, Suck-Hyun Lee *

Department of Molecular Science and Technology, AJOU University, 5 Wonchon-dong, Youngtong, Suwon, Kyunggi-do 443-749, South Korea

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Abstract

We structurally designed and synthesized a novel class of self-layered supramolecular polymers containing DA derivatives that can be obtained as film-forming materials and processed into a various forms. We found that double H-bonds between the acid hard cores together with a remarkable molecular DA recognition allow for retaining more favorable packing of the reactive groups in spin-coated films or even in dispersed solutions with a high degree of local ordering, suitable for topochemical polymerization. The sample molecularly designed here could be topochemically polymerized by UV irradiation through 1,4 addition of the conjugated triple bonds between adjacent stacking molecules. A reversible thermochromism in the absorption characteristics of spin-coated terephthalic acid/diacetylene polymers was also observed.

Keywords: Diacetylene; Thermochromism; Hydrogen-bonded assembly

1. Introduction

Conjugated polymers exhibit electronic and optical properties of interest for applications ranging from biosensors to light-emitting diodes owing to the effective conjugation length of the delocalized π-conjugated polymer backbone [1]. The chromic properties of organic molecules have recently become important elements in applications directed toward the optical processing of information [2–4]. It is well known that diacetylene (DA) derivatives are a class of compounds containing the 1,3-butadiyne structure which undergo a solid-state 1,4 addition by UV-light, X- or γ-irradiation or by heating. The solid-state polymerization is a repetitive 1,4 addition of adjacent diyne units to form a conjugated polymer of alternating ene–yne units. This polymerization reaction occurs only in the solid state, and demands that monomers are closely packed in a crystalline solid [5–8]. Numerous studies of the chromatic behavior of polydiacetylenes (PDAs) induced by thermal changes [9–12], mechanical stress [13], biological targets [14–17] have been published. Recent investigations provided insight into the mechanism of chromic shifts observed in the polydiacetylenic sensing systems. The linear polyenyne backbone starts to 'self-fold' to a 'zigzag' shape due to the free rotation of the single bonds within to polymer chain, and thus changing to color from blue to red [18].

As the extension of our previous study with self-layering materials [19,20], we designed and synthesized a novel class of self-layered supramolecular polymer system by using terephthalic acid substituted with DA moieties in two symmetric side chains. In the construction of supramolecular polymers hydrogen bonding plays a prominent role because of its directionality and versatility. We have been able to construct very stable dispersions of supramolecular polymers from the doubly hydrogen bonded compounds of long dialkoxy substituted terephthalic acids [21,22]. The DA units within the side chains could be lying together and suitable for topopolymerization. The rationalization for this layered supramolecular approach is that it would provide a sufficient order of the reactive groups and promote certain flexibility to accommodate structural changes during the polymerization and subsequent color changes of PDA. When the structurally designed diacetylene polymerizes, a conjugated PDA backbone could be created by connecting the adjacent DA units. It is reasonable to believe that the conformation of the PDA backbone and thus the chromic changes must be greatly affected by the packing structure of the DA monomer.

The present study has attempted for the first time to control the hydrogen bonding network on the photopolymerization and the chromic behavior of PDA chains using these concepts of molecular and supermolecular design. We report here a novel

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* Corresponding author. Fax: +82 31 214 1592.
E-mail address: hyja@ajou.ac.kr (S.-H. Lee).

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class of similar supramolecular polymers containing a DA moiety in each of two symmetric side chains. These intermolecular hydrogen-bonded terephthalic acid DA compounds allow very easy preparation of PDAs with characteristic of thermoreversible color switching.

2. Experimental section

2.1. Materials and instrumentation

Most of the chemicals and solvents were purchased from Sigma–Aldrich. 10-Undecyn-1-ol was purchased from the Flucka Chemical Co. Unless otherwise noted, solvents and chemicals were reagent grade and were used as received. All synthesized compounds containing the diacetylene functionality were stored in the absence of light and in refrigerator. The silica gel used in column chromatography was Kieselgel 60. Thin layer chromatography was 25 TLC aluminium sheets Silica gel 60 G254. Melting points were determined on a Meltemp apparatus and were uncorrected. IR spectra were determined as thin films on sodium chloride plates, or as a KBr pellet with a Nicolet 550 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were determined at either 200 or 400 MHz on Varian superconducting FT instruments. UV–vis spectra were recorded on either JASCO V-550 or V570 instruments. GC Mass spectra were obtained on a QUATTRO LC triple quadrupole tandem mass spectrometer equipped with a HP-1100 high performance liquid chromatography. Thermal properties of monomers and polymers were analyzed by Model DSC 2010 and Model TGA 2050 Instruments (heating rate: 10 °C/min). Patterned images were observed with a laser scanning microscope (LSM-5 PASCAL) and a scanning electron microscope (SEM, model S-2400, HITACHI Co). Wide angle X-ray diffraction studies were performed using a GADDS. UV illuminator of Ushio Inc. equipped with a 500 W Hg–Xe lamp.

2.2. Synthesis

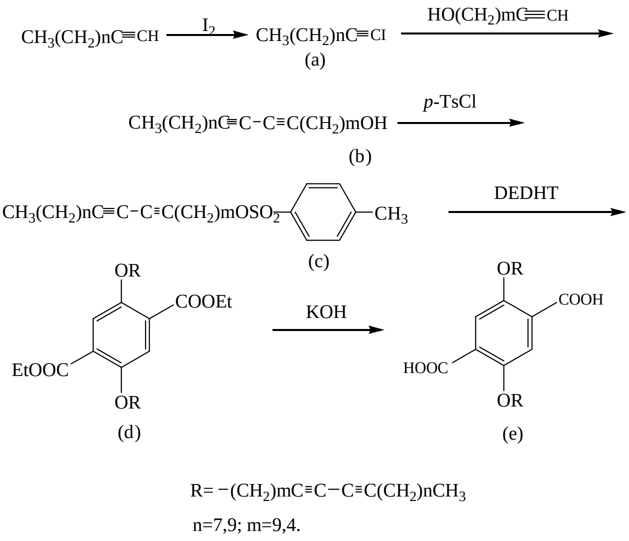
Synthetic routes of the designed diacetylene D(9,8)diacids and D(4,10)diacids are shown in Scheme 1. The detailed synthetic procedures are described as below.

2.2.1. Iodination of 1-decyne

26.6 ml (42.53 mmol) *n*-butyllithium was added to a solution of 6.4 ml (35.44 mmol) 1-decyne in 250 ml hexane cooled in an ice bath. After 20 min, 13.5 g (53.16 mmol) solid iodine was added and the mixture was stirred for 4 h. The solution was washed with 120 ml saturated aqueous sodium thiosulfate solution and the organic phase was dried over sodium sulfate. The product **1a** was used in the coupling reaction without further purification. Yield: 95%.

2.2.2. Preparation of 10,12-heneicosadiyn-1-ol

Fifteen milli liters methanol was added to a mixture of 1.9 ml (9.5 mmol) 10-undecyn-1-ol and 10 ml 10% aqueous potassium hydroxide. 0.066 g (0.954 mmol). Hydroxylamine hydrochloride was added followed by a solution of 0.24 g (2.38 mmol) copper (I) chloride in 3.3 ml ethylamine (70% aqueous). Cooled to <30 °C in a methanol/dry ice bath for 10 min and a solution of 2.1 g (8 mmol) iodinated 1-decyne in 7 ml THF was added dropwise in 20 min. The solution was allowed to stir and warm to room temperature overnight. The solution was then washed with 10% H_2SO_4 and extracted three times with diethyl ether. The combined extracts were dried over anhydrous sodium sulfate, filtered, evaporated the solvent and recrystalized the remaining solid from petroleum ether to produce a slightly yellow solid **1b**. Yield: 52%. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.88 (CH_3, t, 3H), 1.27–1.53 (CH_2 chain, m, 26H), 2.21–2.28 (CH_2, m, 4H), 3.64 (CH_2–O, t, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.11, 19.20, 22.65, 25.70, 27.39, 28.34, 28.43, 28.80, 28.85, 29.01, 29.06, 29.14, 29.34, 29.41, 31.82, 32.78, 63.08, 65.21, 66.10, 76.54, 77.60.



Scheme 1. Synthesis of the investigated compounds: D(9,8)diacid and D(4,10)diacid.

2.2.3. Preparation of 1-(p-toluenesulphonyl)-10,12-heneicosadiyne

1.1 g (3.6 mmol) **1b** was dissolved in 30 ml chloroform and cooled in ice bath. 0.87 ml (10.8 mmol) pyridine was added followed by the addition of 3 equiv *p*-toluenesulphonyl chloride in small portions. The solution was stirred in the ice bath for 8 h. The solution was added 30 ml ether and 7 ml water. The organic layer was washed successively with 2 N HCl, 5% aqueous sodium bicarbonate, and water, and the organic phase was dried over magnesium sulfate, filtered, and concentrated by evaporation. The product **1c** was purified by silica gel chromatography. Yield: 58.8% ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.88 (CH_3, t, 3H), 1.22–1.63 (CH_2 chain, m, 26H), 2.21–2.27 (CH_2, m, 4H), 2.46 (Ar–CH_3, s, 3H), 4.01 (CH_2–O, t, 2H), 7.33–7.81 (Ar–H, $AA'BB'$, 4H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 13.96, 19.02, 21.46, 22.50, 25.13, 28.14, 28.21, 28.48, 28.57, 28.61, 28.70, 28.76, 28.92, 29.01, 31.67, 65.15, 65.24, 70.50, 77.18, 77.35, 127.69, 129.66, 133.03, 144.49.

2.2.4. Preparation of diethyl 2,5-di-[1-(10,12-heneicosadiyneoxy)]terephthalate

In a round bottom flask, 0.2457 g (0.94 mmol) diethyl 2,5-dihydroxy terephthalate (DEDHT) and 0.3897 g (2.82 mmol) K_2CO_3 were dissolved in 4 ml DMF, 0.86 g (1.87 mmol) **1c** in 1 ml DMF was added dropwise to the above solution over a period of 10 min. The reaction solution was allowed to stir at 50 °C for 28 h. Cooled and filtered, the solvent was removed by vaccum distillation. The product **1d** was purified by column chromatography using silica gel as column material and hexane/ethyl acetate (30:1) as eluent. Yield: 80%; ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.87 (CH_3, t, 6H), 1.26–2.27 (CH_2 chain, m, 60H), 1.3 (CH_3 of $COOCH_2CH_3$, 6H), 4.02 (CH_2–O t, 4H), 4.37 ($COOCH_2$, q, 4H), 7.34 (Ar–H, s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.07, 14.18, 14.25, 19.15, 22.60, 22.66, 25.90, 28.30, 28.77, 28.81, 29.02, 29.10, 29.26, 29.36, 31.77, 31.84, 61.24, 65.19, 65.22, 69.74, 77.01, 77.50, 116.48, 124.58, 151.64, 166.05.

2.2.5. Preparation of 2,5-di-[1-(10,12-heneicosadiyneoxy)]-terephthalic acid

A solution of 0.2407 g D(9,8) diester (0.29 mmol) in EtOH(50 ml) was heated at 50 °C under nitrogen. 0.082 g KOH(1.45 mmol) in 10 ml EtOH was added to the above solution. The mixture was stirred for 48 h and TLC indicated the completion of the reaction. Upon completion, the solution was cooled to room temperature, and 35% HCl was added to the reaction mixture until pH to 2–3 and stirred vigorously. The white precipitate was filtered, dried and recrystallized from a cosolvent (MeOH + EA + MC), The pure product **1e** was obtained by filtration and dried under reduced pressure. Yield: 77%; mp: 112–3 °C; ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.88 (CH_3, t, 6H), 1.15–2.32 (CH_2 chain, m, 60H), 4.30 (CH_2–O t, 4H), 7.88 (Ar–H, s, 2H), 11.17 (COOH, s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.09, 19.20, 22.65, 25.72, 28.27, 28.34, 28.39, 28.73, 28.81, 28.93, 29.05, 29.14, 29.21, 31.82, 65.19, 65.30, 71.30, 77.22, 77.40, 117.48, 122.66, 151.72, 163.95; IR(KBr), (cm^{-1}), 3427, 2920, 2851, 1682, 1450, 1223, 1040, 758; GC MS (*m/z*): calcd for $C_{50}H_{74}O_6$ 771.13, found 771.4.

*2.2.6. Iodination of 1-dodecyne **(2a)***

The 1-iodododecyne was synthesized from, 1-dodecyne. Yield: 93.7%.

*2.2.7. Preparation of 5,7-octadecadiyn-1-ol **(2b)***

Yield: 55%. ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.84 (CH_3, t, 3H), 1.22–1.63 (CH_2 chain, m, 20H), 2.16–2.29 (CH_2, m, 4H), 2.38 (OH, s, 1H), 3.60 (CH_2–O, t, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 13.99, 18.88, 19.06, 22.58, 24.56, 28.25, 28.76, 29.00, 29.21, 29.38, 29.47, 31.58, 31.79, 61.99, 65.09, 65.61, 76.79, 77.59.

*2.2.8. Preparation of 1-(p-toluenesulphonyl)-5,7-octadecadiyne **(2c)***

Yield: 53.4% ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.86 (CH_3, t, 3H), 1.24–1.70 (CH_2 chain, m, 20H), 2.17–2.36 (CH_2, m, 4H), 2.43 (Ar–CH_3, s, 3H), 4.02 (CH_2–O, t, 2H), 7.31–7.78 (Ar–H, $AA'BB'$, 4H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.01, 18.41, 19.07, 21.52, 22.58, 24.09, 27.71, 28.20, 28.74, 28.99, 29.20, 29.37, 29.46, 31.79, 64.98, 66.01, 69.73, 75.90, 77.88, 127.74, 129.78, 132.95, 144.68.

*2.2.9. Preparation of diethyl 2,5-di-[1-(5,7-octadecadiyneoxy)] terephthalate **(2d)***

Yield: 83%. Mp: 50–1 °C; ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.91 (CH_3, t, 6H), 1.22–2.45 (CH_2 chain, m, 48H), 1.3 (CH_3 of $COOCH_2CH_3$, 6H), 4.05 (CH_2–O t, 4H), 4.41 ($COOCH_2$, q, 4H), 7.37 (Ar–H, s, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.52, 14.71, 19.28, 19.57, 23.07, 25.29, 28.71, 29.21, 29.47, 29.68, 29.86, 29.94, 32.26, 61.65, 65.45, 66.14, 69.26, 76.92, 77.99, 116.67, 124.79, 151.70, 165.94; IR(KBr), (cm^{-1}), 2957, 2918, 2849, 1697, 1427, 1213, 1057, 785, 725; GC MS (*m/z*): calcd for $C_{48}H_{70}O_6$ 743.1, found 743.2.

*2.2.10. Preparation of 2,5-di-[1-(5,7-octadecadiyneoxy)] terephthalic acid **(2e)***

Yield: 84%. Mp: 138–9 °C; ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.88 (CH_3, t, 6H), 1.26–2.43 (CH_2 chain, m, 48H), 4.33 (CH_2–O t, 4H), 7.88 (Ar–H, s, 2H), 10.96 (COOH, s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.12, 18.85, 19.19, 22.67, 24.51, 27.93, 28.27, 28.86, 29.08, 29.29, 29.47, 29.57, 31.89, 64.89, 66.53, 70.59,75.53, 78.39, 117.51, 122.74, 151.63, 163.84; IR(KBr), (cm^{-1}), 3261, 2957, 2918, 2849, 1697, 1427, 1213, 1057, 785, 725; GC MS (*m/z*): calcd for $C_{44}H_{62}O_6$ 686.97, found 687.4.

3. Results and discussion

3.1. UV-induced photopolymerization

To investigate the UV-induced formation of polymers in the spincoated films and dispersion aggregates, the monomer films and dispersion solutions are irradiated with UV (254 nm) light. These two monomers are capable of polymerizing DA groups either in a simple dispersion medium of chloroform/hexane or in spincoated films. Spincoated films [0.9 wt% of monomer was dissolved in dichloromethane. The solution was filtered through 0.2 μm membrane filter and spincoated using headway research spincoator (2000 rpm, 2 min)] of about 0.2 μm on quarts plate were used here as they can be successfully photopolymerized via a topochemical reaction and thereby easily produce the colored PDAs upon UV irradiation. Solution-phase polymerization of dispersion aggregates [0.9 wt% of monomer was dissolved in dichloromethane. The solution was filtered through 0.2 μm membrane filter. The solution was then diluted in hexane (1% v/v) resulting in semistable dispersions] of DA compounds upon UV irradiation is visible to the eye by a rapid change of the color of the suspension to blue [23]. Due to the conjugated structure of the polymer chains exhibit a strong absorption in visible, the polymerization of DA derivatives can, therefore, easily be monitored by UV–vis absorption spectroscopy. Fig. 1 presents the comparison of the UV–vis spectra for D(9,8)diacid in

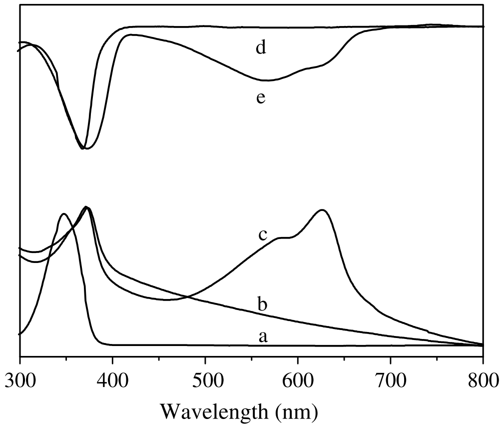


Fig. 1. UV–vis absorption (a)–(c) and transmission spectra (d), D(9,8)diacid in $CHCl_3$ solution (a), a dispersion in $CHCl_3$/hexane (0.5% v/v) unexposed (b) and exposed by UV irradiation (254 nm, 23 mW/cm^2) for 20 m (c), and a spincoated film on quartz unexposed (d) and UV exposed for 1 min (e).

various sample forms. The spectra for D(4,10)diacid are omitted here because the spectra for the two compounds are nearly identical except the relative intensity ratio $I_{\mathrm{PDA}}/I_{\mathrm{DA}}$. The non-polymerized sample in solution of $CHCl_3$ (a), a dispersion of $CHCl_3$/hexane (b), and film (d) show no absorption in the region from 400 to 800 nm and all these samples fluoresce when irradiated with UV light. A characteristic absorption band of the dispersed phase λ_{max} around with 370 nm is red-shifted by 22 nm relative to the corresponding band in solution. A similar absorption band is also observed for the spincoated film. This excitonic absorption shift can be understood as an indication that under given experimental conditions supramolecular polymers form an aggregate by parallel stacking of the aromatic rings of the terephthalic acid cores with the side chains and shifted in the phenyl plane with respect to each other [23]. The assembly of the aromatic groups into a rigid core by stacking is a prerequisite for the formation of the layered architecture, which is required for the DA units to react topochemically. As expected, the absorption spectrum for the dispersion sample has a distinct maximum at 630 nm with a shoulder around 580 nm after UV irradiation, which is characteristic for PDAs. When the irradiation time is extended to 20 min, the absorption intensity of the so-called blue form of the polymer at 630 nm increased and the maximum shifted slightly towards shorter wavelengths. Continuing irradiation for an hour results in a weak blue-form absorption band, leaving the red form at 580 nm dominant. The transmission spectrum for the spincoated PDA sample is similar but has a blue shifted absorption at 600 nm and another at 540 nm ascribable to the red form, which indicates the formation of a mixture of red and blue forms. Note that a fractional monomer conversion after photopolymerization for spincoated film (∼24%) determined by isolating the polymeric insoluble part (from the soluble monomer part owing to incomplete polymerization) was also much lower than for the dispersion specimen (79%). We think that the localized shear stresses and the accompanying changes in samples and molecular dimensions produced during the spinning process drives the films to a more disordered ‘red’ film as a result of the perturbation of the π-conjugation system.

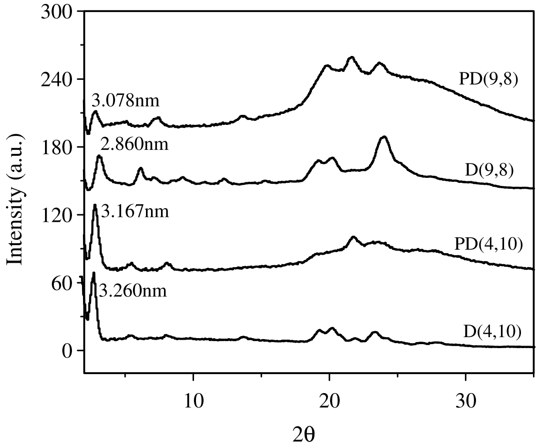
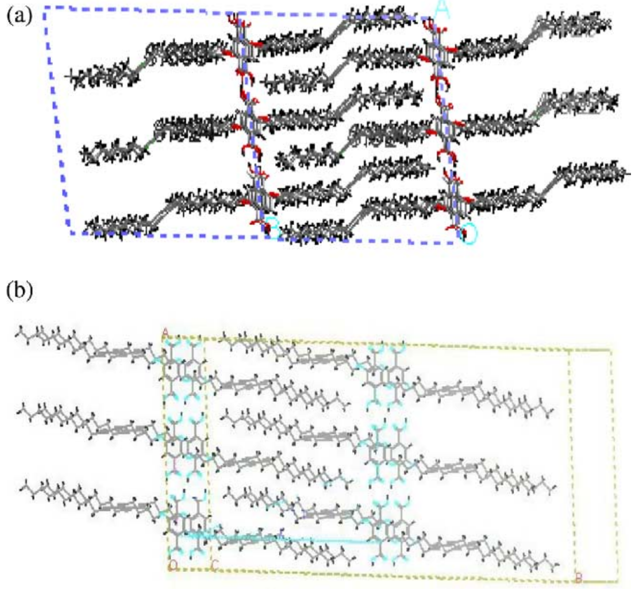


Fig. 2. Powder X-ray diffractograms of D(9,8), PD(9,8), D(4,10), and PD(4,10)diacid at 25 °C. Polymer prepared in dispersion ($CHCl_3$/hexane).

3.2. Structure

The occurrence of the lattice controlled DA polymerization provoked the question for the state of order of the structures, therefore, X-ray diffraction (XRD) is used to investigate the structure of the samples. Powder XRD for the monomers and polymers show that the highly ordered layer structure is preserved while going from monomer to polymer with slightly decreased side chain crystallinities (Fig. 2). The X-ray analysis confirms that they are all assemble into highly ordered layers similar to comb-shaped rod-like polymers [24]. Here, supramolecular polymers are formed by the double H-bond between aromatic dicarboxylic acids enforced through layers of an interdigitating side group. A typical packed structure of



Scheme 2. Packed computational structures of D(9,8)diacid (a) and D(4,10)diacid (b).

D(9,8)diacid in powder form as calculated by X-ray and molecular mechanics is schematically shown in Scheme 2(a). The X-ray results indicate that D(9,8)diacid sample exhibits a smaller layer distance as compared to that of D(4,10)diacid even though the alkyl chain length of D(9,8)diacid is much longer than that of D(4,10)diacid. We think that it is because of the relatively stronger van der Waals forces among adjacent DA groups in D(9,8)diacid, and thus the layer distance is decreased as van der Waals forces are increased. The mismatch in the spatial distance in D(4,10)diacid prevents the inter-digitated assembly of adjacent DA moieties, resulting in a longer spacing. The intensity ratio $I_{\mathrm{PDA}}/I_{\mathrm{DA}}$ (UV absorption spectra) is much higher for D(9,8)diacid, resulting in higher polymerization reactivity of the monomer.

3.3. Reversible thermochromic transition

To investigate the thermochromic transition of the spin-coated films, we measured absorption spectra against temperature based on the results of differential scanning calorimetry (DSC) measurements shown in Fig. 3. These materials exhibit structural and thermal behaviors similar to the side-chain polymers based on a rigid backbone [25,26]. Their general architecture can be described in terms of hydrogen-bonded aromatic rigid backbones separated by layers composed of relatively well packed side chains. D(4,10)diacid and PD(4,10)diacid revealed two endothermic before melting: the higher transition temperature is associated with rigid core motion and the low temperature transition is attributed to the onset of disordering process in the side chain region. But D(9,8)diacid showed no other peak before melting, this is maybe due to the difference of structures. As shown in Fig. 4(a) and (b), polymer PD(4,10)diacid shows reversible spectroscopic changes during the thermal cycles. The blue form which gives rise to the band at 600 nm disappears and the red form appears as the temperature increases. The absorptions of the red form appear at 540 and 500 nm at 350 K and then grow in the intensity up to the melting point of 411 K even though the film was not fully blue to begin with. Upon cooling to room temperature the blue form reappears in a reversible manner. This remarkable thermochromic behavior is not usually observed in PDAs. Thermal stimulus gives the side chains enough energy to impose mechanical strain on the PDAs by rotation around the single bonds between the methylene units although such movement of the side chains must be restricted so that the necessary crystal integrity for reversibility is maintained. The observed reversibility in PD(4,10)diacid corroborates that the layer integrity is retained at higher annealing temperatures. Polymerization of D(4,10)diacid produces the unusual rigid ladder-type bonding in the layer structures and such sterically controlled systems have no degree of freedom to respond to intralayer strain that causes structural modifications. PD(9,8)diacid also shows reversible color changes during thermal cycles. The blue form at 620 nm progressively disappears and the red form appears as the temperature increased. Upon cooling to room temperature, the blue form reappears in a reversible manner. Thus, up to the backbone melting temperature the thermochromic transitions for our material are dominated by the flexibility of the side-chain packing between supramolecular polymers.

3.4. Photolithographic patterns

Significant attention has recently been focused on patterning the chemical properties of surface. By protecting

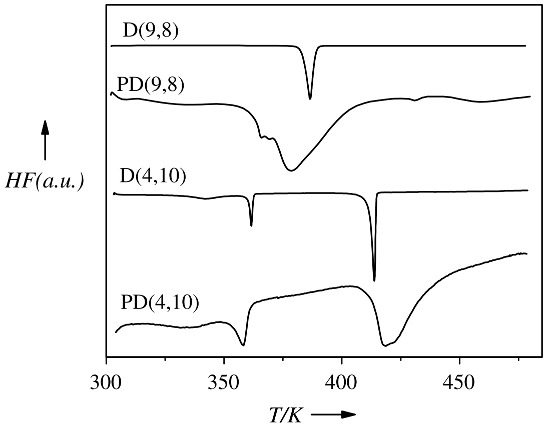


Fig. 3. DSC thermograms of compounds D(9,8), PD(9,8), D(4,10), and PD(4,10)diacid.

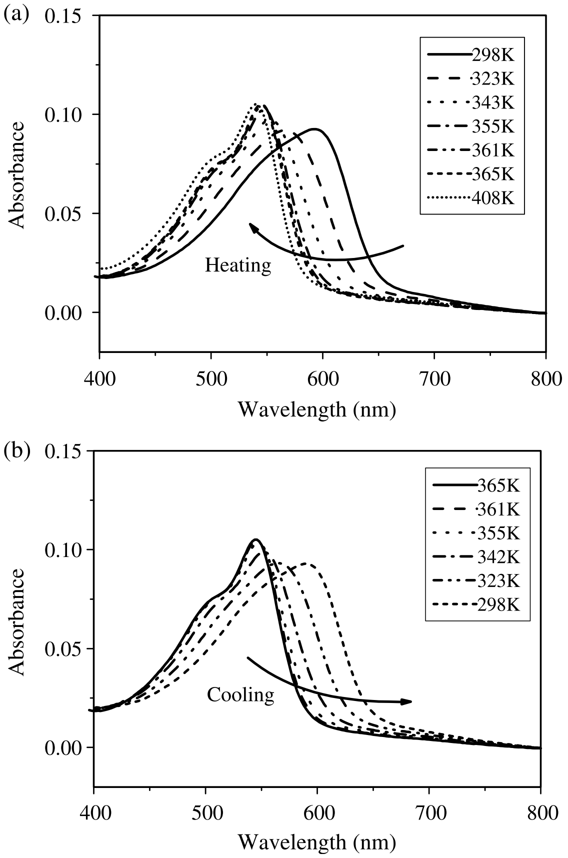


Fig. 4. Reversible colorimetric transitions of a spincoated film made from PD(4,10)diacid as thermal stimulus was imposed (a) and removed (b) at the indicated temperatures.

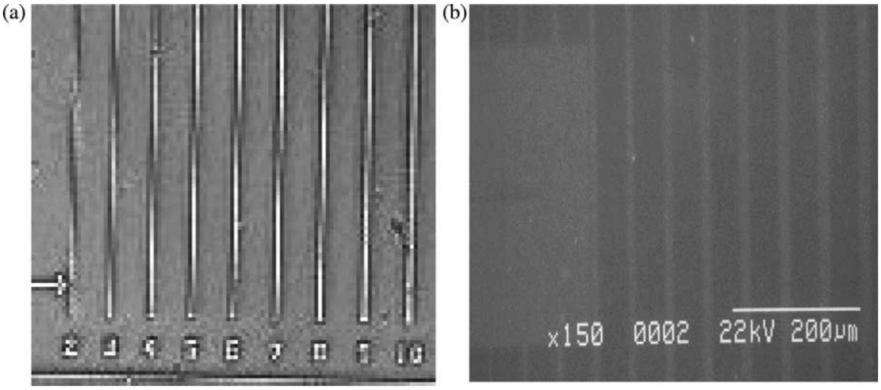


Fig. 5. LSM (left) and SEM patterns (right) on 0.18 μm thick films of D(9,8)diacid on silicon wafers after UV exposure for 3 min followed by development with chloroform for 1 min. The width of dedicated line is 2 μm (left).

these DAs selectively with a photomask upon UV exposure, high-resolution photolithographic micropatterns can be obtained [27,28]. The spincoated DA film on a silicon was irradiated with a 250 nm UV for 360 s through a photomask in a contact mode. The protected DA is soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran and acetone. Once the monomer is photopolymerized, it becomes insoluble in organic solvents. By treatment with organic solvents, monomer parts may be selectively removed, while the polymerized part remains on the substrate. Negative-tone patterns could be obtained by developing the unexposed regions with appropriate solvents. A 3 min UV exposure through a mask resulted in the patterned polymerization of PDA after development with chloroform for 1 min. As shown in Fig. 5, laser scanning and scanning electron microscopy showed the images of parallel lines. For our samples show reversible color changes during thermal cycles, we can easily obtain multicolor pattern by overheating the first UV exposed sample to destroy reversibility and giving a second UV exposure to unpolymerized region. This kind of pattern can be changed color to the same or different color of the background upon thermal stimulus, and is crucial for PDA's envisaged application as sensor design and optoelectronic devices.

4. Conclusions

By using terephthalic acid substituted with DA moieties in each side chains, 1,4 addition polymerization behavior and reversible colorimetric transitions can be found. The self-layered hydrogen-bonded supramolecular polymers demonstrated here offer a new design principle for reversible thermochromism of polymerizable DA units. They can be easily processed by simple spincoating method or other solution techniques and readily patterned using current lithography after development. The reversible property of these materials provides the allowance for the reversible color switching, thus expanding the scope where PDA can be realized and applied.

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