

A Soluble, Low-Temperature Thermochromic and Chemically Reactive Polydiacetylene

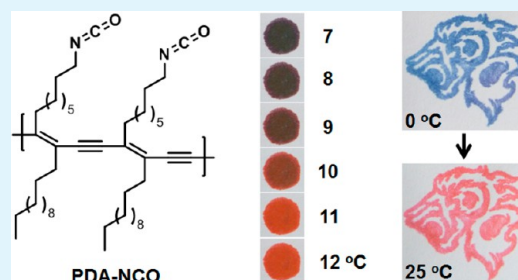
In Sung Park,[†] Hye Jin Park,[†] and Jong-Man Kim^{*,†,‡}

[†]Department of Chemical Engineering and [‡]Institute of Nanoscience and Technology, Hanyang University, Seoul 133-791, Korea

S Supporting Information

ABSTRACT: The majority of polydiacetylenes (PDAs) described to date display thermochromic transitions above room temperature. By following a strategy that employs headgroups that do not participate in strong interactions, we have designed and prepared a liquid diacetylene (DA) monomer that solidifies at a temperature near 0 °C. The isocyanate-containing DA monomer, DA-NCO, having this property does not undergo polymerization in its liquid state at room temperature. However, UV irradiation of frozen DA-NCO at 0 °C causes the instantaneous formation of a blue PDA (PDA-NCO). Interestingly, PDA-NCO was found to display a sharp blue-to-red color transition at a temperature near 11 °C. By taking advantage of its room temperature liquid-phase property, we were able to readily transfer the DA monomer to solid substrates by using common stamping and writing methods used for creating patterned PDA images. In addition, PDA-NCO dissolves in chloroform, giving a yellow solution that becomes red and simultaneously generates polymer aggregates when hexane is added. Finally, the isocyanate moieties present in PDA-NCO have been utilized to differentiate 1° from 2° and 3° amines owing to the fact that a chloroform solution of PDA-NCO undergoes a rapid yellow-to-red color change associated with an insoluble urea-forming reaction with primary amines.

KEYWORDS: polydiacetylene, thermochromism, solvatochromism, conjugated polymer, sensor



INTRODUCTION

Polydiacetylenes (PDAs),^{1–5} a family of conjugated polymers (CPs),^{6–14} are intrinsically supramolecular systems because these polymers are prepared by polymerization (UV and γ irradiation or heating) of self-assembled diacetylene (DA) monomers. The densely packed side chains within PDAs restrict conformations of the conjugated backbone of the main chain and enable the polymer to possess extensive p-orbital overlap. As a result, in many cases, PDAs have absorption maxima at ca. 650 nm that are associated with an apparent blue color. Intriguingly, PDAs undergo a distinct color change (typically blue-to-red) when their arrayed p orbitals are distorted by environmental perturbations such as heating,^{15–21} mechanical pressing,^{22,23} intercalation,^{24–26} ligand–receptor interactions,^{27–33} and exposure to organic solvents,^{34–37} currents,^{38–40} and magnetic fields.⁴¹

Since the discovery of PDAs, investigators have focused a great deal of attention on their thermochromic properties. These efforts have been designed to gain a fundamental understanding of these properties and to develop practical applications of PDAs as temperature sensors.^{42–45} The majority of thermochromic PDAs reported to date undergo blue-to-red color transitions above room temperature (typically >40 °C). In addition, most of the DA monomers, employed to prepare thermochromic PDAs, are solid at room temperature owing to the fact that they contain functional groups, which can participate in hydrogen-bonding, arene–arene, and ionic interactions. Moreover, the thermochromic initiation temper-

atures of the CPs are typically close to the melting temperatures of the corresponding monomers.^{46,47}

From the perspective of practical applications, a thermochromic PDA that undergoes a color transition at or below room temperature should be useful as a temperature indicator for goods that require refrigeration or freezing. Thus, by using these sensors, manufacturers, freight transporters, and customers would be able to judge the temperatures of goods during their storage, delivery, and display. Despite the potential significance of applications of low-temperature thermochromic PDAs, to the best of our knowledge, only one example of a CP displaying this property has been reported.⁴⁷ In the investigation described below, we have developed a new DA monomer that is a liquid at room temperature and that polymerizes to generate a PDA that undergoes a blue-to-red color change at ca. 11 °C. The low-temperature thermochromism of the new PDA can be observed by using the naked eye as well as by employing UV–visible absorption and Raman spectroscopy. Interestingly, the PDA, which contains isocyanate groups, is soluble in selected organic solvents such as chloroform. In addition, chloroform solutions of the PDA undergo a yellow-to-red color transition upon the addition of a solvent, like hexane, in which the PDA is not soluble. Moreover, because it exists as a liquid at room temperature,

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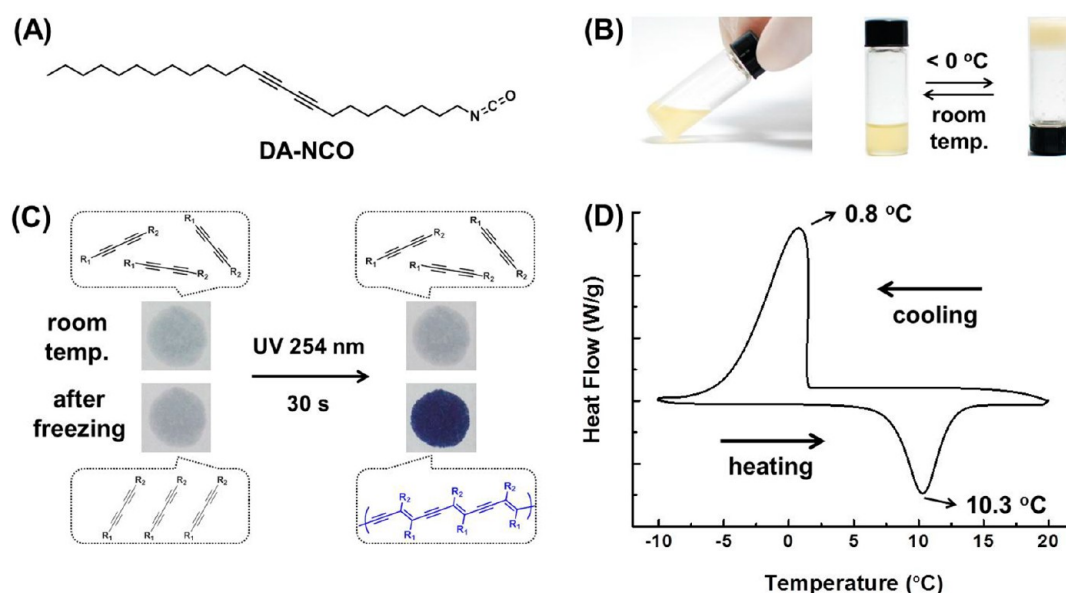


Figure 1. (A) Molecular structure of DA-NCO. (B) Photographs of DA-NCO at room temperature and $0\text{ }^\circ\text{C}$. (C) Photographs of DA-NCO immobilized on paper before and after UV irradiation (254 nm , 1 mW/cm^2) for 30 s at room temperature ($20\text{ }^\circ\text{C}$) and $0\text{ }^\circ\text{C}$, respectively. (D) DSC thermogram of DA-NCO upon application of a thermal cycle.

the DA monomer can be readily transferred to solid substrates by employing stamping and writing methods for PDA image generation. Finally, the new PDA can be used to colorimetrically distinguish a 1° from a 2° and 3° amine based on the fact that only primary amines react rapidly with its isocyanate moieties to form ureas, a reaction that induces a color change.

EXPERIMENTAL SECTION

Materials and Instruments. Oxalyl chloride, sodium azide, and anhydrous solvents were purchased from Sigma-Aldrich. 10,12-Pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals. ^1H and ^{13}C NMR spectra were recorded on a Varian UnityNova (300 MHz) spectrometer. A differential scanning calorimetry (DSC) thermogram was monitored on a DSC2010 calorimeter (TA Instruments). IR spectra were recorded on a MAGNA-IR ESP (Thermo Fisher Scientific, Inc.). Absorption spectra were recorded on an USB2000 miniature fiber-optic spectrometer (Ocean Optics). A homemade Peltier device was used to investigate the thermochromism of the PDA at low temperatures (Figure S1 in the Supporting Information, SI).

Preparation of 1-Isocyanatotetracos-9,11-diyne (DA-NCO). Oxalyl chloride (1.36 g , 10.68 mmol) was added dropwise to a solution of PCDA (2.00 g , 5.34 mmol) in 40 mL of anhydrous methylene chloride. Following the addition of several pipet drops of N,N -dimethylformamide, the solution was stirred at room temperature for 6 h . After removal of the precipitate by filtration, the filtrate was concentrated in vacuo to afford 10,12-pentacosadiynoyl chloride, which was used in the next step without further purification. Sodium azide (419 mg , 6.35 mmol) was added to a solution of the crude 10,12-pentacosadiynoyl chloride (1.00 g , 2.54 mmol) in 50 mL of anhydrous acetonitrile. The reaction mixture was vigorously stirred at room temperature for 24 h under a nitrogen atmosphere and then concentrated in vacuo. Hexane was added to the residue, giving a suspension, which was filtered. Concentration of the filtrate afforded the desired DA-NCO (897 mg , 95%). Mp: $10.3\text{ }^\circ\text{C}$. IR (CHCl_3 , cm^{-1}): ν_{max} 1324 , 1357 , 1427 , 1465 , 1712 , 2275 , 2854 , 2931 , 3020 . ^1H NMR (300 MHz , CDCl_3): δ 3.29 (2H , t , $J = 6.8\text{ Hz}$), 2.24 (4H , t , $J = 7.0\text{ Hz}$), 1.63 – 1.47 (6H , m), 1.42 – 1.20 (26H , m), 0.88 (3H , t , $J = 7.0\text{ Hz}$). ^{13}C NMR (75 MHz , CDCl_3): δ 14.73 , 19.77 , 19.80 , 23.32 , 27.09 , 28.88 , 28.98 , 29.31 , 29.41 , 29.48 , 29.54 , 29.73 , 29.98 , 30.12 , 30.24 ,

30.26 , 30.28 , 31.88 , 32.55 , 43.56 , 65.84 , 65.99 , 77.86 , 122.57 . HRMS. Calcd for $\text{C}_{25}\text{H}_{41}\text{NO}$: m/z 371.3188 . Found: m/z 371.3186 .

Preparation of 1,1-Diethyl-3-(tetracos-9,11-diyne-1-yl)urea (DA-Urea). Diethylamine (1.67 mL , 16.78 mmol) was added dropwise to the solution of DA-NCO (300 mg , 0.84 mmol) in anhydrous methylene chloride (3 mL). The mixture was stirred at room temperature for 2 h . The solvent and unreacted amine were removed in vacuo to afford the desired DA-Urea (350 mg , 97%). IR (KBr , cm^{-1}): ν_{max} 1039 , 1097 , 1198 , 1279 , 1376 , 1406 , 1459 , 1536 , 1627 , 2853 , 2924 , 3348 . ^1H NMR (300 MHz , CDCl_3): δ 4.28 (1H , s), 3.29 – 3.19 (6H , m), 2.24 (4H , t , $J = 6.8\text{ Hz}$), 1.53 – 1.47 (6H , m), 1.42 – 1.26 (26H , m), 1.14 (6H , t , $J = 7.0\text{ Hz}$), 0.88 (3H , t , $J = 6.6\text{ Hz}$). ^{13}C NMR (75 MHz , CDCl_3): δ 14.42 , 14.67 , 19.71 , 19.73 , 23.24 , 27.47 , 28.85 , 28.90 , 29.28 , 29.40 , 29.56 , 29.65 , 29.75 , 29.90 , 30.03 , 30.18 , 30.20 , 30.95 , 32.47 , 41.35 , 41.65 , 65.79 , 65.85 , 77.91 , 78.03 , 157.86 .

Colorimetric Response to Amines. To a chloroform solution (1.0 mL) containing PDA-NCO (1.0 mg) was added a chloroform solution (1.0 mL) of amine (10 mM), and the resultant mixture was analyzed by spectroscopic methods [UV–visible, Fourier transform infrared (FTIR), dynamic light scattering (DLS), etc.] after 5 min of incubation. The amines tested were n -octylamine, N,N -diethylamine, and triethylamine, respectively.

Preparation of Polymerized DA-Urea. DA-Urea powder (50 mg) was ground and polymerized with UV irradiation (254 nm , 1 mW/cm^2) for 1 h at $-5\text{ }^\circ\text{C}$. The polymerized DA-Urea was purified by removing unreacted monomers using a cotton-filled syringe filter with hot ethyl acetate. The residual red precipitate was extracted with hot chloroform, and the organic solvent was concentrated in vacuo to afford poly(DA-Urea) (23 mg , 46%).

RESULTS AND DISCUSSION

The DA monomer DA-NCO (Figure 1A) was prepared by using a two-step process involving conversion of PCDA to the corresponding acid chloride by treatment with oxalyl chloride followed by reaction of the chloride with sodium azide. In contrast to DA monomers that contain amide and arene moieties, which are solids at ambient temperatures, DA-NCO, which possesses an isocyanate headgroup, is a liquid at room temperature. This phenomenon is likely a result of the fact that attractive forces between isocyanate headgroups in DA-NCO

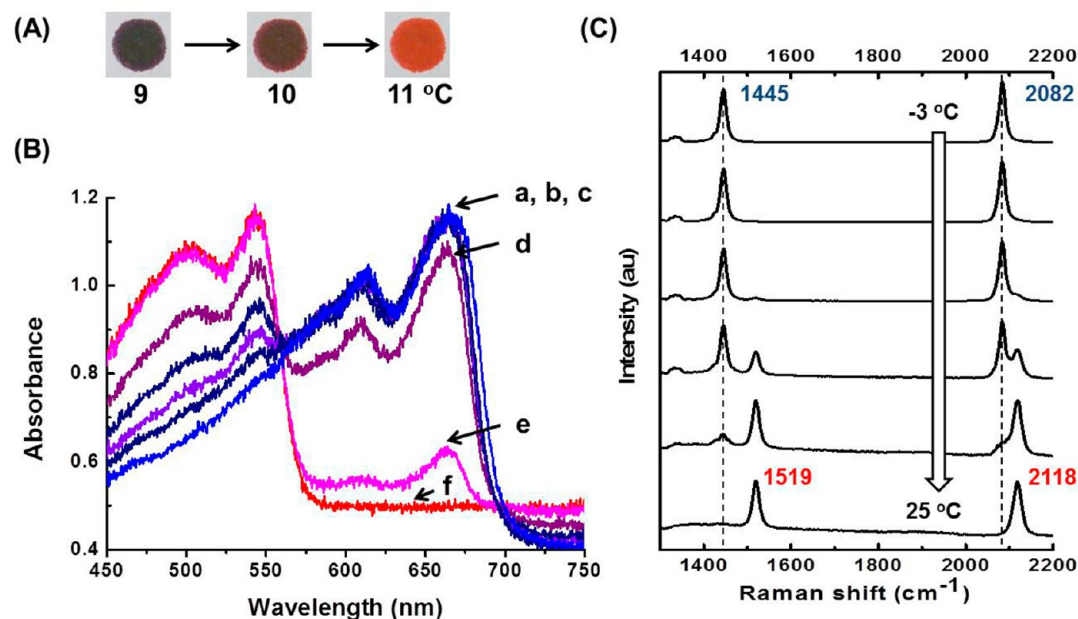


Figure 2. (A) Photographic images of polymerized DA-NCO at 9, 10, and 11 °C. (B) Visible absorption spectra of PDA-NCO at 7 (a), 8 (b), 9 (c), 10 (d), 11 (e), and 12 °C (f). (C) Raman spectroscopic monitoring of the blue-to-red color transition with gradual heating from -3 to $+25$ °C.

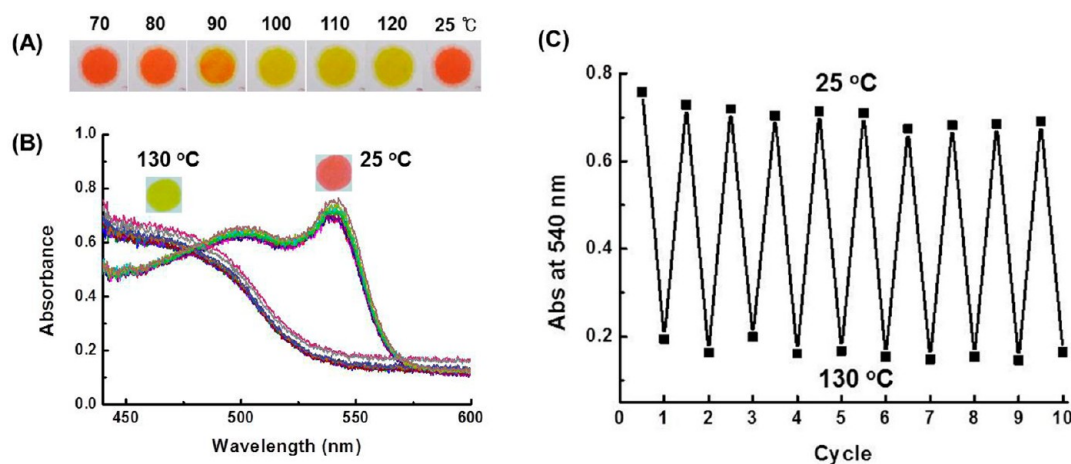


Figure 3. (A) Photographic images of a paper immobilized with polymerized DA-NCO at various temperatures. (B) Absorption spectra of the reversible red-to-yellow color transition of PDA-coated paper upon being subjected to thermal cycles ($130 \leftrightarrow 25$ °C). (C) Plots of the absorption intensity at 540 nm as a function of the thermal cycles ($130 \leftrightarrow 25$ °C).

are not strong. Solidification of a liquid DA-NCO was observed to occur when it was placed in a freezer (Figure 1B).

Irradiation of the solid sample of DA-NCO, formed by standing in a freezer at -15 °C, with a hand-held laboratory UV lamp (254 nm, 1 mW/cm²) results in polymerization to form the corresponding PDA (PDA-NCO). Because solid-state polymerization of DA-NCO at low temperatures is interesting, the phenomenon was investigated in greater detail. For this purpose, a small-scale Peltier device was fabricated (Figure S1 in the SI) and used to control the surface temperature, which was monitored by using a real-time probe thermometer. A small amount of the liquid DA-NCO was applied to an unmodified paper immobilized on the top of the Peltier device. Irradiation of the DA-NCO immobilized paper with a 254 nm hand-held laboratory UV lamp (1 mW/cm²) at room temperature did not induce a noticeable color change associated with PDA formation (Figure 1C, top). In contrast, a solidified DA-NCO sample formed by lowering the temperature of the sample to

below 0 °C underwent a significant blue-color-forming change upon UV irradiation (Figure 1C, bottom), indicative of the formation of PDA supramolecules. Efficient polymerization of DA-NCO observed in the solid versus liquid state of DA-NCO indicated that the monomer was randomly distributed in the latter state and not aligned properly for UV-irradiation-induced formation of the CP. Lowering the temperature below the freezing point of the monomer caused the self-assembly of DA-NCO molecules and, as a result, enabled PDA generation upon UV irradiation. Monitoring DA-NCO by using DSC revealed that it underwent a freezing transition at 0.8 °C and a melting transition at 10.3 °C (Figure 1D).

In Figure 2A are shown photographs of polymerized DA-NCO at three different temperatures. Through inspection of these images, it is clear that the dark blue of the PDA (PDA-NCO) becomes purple at 10 °C and eventually is transformed to red at 11 °C (see also movie clip 1 provided in the SI). The low-temperature, thermochromic behavior of PDA-NCO is

further evidenced by using absorption spectroscopy (Figure 2B). No significant spectral changes are observed to take place below 9 °C (Figure 2B, a–c) but the absorbance at 650 nm begins to decrease when the temperature rises above 10 °C (Figure 2B, d). A sharp decrease of absorption at 650 nm occurs at 11 °C (Figure 2B, e), and the complete disappearance of the band takes place at 12 °C (Figure 2B, f). The blue-to-red color transition, observed at ca. 11 °C, is very close to the melting temperature of the monomer DA-NCO (Figure 1D).

The temperature-dependent thermochromic behavior of PDA-NCO was also probed by using Raman spectroscopy. As seen by inspection of the spectra displayed in Figure 2C, bands associated with the conjugated alkyne–alkene groups in the blue-phase PDA-NCO appear at 2082 (C≡C) and 1445 cm^{-1} (C=C), respectively. Gradual heating of the PDA-NCO immobilized paper from –3 to +25 °C results in the appearance of the typical red-phase PDA alkyne–alkene bands at 2118 (C≡C) and 1519 cm^{-1} (C=C), respectively. The relative intensities of the Raman bands corresponding to the red phase of PDA-NCO increase as the temperature of the paper increases, and the blue-phase PDA bands disappear at 25 °C. Because the color transition process is irreversible, the blue-phase PDA bands are not recovered upon cooling of the paper to 0 °C. It should be noted that monitoring of Raman spectra at specified temperatures is technically difficult. Consequently, the spectra displayed in Figure 2C were recorded first at –3 °C and then at various times as the temperature of the sample rose to 25 °C. Thus, it is believed that Raman spectra between 12 and 25 °C are almost identical because most of the blue-phase PDAs should be transformed to red counterparts in this temperature range.

In addition to undergoing a low-temperature blue-to-red color transition, PDA-NCO displays red-to-yellow thermochromic behavior at high temperatures. The temperature-induced color response of PDA-NCO on paper is seen by viewing the images displayed in Figure 3A. Red-colored PDA-NCO undergoes a red-to-yellow colorimetric transition at 100 °C. The red color of the printed PDA-NCO image is reformed when the paper is cooled to 25 °C, indicating that the red-to-yellow color transition is reversible. Complete colorimetric reversibility (red–yellow) takes place between 25 and 130 °C (see also the movie clip 2 provided in the SI). In Figure 3B are shown absorption spectra of red and yellow PDA-NCOs upon exposure to thermal cycles. It is clear from viewing the spectra that the shifts in the absorption bands are reversible and that no loss takes place in the original intensities during repeated heating and cooling cycles. A plot of the absorbance at 540 nm as a function of thermal cycles adds further evidence to the existence of complete colorimetric reversibility (Figure 3C).

A meritorious feature of the fact that the DA-NCO monomer is a liquid at room temperature is that it enables ready transfer of the monomer to solid substrates by using simple stamping and printing methods. For instance, an ordinary rubber stamp method, involving loading and softly pressing the stamp, can be utilized to transfer monomeric DA-NCO to a paper substrate. By employing a routine rubber stamp application, freezing, irradiation, and heating sequence, we were able to create images on paper, such as that of the Hanyang University logo (Figure 4A). The university logo is almost invisible after stamping with DA-NCO (Figure 4A, left), but the latent image appears when the paper is cooled to 0 °C and irradiated with UV light (Figure 4A, middle). Upon standing at ambient temperature, the generated blue image turns red (Figure 4A, right). The

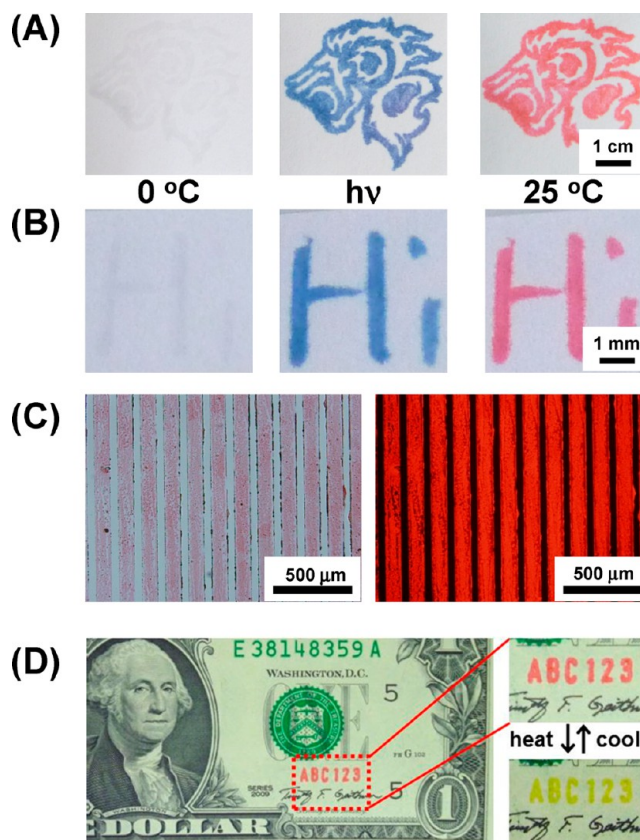


Figure 4. (A and B) Photographic images of papers immobilized with DA-NCO by stamping (A) and hand writing using a jelly-roll pen that is filled with the liquid monomer (B) at 0 °C (left), after 254 nm (1 mW/cm^2) of UV irradiation for 30 s (middle), and at room temperature (right). (C) Optical (left) and fluorescence (right) images of μ -contact-printed and low-temperature (0 °C) polymerized DA-NCO at room temperature. (D) Photograph of a one dollar banknote printed with PDA-NCO upon thermal cycles.

flexibility of the new ink system was demonstrated by its application to a pen-on-paper writing method. Accordingly, a jelly-roll pen was loaded with DA-NCO ink and then employed to handwrite the word “Hi”. As expected, subsequent subsection of the paper to a freeze–irradiation–warming process results in the generation of a blue–then–red PDA image (Figure 4B).

Microcontact printing (μ -CP) is one of the most reliable methods for the generation of micrometer-sized features on solid substrates.^{48–50} An experiment was conducted to determine if the liquid DA-NCO monomer could be transferred to a solid substrate using a patterned poly-(dimethylsiloxane) (PDMS) stamp. For this purpose, the liquid monomer was deposited on the surface of a patterned PDMS stamp. The DA-NCO-loaded PDMS stamp was then gently pressed on a glass substrate. The glass substrate was then subjected to low-temperature (0 °C) photopolymerization and room temperature thermochromic transition, giving the optical (left) and fluorescence (right) microscopic images displayed in Figure 4C. Although the optical microscopic images of the patterned PDA-NCOs are not extremely clear, the corresponding fluorescence microscopic images are sharp, thus confirming that micrometer-sized PDA patterns displaying red-phase fluorescence are produced. Attention next was focused on the application of the colorimetrically reversible PDA-NCO as a potential counterfeit-preventing material for banknotes. To

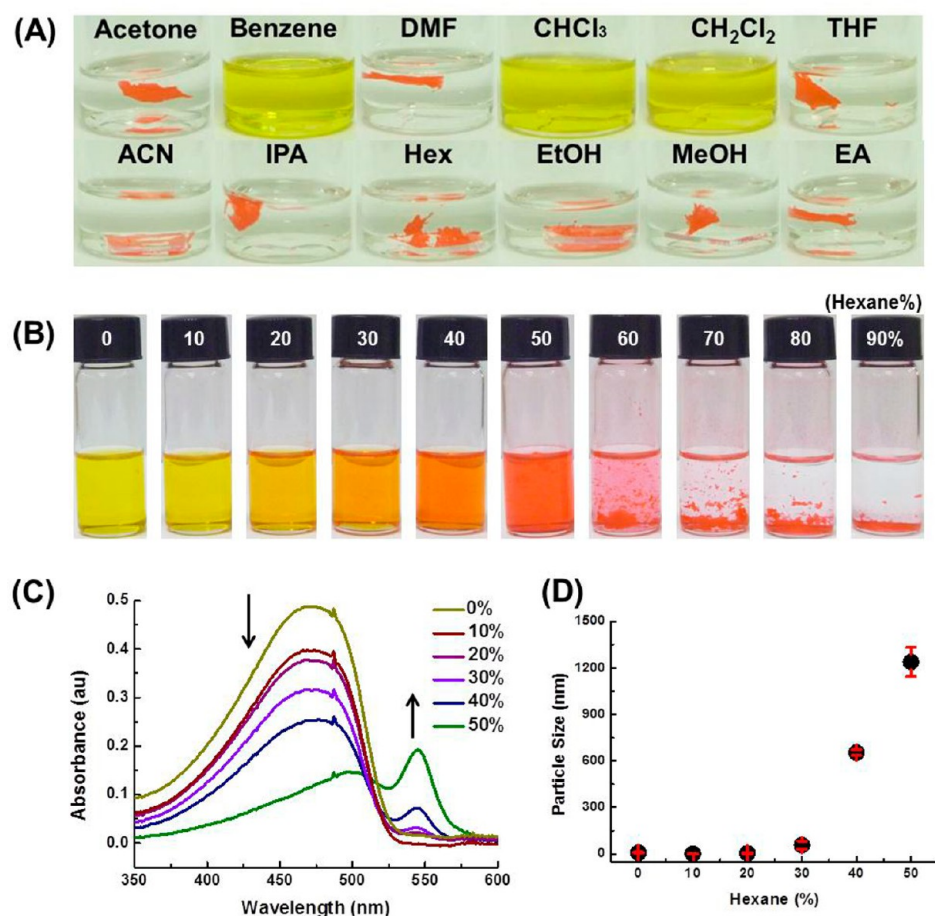


Figure 5. (A) Photographs of vials containing polymerized DA-NCO in various solvents. (B) Photographs of vials containing polymerized DA-NCO (1 mg/mL) in chloroform–hexane mixtures with different hexane contents. (C and D) UV–visible spectra (C) and particle sizes (D) reflecting the effect of varying volume percentages of hexane in chloroform–hexane solutions.

accomplish this, a red PDA-NCO image (Figure 4D) was created on a one-dollar bill by printing with DA-NCO. The bill was then subjected to UV-induced polymerization at 0 °C and heated to 25 °C. The red color of the PDA image at room temperature transformed to a yellow color when the banknote was placed on a hot plate (130 °C). A reverse yellow-to-red colorimetric transition took place upon removal of the note from the hot plate. The reversible thermochromic transitions can be repeated numerous times (>100 times) without loss of color contrasts.

PDA-NCO, derived from the isocyanate-containing DA monomer DA-NCO, is soluble to varying extents in selected organic solvents such as chloroform, dichloromethane, and benzene (Figure 5A). For instance, the polymer is soluble in hot benzene and dichloromethane, but it forms aggregates when these solutions are cooled to room temperature (Figure S2 in the SI). In addition, a yellow-to-red color transition occurs upon aggregation. In contrast, a chloroform solution of PDA-NCO retains its yellow color with no precipitation occurring upon prolonged storage (7 days) at room temperature. The addition of a solvent like hexane, in which the polymer is not soluble, to the chloroform solution results in precipitation of the polymer with a gradual color change from yellow-to-orange-to-red as the amount of hexane is increased (Figure 5B). In Figure 5C are shown absorption spectra of PDA-NCO in hexane–chloroform solutions containing varying volume percentages of hexane. The observation that a red shift

of the absorption maximum from 470 to 545 nm takes place upon the addition of increasing amounts of hexane shows that a solvent in which PDA-NCO is insoluble induces a chromic transition. It should be noted that reliable spectroscopic data could not be obtained when the solution was greater than 50% (v/v) content owing to the occurrence of severe aggregation. The particle size of PDA-NCO, measured by using a DLS method, is found to be ca. 8 nm in pure chloroform. The particle size of the polymer is found to increase to 57 nm in 30% hexane–chloroform and to 650 nm in 40% hexane–chloroform (Figure 5D). A further increase of the hexane content to 50% results in generation of the micrometer-sized (1.2 μm) polymer particles. No attempt was made to measure the particle size in solutions containing greater than 50% hexane because of polymer precipitation.

The “insoluble solvent”-induced red shifts observed by the addition of hexane to chloroform solutions of PDA-NCO parallel those reported with other soluble PDAs derived from urethane-substituted DA monomers. Thus, it appears that the side chains of the polymer in a “good” solvent can rotate to bring about maximum utilization of the entropic effects. The addition of an “insoluble solvent” like hexane causes aggregation of the polymer as a likely consequence of restriction of free rotations of side chains, which enables effective overlap of p orbitals of the conjugated moieties responsible for the red shift in the absorption spectra.

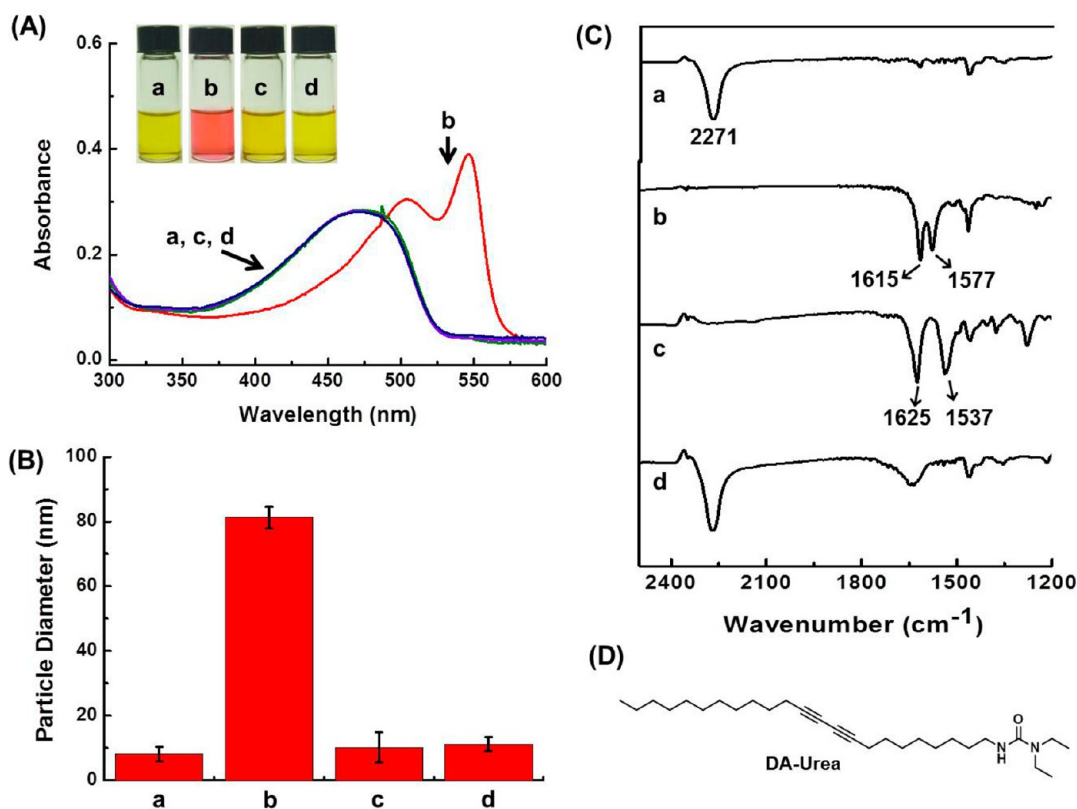


Figure 6. UV-visible absorption spectra (A) and particle size (B) of chloroform solutions containing PDA-NCO (a) in the presence of *n*-octylamine (b), diethylamine (c), and triethylamine (d), respectively. The inset in Figure 6A contains photographs of the corresponding PDA-amine solutions (PDA, 0.5 mg/mL; amine, 5 mM). (C) FTIR spectra of PDA-NCO (a) and after treatment of *n*-octylamine (b), diethylamine (c), and triethylamine (d), respectively. (D) Structure of an independently prepared urea group containing DA from DA-NCO and diethylamine.

Studies were carried out to determine if the chemoselective reactivity of isocyanate groups present in PDA-NCO and the solubility of the polymer in organic solvents could be used advantageously in the design of chemically selective sensors, in particular one that can be employed to distinguish between primary versus secondary and tertiary amines. To evaluate the feasibility of this approach, chloroform solutions containing PDA-NCO were individually treated with primary, secondary, and tertiary amines. Interestingly, the yellow color of the polymer solution changes to red upon the addition of a solution of the primary amine, *n*-octylamine, or *n*-propylamine (final concentration, 0.5 mg/mL; Figures 6A and S3 in the SI). In contrast, no color change takes place when either *N,N*-diethylamine or *N,N,N*-triethylamine is added to the polymer solution under identical conditions. These observations indicate that the isocyanate-containing PDA-NCO can serve as a primary amine colorimetric sensor. The amine-selective colorimetric changes described above were also monitored by using UV-visible spectroscopy. A red shift of the absorption maximum from 465 to 550 nm occurs when PDA-NCO is mixed with the primary amine, while no spectral changes take place when the secondary or tertiary amine is utilized (Figure 6A). Aggregate formation in the primary amine-treated polymer solution was demonstrated by determining particle sizes using the DLS method. As seen by inspection of the graph in Figure 6B, the diameter of the polymer increases approximately 10 times in the presence of primary amine. In contrast, only a negligible size increase takes place in the secondary or tertiary amine-treated sample.

Decisive information on the primary amine-selective colorimetric change was derived from a comparison of their FTIR spectra (Figure 6C). The isocyanate group of the polymerized DA-NCO shows a strong absorption at 2271 cm⁻¹ (Figure 6C, a). A complete disappearance of the isocyanate peak was observed with the sample treated with *n*-octylamine with the appearance of two absorptions at 1615 and 1577 cm⁻¹ (Figure 6C, b). The peaks at 1615 and 1577 cm⁻¹ are typical of dialiphatic hydrocarbon-substituted ureas.⁵¹ Thus, the new peaks produced are most likely associated with the rapid urea-forming reactions between the isocyanate groups and primary amines. It is believed that rapid transformation of the isocyanate groups in PDA-NCO to the corresponding urea moieties leads to a decrease in the solubility of the polymer, resulting in red-color-associated aggregate generation. Interestingly, the secondary amine (diethylamine) also was found to react with the isocyanate moieties in the polymer and form urea groups (Figure 6C, c). To confirm the formation of urea groups from the secondary amine reaction, the DA-Urea shown in Figure 6D was independently prepared from DA-NCO and diethylamine. PDA was readily prepared by UV irradiation of self-assembled DA-Urea, and a FTIR spectrum was recorded. As displayed in Figure S4 in the SI, the two urea carbonyl stretching bands observed with the polymerized DA-Urea are almost identical with those shown in Figure 6C (c). In addition, the polymerized DA-Urea was found to be soluble in chloroform, and a yellow solution was obtained. Thus, the soluble nature of the product from the reaction between PDA-NCO and diethylamine is responsible for the yellow solution in

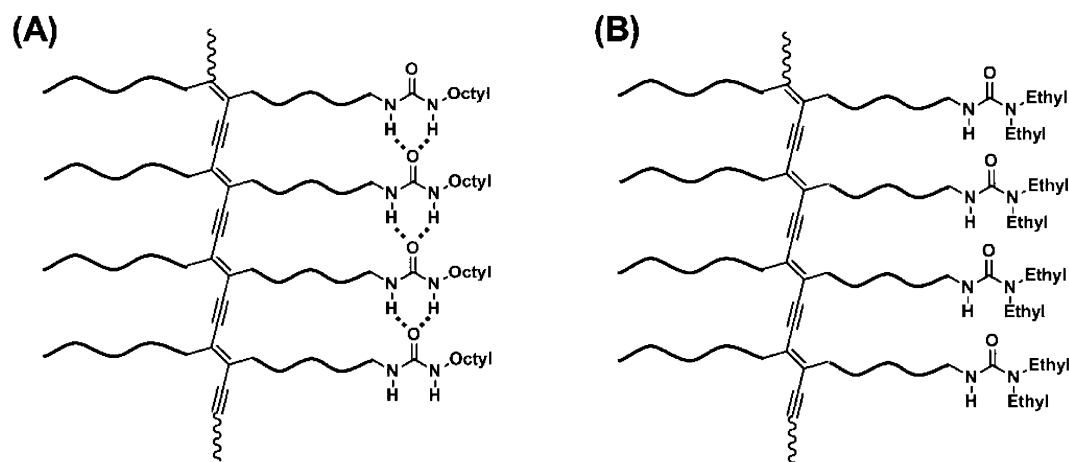


Figure 7. Schematic representation of urea-containing PDAs derived from DA-NCO and *n*-octylamine (A) and diethylamine (B).

Figure 6A (inset). In comparison, tertiary amines are unreactive with isocyanates (Figure 6C, d).

The solubility differences observed between the primary and secondary amine adducts can be rationalized in terms of hydrogen-bonding capability. In the case of a primary amine, the generated urea groups can form extensive hydrogen-bonding interactions, as shown in Figure 7A, and this makes the resulting polymer insoluble in chloroform. In contrast, the secondary-amine-derived urea-containing polymer is not capable of strong hydrogen bonding as much as the primary amine adduct, with only one hydrogen-bondable proton source (Figure 7B). In addition, the bulky substituents disfavor the formation of efficient hydrogen-bonding interactions for the secondary-amine-derived polymer.

CONCLUSIONS

The studies described above have led to the development of a PDA that displays low-temperature thermochromism. The isocyanate-containing DA, DA-NCO, was observed to be liquid at room temperature, and it solidifies at ca. 0 °C. UV irradiation of DA-NCO in its solid state results in generation of the blue PDA, PDA-NCO, that undergoes a sharp blue-to-red color transition at ca. 11 °C. The room temperature liquid-nature DA-NCO was advantageously employed to create patterned PDA images on solid substrates by using stamping and writing methods. Interestingly, PDA-NCO is soluble in chloroform. The addition of hexane, a solvent in which it is not soluble, to a chloroform solution of PDA-NCO induces a significant red shift. Finally, the isocyanate-containing polymer was found to display a yellow-to-red chromic transition with formation of polymer aggregates upon exposure to a primary amine solution. It is believed that the strategy described above, which is based on weak headgroup interactions in both the DA monomer and resulting PDA polymer, should be useful in the design of new low-temperature thermochromic PDAs.

ASSOCIATED CONTENT

Supporting Information

Photographs of a Peltier device, time-dependent aggregation behaviors of PDA derived from DA-NCO in benzene, dichloromethane, and chloroform, UV-visible spectra, FTIR spectrum of DA-urea, ¹H and ¹³C NMR spectra of DA-NCO, and movie clips. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jmk@hanyang.ac.kr.

Notes

The authors declare no competing financial interest.

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