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Characterization of ladder-type polydiacetylene exhibiting reversible thermochromism with wide temperature range

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Abstract : Thin film of ladder-shaped polydiacetylene (PDA) is fabricated by photo-polymerization of bis(diacetylene) monomer, LDA with a phenylenedicarbamate. The polyLDA exhibits thermochromism in the wide temperature range. The analyses by IR and XRD suggest that conformation of alkyl chains induces the torsion of PDA resulting in the thermochromism. The reversibility can be explained by the fact that packing between dicarbamate

moieties prevents from a drastic change. The blended film with polystyrene exhibits the similar thermochromism as that of polyLDA.

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Keywords : Conjugated polymers; Optically active materials; Self-assembly; Stimuli-responsive materials.

INTRODUCTION

The stimuli-responsive chromic materials have attracted much interests^[1-4]. These materials could provide the signal to inform the environment status, and are applied to the colorimetric indicators^[5-7]. Polydiacetylenes (PDAs), comprised of alternating ene-yne structure, are an intriguing class of color change materials, and have been investigated as potential colorimetric sensors. PDAs shows absorption in the range from 500 to 700 nm, and exhibits drastic color change from blue to red upon exposure to various stimuli such as heat, mechanical stress,

change of chemical environment, etc^[8-16]. According to the first principles calculations, this transition is related to the formation of torsional isomers with a twist of the lateral groups^[17]. It is well-known that the blue to red transition is not reversed when the external stimulus is removed in many cases, which prevents PDAs-based sensors from the repeated utilizations. In order to achieve reversible colorimetric transition, chemical modifications of DA monomers to induce the interaction between head groups in the side chains have been carried out (refs). Many sensors based on the reversible chromic materials have been reported by Kim's group^[18-22].

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Meanwhile, ladder-type PDA materials have also been investigated extensively due to the ability for constructing nano-scale insoluble frameworks^[23-26], such as tube, wire, sheet and so on, where the resulting morphology is dependent on the aggregated structure of monomer. As well as the structural studies for ladder-type PDA materials, their chromic nature has been investigated. For example, Ampornpun et al. reported the color changeable ladder-type PDA^[27]. In their report, it is assumed that oligomethylene-spacer between two hydrophilic amide groups on PDA side chains affects thermochromic reversibility. With even number of methylene spacers, complete reversible thermochromic behaviors are observed, but with odd number, partially reversible or irreversible. This odd-even effect was speculated to be resulted from the combination of appropriate hydrogen bonds and hydrophobic packing of alkyl chains. More recently, Lee et al. reported a new type of PDA, (Bis-PDA-Ph) with thermochromic reversibility, in which two PDA moieties are connected via *p*-phenylenegroup^[28]. According to the theoretical simulation, reversibility is explained by the existence of unique hydrophobic interactions between alkyl chains as well as π - π interactions between aryl groups. In this material, the wide temperature range of 20 to 120°C is observed for the color change. There is still room for improvement of temperature range (especially lower temperature region).

Hitherto, no experimental evidences such as spectroscopic data are presented to justify the as-

sumption or simulation. It is of importance to conduct the structural analyses in order to elucidate the relationship between the color and structure.

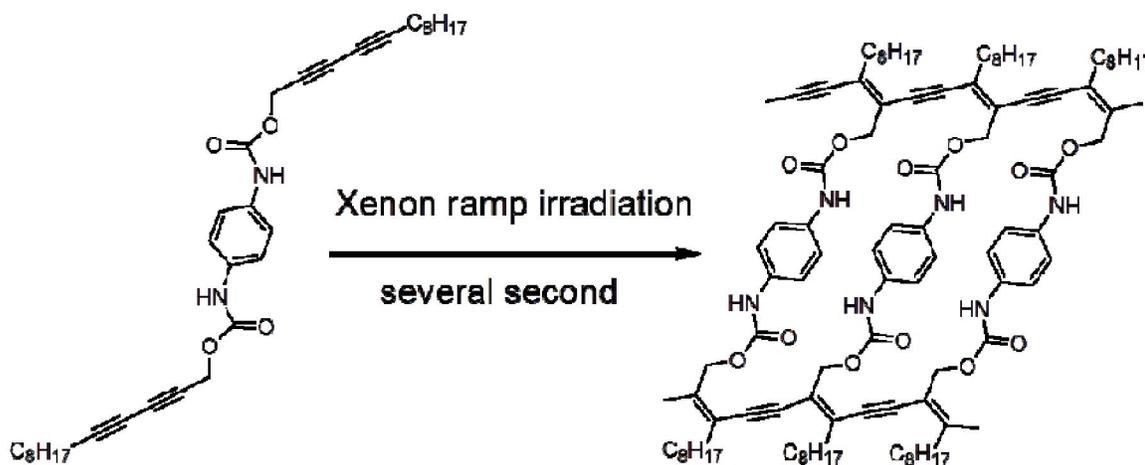
In this paper, we report the novel ladder-type PDA materials with reversible thermochromic nature in the wide temperature range from -60 to 150 °C. Thin films of bis(alkyldiacetylene) monomer, LDA, with phenylenedicarbamate core (scheme 1) were fabricated via wet processes, and irradiated with Xenon lamp to obtain the ladder type polymers. The relationships between chromic behavior and structural changes of polyLDA were clarified by variable-temperature UV-vis, IR and two-dimensional X-ray diffraction. Composite films with polystyrene were also fabricated, and it is found that the thermochromic nature with reversibility remained.

EXPERIMENTAL SECTION

Methods: Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Dry THF was obtained by distillation from sodium / benzophenoneketyl. 2,4-Tridecadiyne-1-ol was synthesized according to literature^[29].

Synthesis of 1,4-bis(2,4-tridecadiynyl) phenylenedicarbamate (LDA)

1,4-Phenylene diisocyanate (0.809 g, 4.20 mmol) was placed in a 10-mL round bottom flask under nitrogen atmosphere, and dissolved with dry THF (1 mL). To the mixture 2,4-tridecadiyne-1-ol (0.320



Scheme 1 : Chemical structure of LDA and polyLDA

g, 1.98 mmol) and dry THF (1 mL) were added, and the reaction mixture was stirred for 1 h at 60°C. The mixture was placed into hexane (30 mL). After stirring for 30 min. the precipitated solid was collected by filtration. Obtained white solid 1 was dried under vacuum. Yield was 0.743 g (1.36 mmol, 69.1%) ^1H NMR (300 MHz, CDCl_3 , 25°C, δ): 9.73 (s, 2H, NH), 7.32 (s, 4H, ArH), 4.81 (s, 4H, CH_2), 2.30 (t, $J = 7\text{Hz}$, 4H, CH_2), 1.43 (m, 4 H, CH_2), 1.31 – 1.1 (m, 20 H, CH_2), 0.82 (t, $J = 6.6\text{ Hz}$, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, CDCl_3 , δ): 153.09, 134.30, 119.47, 83.13, 71.98, 71.15, 64.63, 52.85, 31.76, 29.08, 28.91, 28.74, 28.01, 22.61, 18.85, 14.49 ppm. HRMS (FAB) m/z : $[\text{M}]^+$ calcd for $\text{C}_{34}\text{H}_{44}\text{N}_2\text{O}_4$, 544.3301; found 544.3339.

Film fabrication and photo-polymerization

Thin film of LDA was fabricated on a glass slide or aluminum plate by drop-casting a 10 mg/mL solution of LDA in THF. After drying in vacuo, the samples were subjected to exposure with Xenon lamp for 1 min. Hamamatsu photo cure 200 (11 mW/cm²) was used as a light source.

Measurements

^1H and ^{13}C NMR measurements were carried out in CDCl_3 using JEOL ECX 300 at 300 and 75 MHz, respectively. DSC thermograms were recorded on RigakuThermo plus DSC8230 at a heating or cooling rate of 10 K min⁻¹ under nitrogen atmosphere. Visible-light absorption spectra in a film state were recorded with Ocean Optics USB 4000 spectral apparatus and Nikon optical fiber BIS-VIS-NIR mounted on Nikon eclipse lv 100 POL polarized microscope. IR reflection spectra in film state were recorded with JASCO MFT-2000 microscopic Infrared spectrometer. Temperature-variable spectroscopic measurements were carried out with Linkam 10039 Hot stage was mounted on each instrument. Raman scattering measurement in a film state was conducted by Nicolet Almega XR microscopic Raman spectrometer (laser wavelength 532 nm, photon flux 600 kW cm⁻²). $2\theta/\theta$ XRD measurements were conducted on RIGAKU SmartLab (Cu K α 45 kV, 200 mA). 2D-GIXRD measurements were conducted on Bluker AXS D8 DISCOVER X-ray diffraction ap-

paratus (Cu K α , 40 kV, 40 mA, camera length was aligned by silver behenate and adjusted to 100 mm), VANTEC-500 two-dimensional CCD detector and Anton Paar TCU 150 Temperature control unit for temperature-variable measurement.

RESULTS AND DISCUSSION

Monomer synthesis and physical property

Monomer, LDA, was successfully synthesized by the addition reaction of 1,4-phenylene diisocyanate with 1,3-tridecadiyne-1-ol in a yield of 70%. The monomer was obtained as cream white powder. Chemical structure of a product was determined by ^1H -NMR (Figure S1), ^{13}C -NMR (Figure S2), and mass spectroscopies. Since LDA easily reacts under natural light, purified monomer was stored in a light-shielded bottle (aluminum-foil covered glass bottle). Without shield, the color of LDA powder gradually turned from white to purple. The solubility of LDA in common organic solvents were evaluated by simple solvent adding and ultrasonication method, and those were determined to be 20.3 and 2.9 mg/mL in THF and chloroform, respectively. As THF has hydrogen-bonding accepting property, intermolecular-hydrogen bonding still plays an important role for aggregation.

Thermal property of LDA was evaluated by the differential scanning calorimetric (DSC) measurements. Figure S3 showed the thermal history of LDA. In the first heating scan, an exothermic peak was detected at 166°C. It is thought that this peak was derived from melting. From the peak area, ΔH was calculated to 7.97 kcal mol⁻¹. After the melting, an endothermic peak was observed from around 199°C. In the cooling, no transition was observed as well as in second heating scan, indicating that endothermic peak in the first heating was resulted from the thermal polymerization of LDA. This thermo-stimulated polymerization was also observed in other diacetylene monomers^[30,31].

Photo-polymerization and properties of resulting polymers

Photo-polymerization of LDA (powder or drop-casted films) was carried out by light-exposure of

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the xenon-lamp (11 mW cm^{-2}). The color of LDA turned from white to deep purple in the powder and drop-casted film. The polymerized solids could not be dissolved in any organic solvents (such as acetone, chloroform, methanol, THF, DMF, and etc.), but the color of the solid was changed by immersion in organic solvents, and that is dependent on the solvent's character. In polar solvents such as DMF, acetone and THF, the color tends to turn to reddish one. But in soaking in methanol, almost no color change was observed. In non-polar solvents, such as toluene, hexane, the color remained deep purple. Up to now, however, the origin for color change induced by solvents is not clear. The behavior suggests that not only the polarity or hydrogen bonding ability, but also the affinity of solvent to polymer matrix plays a significant role in the solvent induced color change.

Photo-polymerization was confirmed by UV-vis absorption spectroscopy. Figure 1 shows the UV-vis spectra of a spin-coated film before and after the light-irradiation. Before irradiation, any characteristic peaks were not observed, while after irradiation, a characteristic peak was observed about 546 nm. Thus, photo-polymerization of LDA was easily proceeded with xenon light-source.

The photo-polymerization was also confirmed by laser Raman scattering experiments. Since the monomeric film underwent photo-polymerization by

the laser irradiation in measurements, scattering experiments were carried out for polymeric films only. As shown in Figure S4, the two characteristic peaks at 1508 and 2115 cm^{-1} were observed, which correspond to $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ vibrations of the typical polydiacetylene, respectively. Therefore, Photo-polymerization was proceeded in a topochemical manner (i.e., 1,4-addition reaction).

Structural information of the polymer

XRD measurements were carried out for drop-casted film of polyLDA. In order to obtain the orientational information, two kinds of XRD measurements were conducted, out-of-plane measurements (i.e., $2\theta/\theta$ scan) for the stacking structure where the axis is normal to the substrate and in-plane measurements (i.e., $2\theta/\chi/\varphi$ scan) for the stacking structure where the axis is parallel with the surface. Figure 2a shows the out-of-plane XRD pattern in a drop-casted film of polyLDA. A strong diffracting peak in a small angle region was observed at 2.98 degree, and corresponding d -spacing is 29.6 \AA . Furthermore, weak second, third, and fourth order diffractions were observed at 5.93 , 8.93 , and 12.0 degree (Figure 2a inset), respectively. These diffractions are resulted from layered-structure of polyLDA. Moreover, weak trimodal diffractions were observed from 15 to 30 degree (Figure 2a inset). As shown in Figure 2b, these trimodal diffractions were exaggerated in-plane

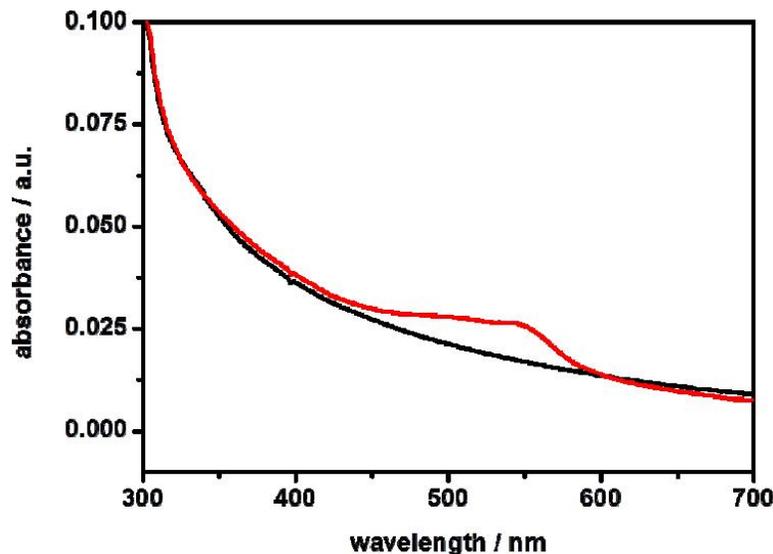


Figure 1 : UV-vis absorption spectra of spin-coated film of LDA. Black and red lines represent before and after xenon lamp irradiation, respectively

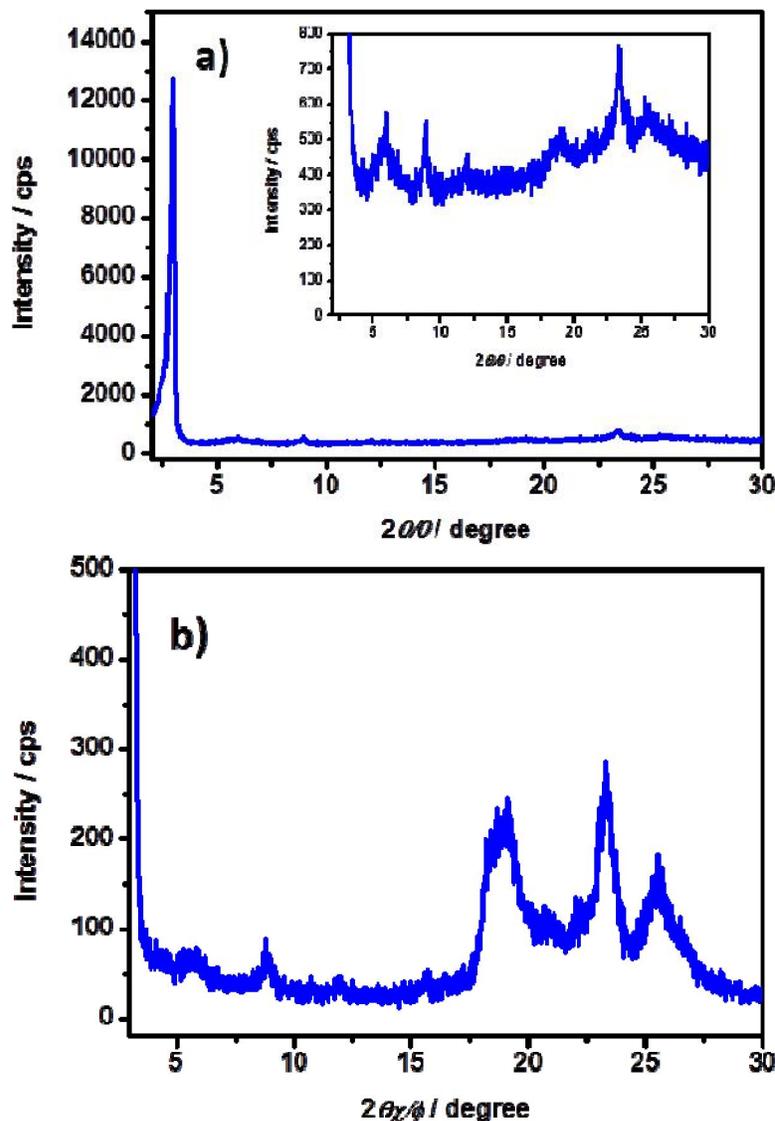


Figure 2 : Film-state X-ray diffraction (XRD) patterns of drop-casted film of polyLDA, a) out of plane XRD (inset: magnified pattern), and b) in-plane XRD

XRD pattern at 19.13, 23.26, and 25.49 degree (identical angles to those in out-of-plane). The corresponding d -spacing are 4.6, 3.8, and 3.5 Å, respectively. These results suggest that film orientation occurred even in the drop-casted film of polyLDA, and the orientational distortion also occurred. This structural anisotropy is correlated with molecular structure of LDA, and it is considered that partially oriented framework was formed in a drop-casted film after photo-irradiation, resulting from self-organization via strong hydrogen-bonding interaction and hydrophobic alkyl-chain aggregation.

Thermochromic properties

In order to investigate the temperature depen-

dencies of the color and structure, we carried out the variable-temperature (VT) measurements including UV-vis, IR, and XRD. The color change of the drop-casted polymerized film was evaluated by the temperature-variable visible absorption spectroscopic measurements. Figure 3 shows the temperature dependencies of absorption spectra. At -60°C , the bimodal absorption band was observed around 560 and 627 nm. This absorption band is known to be observed in the blue-phase for typical polydiacetylene based materials. With the increase of temperature, the wavelength at absorption maximum (λ_{max}) around 627 nm was blue-shifted, and the intensity was decreased. Consequently, this band

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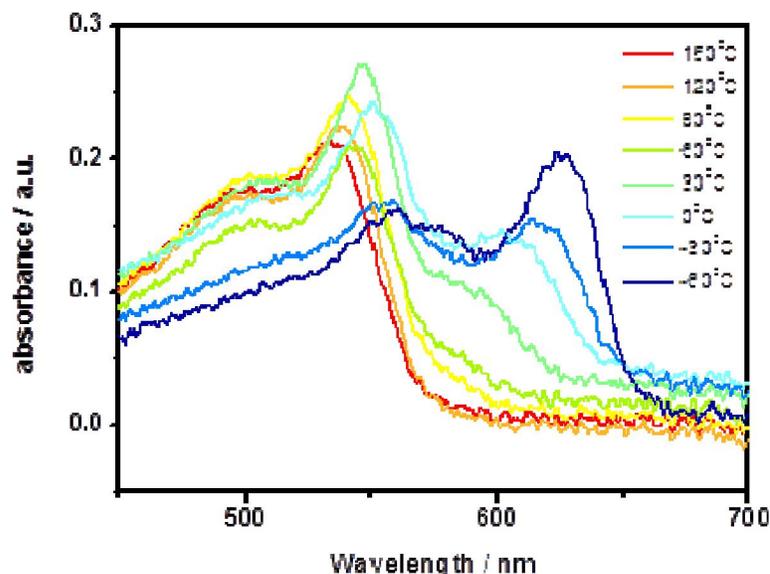


Figure 3 : Variable-temperature visible absorption spectra of drop-casted film of polyLDA

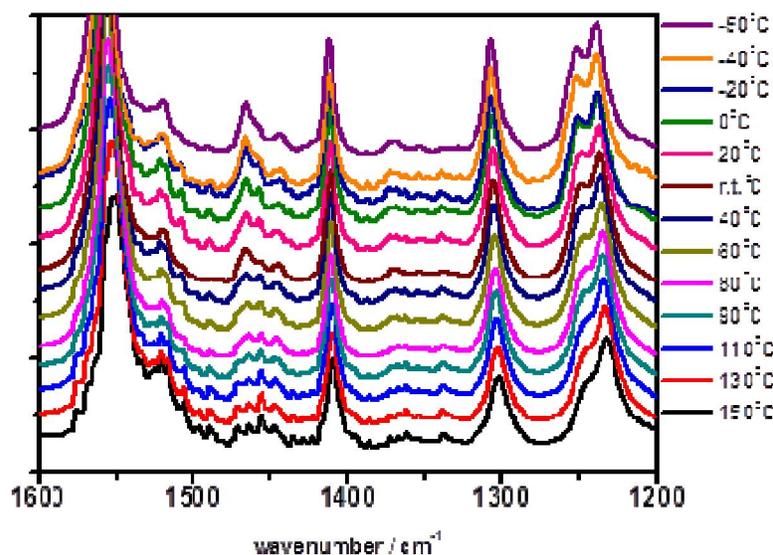


Figure 4 : Variable-temperature infrared spectram of drop-casted film of polyLDA in the range of 1200-1600 cm^{-1}

disappeared above 60°C. On the other hand, the intensity of the absorption around 560 nm was increased with the increase of temperature accompanied with the blue shift. At 80°C, λ_{max} reached 542 nm. In addition, new absorption band appeared around 500 nm. This new band is characteristic for the red-phase in typical polydiacetylene based materials. Red-phase band persisted up to 150°C. It is noteworthy that these transitions of the absorption bands were reversible in the temperature range we examined, whereas the transitions in many PDAs are irreversible as mentioned in Introduction. It is suggested that our molecular design including ladder-shaped structure, flexible alkyl chains, and

phenylenedicarbamate moiety adjacent to the conjugated backbone induces remarkable thermal stability and reversibility. Recently several thermally stable PDAs with reversible thermochromic nature have been reported. One of these materials is polydiacetylene including the carboxy and 4-carboxyphenyl groups as the side-chain substituents adjacent to the conjugated main chain^[32]. However, the reversibility diminished after the heating at 150°C. Another example is ladder-shaped phenylene ester based PDA reported by Lee et.al, namely Bis-PCDA-Ph^[28]. The temperature range window for color change in polyBis-PCDA-Ph is from 20 to 120°C.

Temperature dependency of structure

In general, it is known that the conformational change of PDA backbone induces the absorption-band shift. It is expected that the conformation is manipulated by controlling of the packing and arrangement of the substituents attached to the conjugated chain. Thus, it is important to investigate the temperature induced structural changes in order to understand the thermochromic property. Figure 4 shows temperature-variable IR spectra of the drop-casted films after polymerization in the range from 1200 to 1800 cm^{-1} . In 1420-1480 cm^{-1} , CH_2 scissoring (1466 and 1460 cm^{-1} as shoulder) and CH_3 rocking (1450 cm^{-1}) bands were observed at -50°C . The

bands at 1466 and 1460 cm^{-1} are assigned to *trans* and next to *gauche* conformer, respectively, indicating the relatively regular conformation of alkyl chain^[33,34]. With the increase of temperature, the intensity of band for *trans* conformation decreased, and a series of small bands appeared. This observation suggests that alkyl chain exhibits a variety of conformation at elevated temperature. In addition the intensity of band at 1250 cm^{-1} decreased as the temperature increased, which is difficult to be interpreted. As for other bands, both N-H, and C=O stretching bands shifted monotonously to a lower wavenumber with the increase of temperature (see Figure S5 in supporting information, and Figure S6

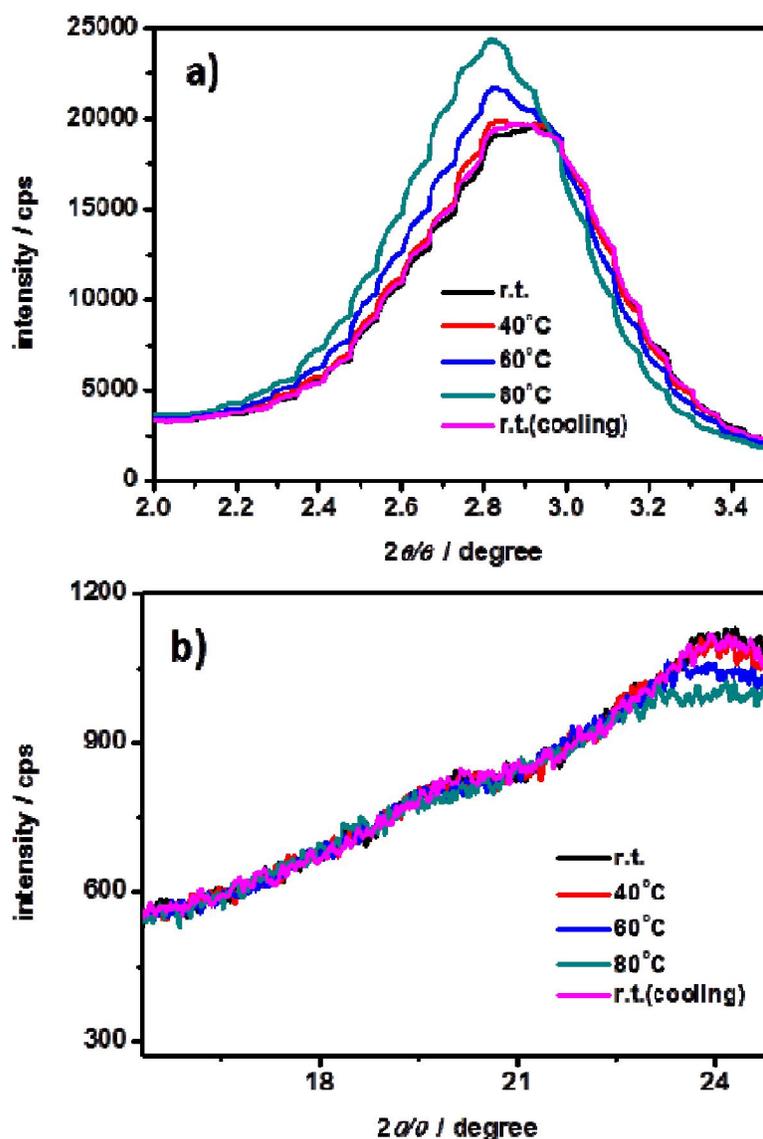


Figure 5 : Variable-temperature two-dimensional XRD profiles of drop-casted film of polyLDA. (q_z axis). a) from 2.0 to 3.5 degree, and b) from 15 to 25 degree

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shows overall VT-IR spectra), whereas C-O stretching band to a higher wavenumber. According to these results, it is considered that no drastic structural change for phenylenedicarbamate moieties occurred with the increase of temperature, although the small extent of change for hydrogen bonding strength was observed. These results suggested that order-disorder transition of alkyl chains induces the conformational torsion of PDA backbone resulting in the color change, and preservation of packing between dicarbamate moieties adjacent to conjugated chains prevented from a drastic change of arrangement of each moiety. This interpretation reasonably explains the observed reversibility.

In order to evaluate the change of arrangement via thermal stimulus, the temperature-variable two dimensional grazing incident XRD (2D-GIXRD) measurements were carried out for drop-casted film of polyLDA. Figure S7 shows the 2D-GIXRD pattern in polymer film at room temperature. In out of plane axis (*i.e.* q_z axis), five diffractions were observed which is corresponding to the out of plane XRD profiles of polyLDA. These patterns are recognized as an arch-like shape reflecting the structural distortion and/or the orientational disorder as mentioned in section 3.3. Figure 5a shows (100) diffractions along with out of plane axis at various temperatures up to 80°C. These diffractions were gradually shifted to small angle side. However, the change of d -spacing was calculated to no more than 1 Å. In addition, d -spacing became almost constant over 80°C. It is noteworthy that the change of d -spacing caused by thermo-stimulus reversible. These observations suggest that the overall layered structure in the film exhibit no drastic change of arrangement, nevertheless the order-disorder transition of alkyl side-chain is induced by heating as mentioned in

former section. In the wide angle region along with q_z axis, the intensity of diffraction at 24 degree slightly decreased with the increase of temperature (Figure 5b). Although this broadening is due to the disorder of the stacking structure of phenylenedicarbamate units, reversibility was also observed with the temperature cycle. These results strongly support the interpretation for IR measurements.

Polymer-composited film

In former sections, the thermochromic behavior of the drop-casted film of polyLDA was characterized. From the practical point of view, the thermochromic property for a free-standing composite film consisting of polyLDA and polystyrene (PSt) (weight ratio is 1:5 = polyLDA :PSt) was investigated. The composite films with ca. 25 μm thickness were fabricated by casting of THF solution on a glass-slide. Before xenon-lamp irradiation, the appearance of the composite was white opaque, indicating that phase separation between LDA and PSt occurred. After irradiation, the color turned purple resulting from photo-polymerization. Figure 6 shows the photo-images of the composite films at various temperatures. On heating the composite film on a hotplate at 80°C, the color turned to bright red, and on cooling on dry ice to deep blue. Moreover, when the composite film was placed to ambient conditions, the color was immediately returned to purple. As expected, this color change was also reversible. Therefore, it is suggested that in the phase-separated heterogeneous composite film, LDA domain possesses the similar crystalline structure to that in bulk, and is polymerized in a similar manner. In order to confirm this speculation, XRD measurements of composite films were conducted to evaluate the crys-

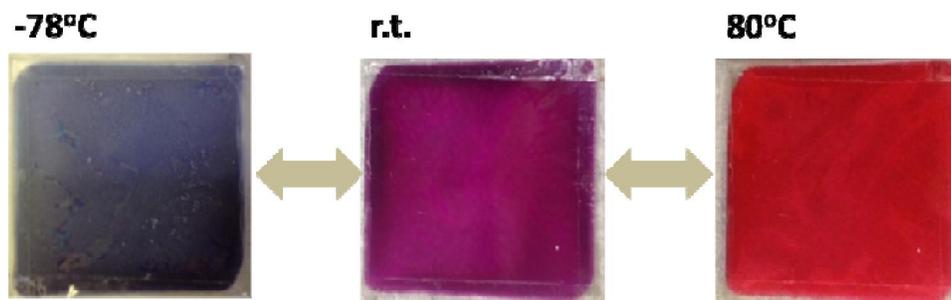


Figure 6 : Optical images of the composited film at various temperatures

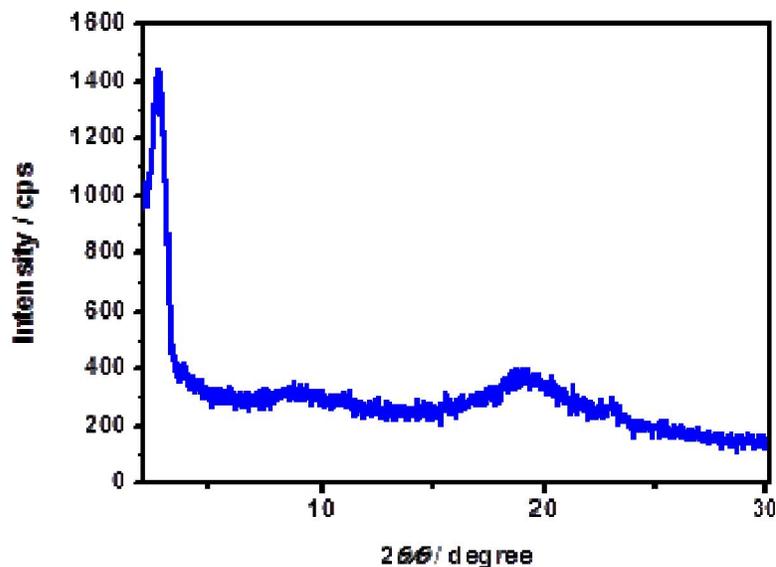


Figure 7 : Out of plane XRD pattern of the composited film

tal structure.

Figure 7 shows out of plane XRD pattern in composite film. The characteristic patterns derived both from polyLDA and PSt domains were observed. The broadened peak at 2.75 degree was almost the same as that of the polyLDA bulk sample. The broader diffractive pattern indicates that the domain size in the composite is smaller than that of bulk. Weak amorphous halos from 7 to 12 degree, and from 15 to 24 degree were derived from PSt domain. As a consequence, the composite films can be applied to thermo-sensor with repeated utilizations.

CONCLUSION

In this article, we reported the two-dimensional ordered polydiacetylene material which exhibited reversible thermochromic property in the wider temperature range. Drop-casted LDA is easily polymerized with xenon lamp-irradiation to produce ladder type of polydiacetylene derivative (polyLDA). This photo-polymerization was proceeded in a topochemical manner. According to the XRD profile and the SEM image, the polymerized film with highly ordered structure was fabricated by a simple drop-casting method. The thermochromic behavior was evaluated by variable-temperature UV-vis spectroscopy, and the origin of color change and its reversibility were explained from the data of IR and XRD measurements. Order-disorder transition of

alkyl chains activated by the thermal stimulus induces the conformational torsion of PDA backbone resulting in the color change, and preservation of packing between dicarbamate moieties adjacent to conjugated chains prevented from a drastic change of arrangement of each moiety. Reversibility can be explained by this rigidity. Finally, the free-standing composite film consisting of LDA monomer and polystyrene was fabricated, and photo-polymerization behavior and thermochromic property were investigated. Reversible thermochromic nature of the composite makes it possible to apply it to a thermochromic sensor with repeated utilization.

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