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Thermochromism of Polydiacetylenes in the Solid State and in Solution by the Self-Organization of Polymer Chains Containing No Polar Group

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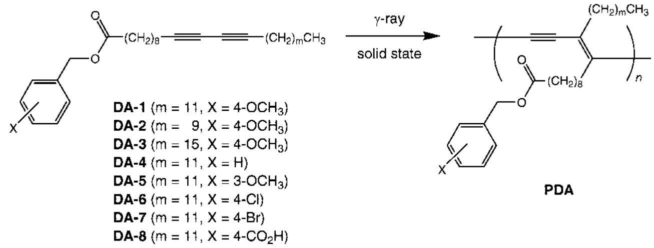
ABSTRACT: We prepared partly crystalline polydiacetylenes (PDAs) by the solid-state polymerization of substituted benzyl 10,12-alkyldiynoates followed by the dissolution of the resulting polymers in refluxing 1,2-dichlorobenzene and subsequent reprecipitation. The obtained PDAs were soluble in organic solvents, such as chloroform and tetrahydrofuran, at room temperature. They showed thermochromism not only in the bulk and polymer matrices but also in solution. The UV–vis absorption spectrum of PDAs in solutions changed depending on the temperature along with a large hysteresis. The thermochromic properties were dependent on the structure of the PDAs, that is, the length of the alkyl side chains and also the structure of the substituent on the phenyl group. We have found that aggregates are formed in the solution when the temperature decreased on the basis of the NMR and dynamic light scattering measurement results.

Introduction

Solid-state polymerization is unique method for the synthesis of the highly crystalline polymers of diacetylene and diene compounds with well-controlled regio- and stereochemical structures.[1–6] It is required that monomer molecules are stacked in the columnar structure characterized by the stacking distance of 5 Å for the process of the solid-state polymerization of these monomers.[1,7] Hydrogen bonding is useful for the design of the desired monomer stacking structure in the solid state, but such a strong intermolecular interaction often produces insoluble diene polymers and polydiacetylene (PDA) as the product. Accordingly, functional materials are fabricated in the form of bulk crystals,[8] gels,[9] mono- and multilayer membranes,[10] and any other solid materials[11] or as a dispersion including nanocrystals[12] and vesicles[13] without further polymer processing after the in-situ polymerization of the molecular-designed diacetylenic compounds.[14] In contrast to the wide range of investigations of the characteristics of PDAs in the solid state, only a limited number of soluble PDAs have been investigated in order to characterize their properties in solution.[15–18] In recent years, conjugated polymers, such as PDAs, have been one of the key materials for developing advanced systems and devices in various fields including optoelectronics due to the intrinsic electronic, photonic, magnetic, and spectroscopic properties of the polymers.[19,20]

During the course of our study on the topochemical polymerization of diene monomers, we found that amorphous or partly crystalline polymers were isolated as readily soluble polymers when highly crystalline diene polymers obtained by the polymerization were dissolved in a polar solvent at a high temperature during refluxing and were then subsequently reprecipitated.[21] A similar dissolution−reprecipitation method is also used for not only diene polymers but also for PDAs.[22] Actually, we synthesized PDAs, which are soluble in common organic solvents, without introducing any strong intermolecular interaction and polar groups as a strategy for the structural design of polymerizable monomers. The PDAs obtained from the solid-state polymerization of substituted benzyl 10,12-alkyldiynoates (Scheme 1) were highly crystalline and insoluble in organic solvents just after the polymerization, but they were readily converted into partly crystalline and soluble polymers by dissolution and reprecipitation. We also found that these PDAs showed a reversible thermochromism in the solid state and in solution. Many studies have been carried out regarding the chromism of PDAs[8–18,23–25] and other conjugated polymers[26] responsible for various external stimuli and the conditions including changes in temperature, solvent, pressure, pH, and any other physical, chemical, and biological interactions, but very few reports on the thermochromism in solution.[15–17] We now describe the thermochromism and solvatochromism of nonpolar PDAs, of which the color change is controlled by the self-organization of the PDA chains in the solid state and in solutions. The chromism is caused by the formation of PDA aggregates dispersed in solution.

Scheme 1



Experimental Section

General Procedures. The NMR spectra were recorded using a JEOL JMN A400 spectrometer in $CDCl_3$ or THF-d_8. The molecular weight of the polymers was determined in THF by gel permeation chromatography (GPC) at 38 °C using a Tosoh CCPD RE-8020 system and polystyrene standards. The FT-IR spectra were recorded using a JASCO FT/IR 430 spectrometer equipped with a JASCO Intron IRT-30 and Mettler-Toledo FP900 as infrared microscope and temperature controller, respectively. The wide-angle X-ray diffraction data were collected using a Rigaku RINT-Ultima 2100 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The thermogravimetric and differential thermal analyses (TG and DTA, respectively) were carried out using a Seiko TG/DTA 6200 in a nitrogen stream at the heating rate of 10 °C/min. The onset temperature of decomposition (T_{init}) was determined as the tem-

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perature at which 5% weight loss was observed. The differential scanning calorimetry (DSC) was carried out using a Seiko DSC-6200 at the rate of 10 °C/min. The melting and crystallization temperatures (T_m and T_c) were determined as the peak top temperature. The UV–vis spectra were recorded using a JASCO V-550 spectrophotometer equipped with a JASCO ETC-505 temperature controller in the temperature range from −10 to 50 °C for the PDA solutions. The sample was kept at each temperature for 10 min before measurement. For the measurement during the heating process, the sample solution was first cooled to −78 °C and then set to −10 °C. The UV–vis spectra of the solid PDA samples were recorded in the temperature range from 40 to 130 °C using a Nikon ECLIPSE E600 POL optical microscope equipped with a Hamamatsu PMA-11 detector and a Mettler-Toledo FP900 temperature controller. The fluorescence spectra were recorded at ambient temperature using a JASCO FP-6600 spectrometer. The dynamic light scattering (DLS) analysis was carried out using an Otsuka Electronics FPAR-1000. The THF solution of the polymer samples (ca. 1 mg/mL) was kept at each temperature for 10 min before measurement in the temperature range between 10 and 50 °C during the heating and cooling processes. The average particle size was calculated by the cummurant method. Transmission electron microscopy observations of PDA-embedded polymer films with a 300 nm thickness were carried out using a JEOL JM-2100 at a 200 kV accelerating voltage after osmium staining.

Synthesis of Monomers. The diacetylenic monomers, **DA-1** to **DA-8,** were prepared from commercially available 10,12-alkadiynoic acids (Alfa Aesar, A Johnson Matthey company Japan, Tokyo) by a reaction with the corresponding benzyl bromides.[27] A typical procedure for the preparation of **DA-1** is as follows.

To *N*-methyl-2-pyrrolidone (20 mL) in a 50 mL round-bottom flask, 1.5 g (4.0 mmol) of 10,12-pentacosadiynoic acid, 0.96 g (4.8 mmol) of 4-methoxybenzyl bromide, and 0.66 g (4.8 mmol) of potassium carbonate were added and stirred for 3 days at room temperature. The *N*-methyl-2-pyrrolidone solution of the acid was used after filtration in order to remove a small amount of the polymer contained in the commercial acid. The reaction mixture was then poured into a large amount of water. The precipitated solid was filtered and washed with methanol. The benzyl ester was isolated as a pale red powder. The yield was 82%. Spectral data are shown in the Supporting Information.

Polymerization Procedures. The polymerization was carried out in the crystalline state under γ-ray radiation in a Pyrex tube, which was degassed and sealed. γ-Radiation was carried out at a radiation dose of 200 kGy (a dose rate of 9.7–20.4 kGy/h) using ^{60}Co at the Osaka Prefecture University. The polymer was isolated by removing any unreacted monomer with acetone after the polymerization. The substituted benzyl ester polymers were dissolved in 1,2-dichlorobenzene; the solution was refluxed for 1 h and then poured into methanol to precipitate the polymer. The obtained polymers, **PDA-1** to **PDA-7**, were confirmed to be partly crystalline on the basis of powder X-ray diffraction measurements. **PDA-8** was insoluble in 1,2-dichlorobenzene under reflux conditions.

PDA-1. Yield 81%. Red powder, T_m = 129.3 °C by DSC; M_n = 5.0 × 10^4, M_w/M_n = 3.0 by GPC. ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.14 (CH$_3$), 22.71, 24.99, 28.78, 29.29, 29.43, 29.62, 29.74, 29.81, 31.96, and 34.34 (CH$_2$), 55.23 (OCH$_3$), 66.84 (CO$_2$*C*H$_2$), 113.88, 128.28, 130.00, and 159.55 (C$_6$H$_4$), 173.60 (C=O). IR (KBr): 1721 ($\nu_{C=O}$) cm^{-1}. UV (THF): λ_{max} = 464 nm; UV (diffuse reflectance): λ_{max} = 493 nm.

PDA-2. Red powder, T_m = 130.5 °C by DTA. ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.14 (CH$_3$), 22.71, 25.00, 28.78, 29.43, 29.74, 31.97, 34.36, and 35.45 (CH$_2$), 55.25 (OCH$_3$), 65.84 (CO$_2$*C*H$_2$), 113.90, 128.30, 130.00, and 159.57 (C$_6$H$_4$), 173.60 (C=O). UV (THF): λ_{max} = 461 nm.

PDA-3. Red powder, T_m = 125.9 °C by DSC; M_n = 2.6 × 10^4, M_w/M_n = 3.3 by GPC. UV (THF): λ_{max} = 462 nm.

PDA-4. Yield 28%. Red powder, M_n = 2.8 × 10^4, M_w/M_n = 3.1 by GPC. ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.13 (CH$_3$), 22.71, 24.99, 28.77, 29.27, 29.42, 29.61, 29.74, 29.80, 31.96, and 34.30 (CH$_2$), 66.01 (CO$_2$*C*H$_2$), 128.12, 128.51, and 136.15 (C$_6$H$_5$), 173.50 (C=O); UV (THF): λ_{max} = 455 nm; UV (diffuse reflectance) λ_{max} = 487 nm.

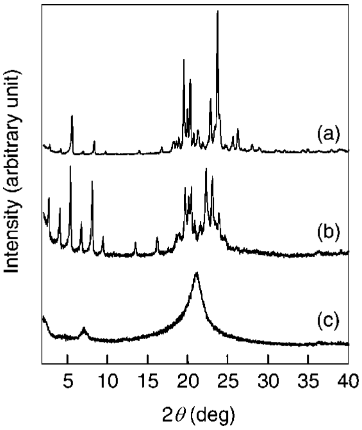

Figure 1. Wide-angle X-ray powder diffraction of **DA-1** and **PDA-1**: (a) **DA-1** monomer, (b) **PDA-1** obtained after γ-ray radiation without isolation (conversion 81%), and (c) **PDA-1** isolated after dissolution and reprecipitation.

PDA-5. Yield 34%. Red powder, M_n = 2.7 × 10^4, M_w/M_n = 2.9 by GPC. ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.14 (CH$_3$), 22.71, 24.99, 28.79, 29.43, 29.81, 31.95, 34.28, and 35.43 (CH$_2$), 55.16 (OCH$_3$), 65.86 (CO$_2$*C*H$_2$), 113.55, 120.25, 129.57 137.65, and 159.66 (C$_6$H$_4$), 173.48 (C=O). UV (THF) λ_{max} = 452 nm; UV (diffuse reflectance) λ_{max} = 487 nm.

PDA-6. Yield 38%. Red powder. ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.15 (CH$_3$), 22.71, 24.95, 28.77, 29.26, 29.43, 29.60, 29.75, 29.81, 31.96, 34.23, and 35.27 (CH$_2$), 65.19 (CO$_2$*C*H$_2$), 128.70, 129.53, 134.03, and 134.62 (C$_6$H$_4$), 173.39 (C=O). UV (THF) λ_{max} = 458 nm; UV (diffuse reflectance) λ_{max} = 487 nm.

PDA-7. Yield 42%. Red powder, M_n = 2.4 × 10^4, M_w/M_n = 2.9 by GPC. ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.15 (CH$_3$), 22.72, 24.96, 28.79, 29.27, 29.43, 29.75, 29.81, 31.97, 34.24, and 35.44 (CH$_2$), 65.21 (CO$_2$*C*H$_2$), 122.18, 129.81, 131.68, and 135.16 (C$_6$H$_4$), 173.36 (C=O). UV (THF) λ_{max} = 460 nm; UV (diffuse reflectance) λ_{max} = 486 nm.

PDA-8. Red and insoluble powder.

Preparation of PDA-Embedded Polymer Films. The embedding of PDA in polymer matrices was carried out as follows. Commercial poly(vinyl alcohol) and poly(methyl methacrylate) were used after reprecipitation. A 10 mL PDA solution (0.2 mmol/L) in THF was combined with 20 mL of an aqueous solution of poly(vinyl alcohol) (10 wt %) or a THF solution of poly(methyl methacrylate) (10 wt %), and then the mixture was cast on a Teflon plate and dried at room temperature for 3 days. An apparently transparent polymer film containing PDA was obtained.

Results and Discussion

Preparation of Soluble PDAs. PDAs were obtained by the solid-state polymerization of the diacetylene monomers, **DA-1** to **DA-8**, under γ-ray radiation and isolated as red powders with a high crystallinity and low solubility to organic solvents. The PDAs except for **PDA-8** were readily transformed into partly crystalline polymers based on dissolving in 1,2-dichlorobenzene at reflux and the subsequent reprecipitation by pouring the solution into a large amount of methanol. The partly crystalline polymers recovered after filtration and dried in vacuo were soluble in various solvents including chloroform and THF at room temperature. This differed from the limited solubility of the original polymer crystals just after the solid-state polymerization. Figure 1 shows the powder X-ray diffraction profiles of the **DA-1** monomer, **PDA-1** obtained after γ-radiation without isolation, and the recovered **PDA-1** after dissolution and reprecipitation. It was confirmed that **PDA-1** kept its high crystallinity after the polymerization, but the polymer recovered

Table 1. TG/DTA and DSC Analyses of Crystalline and Partly Crystalline PDA-1s[a]

	DTA		TG		DSC		
PDA-1	T_β (°C)	T_m (°C)	T_{init} (°C)	residue at 500 °C (%)	T_β (°C)	T_m (°C)	T_c (°C)
crystalline	70.3	136.2	336.3	19.0	61.5	131.7	101.6
partly crystalline	*b*	131.4	329.6	19.1	*b*	129.3	103.5

[a] Crystalline and partly crystalline **PDA-1**s were obtained by solid-state polymerization and the subsequent dissolution and reprecipitation processes, respectively. T_β is the crystal-to-crystal transition temperature. T_m and T_c are the melting and crystallization temperatures observed during the heating and cooling processes, respectively. The heating and cooling rates were 10 °C/min. [b] Not detected.

after the dissolution and reprecipitation processes had a lower crystallinity.

Most PDAs reported in the literature[1–4] are insoluble in organic solvents, except for a few cases in which the soluble PDA was synthesized and characterized in solutions.[15–18] This is because the structure of the PDAs in the solid includes strong hydrogen bonds and other intermolecular interactions, which are required for the construction of the ladderlike monomer molecular stacking appropriate for the solid-state polymerization in the crystals. Simultaneously, such strong interactions results in the robust structures of the obtained polymer crystals having a high crystallinity. In contrast, the monomer crystals used in the present study include only weak intermolecular interactions such as the CH/O or CH/π interaction[28] and alkyl chain packing. As a result, the obtained PDAs have a melting temperature below their decomposition temperature and are soluble in an organic solvent by refluxing. These characteristics enable us to readily fabricate the partly crystalline PDAs by the reprecipitation process, as already described. The introduction of a polar group, which can form intermolecular hydrogen bonds, results in the formation of an insoluble PDA even for the series of benzyl alkadiynoates shown in Scheme 1 in the present study. For example, the monomer including a carboxy group (**DA-8**) polymerized to give a polymer similar to the other PDAs, but the obtained **PDA-8** was insoluble even in a polar solvent under reflux conditions. Eventually, a partly crystalline and soluble polymer was not obtained for **PDA-8**.

Table 1 shows the results of the TG/DTA measurements for the crystalline and partly crystalline **PDA-1**s before and after the reprecipitation process. In the DTA curve of the crystalline **PDA-1**, two peaks were observed at 70.3 and 136.2 °C, while the partly crystalline **PDA-1** had a single endothermic peak at 131.4 °C. Based on the DSC measurements, similar results were obtained (Figure 2). In the first run of the DSC traces for the crystalline **PDA-1** before reprecipitation, an endothermic peak was observed at 61.5 °C. This is due to the crystal-to-crystal transition with a change in the conformation. Figure 3 shows a change in the temperature-controlled powder X-ray diffraction profile of the crystalline **PDA-1** isolated by removing the monomer with acetone after the polymerization. The intensity of the peaks observed at 2.36, 3.66, 5.94, 7.22, and 20.64° of 2θ values, which correspond to 37.4, 24.1, 14.9, 12.2, and 4.3 Å of *d* values, respectively, increased when the temperature increased from 20 to 90 °C, as shown in the profiles a−e. These diffraction peaks cannot be assigned because the crystal structures of **DA-1** and **PDA-1** are unknown. The diffraction profiles shown in Figure 3 indicate that this structural change is irreversible. The sharp diffractions observed at lower angles retained after cooling. This is related to the relaxation of the crystal strain that had accumulated in the crystals during the solid-state polymerization.[9c,10h,24] The **PDA-1** in the melt at 160 °C provided a broad peak, and the **PDA-1** with low crystallinity was recovered after cooling to 20 °C. The results of the X-ray diffraction experiments in Figure 3 are quite consistent with the results of the thermal analyses in Figure 2.

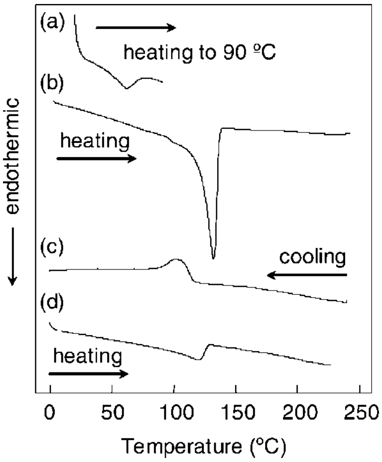

Figure 2. DSC curves of crystalline and partly crystalline **PDA-1**s: (a) first heating of the crystalline **PDA-1** from room temperature to 90 °C, (b) second heating of the crystalline **PDA-1** to 250 °C, (c) cooling and (d) heating of the partly crystalline **PDA-1**. The heating and cooling rate was 10 °C/min.

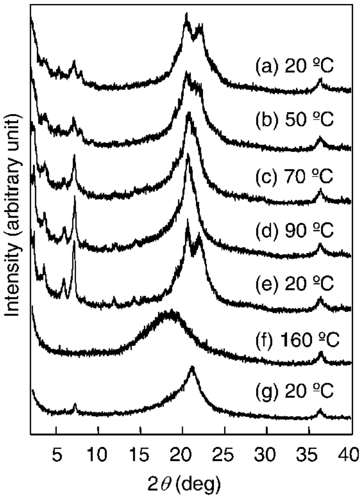

Figure 3. Powder X-ray diffraction profiles of **PDA-1**: (a−d) the crystalline **PDA-1** during the first heating from 20 to 90 °C, (e) the crystalline **PDA-1** at 20 °C (after heating to 90 °C), (f) **PDA-1** in the melt at 160 °C, and (g) the recovered **PDA-1** at 20 °C (after heating to 160 °C).

Thermochromism in the Solid State. The solid film of **PDA-1** was obtained by casting the chloroform solution on a glass plate and then drying at room temperature. Figure 4 shows the reversible change in the UV–vis absorption spectrum under temperature control in the range 40−130 °C. The red solid film at 40 °C had absorption bands consisting of a broad peak around 490 nm due to the π-conjugated system of the main chain and another sharp one at 530 nm. The broad peak gradually shifted to a lower wavelength region during the heating process from 40 to 130 °C. At the same time, the intensity of the peak observed at 530 nm decreased without any shift in the wavelength. A single broad peak was observed at 445 nm at 130 °C. The solid film changed from red to yellow in appearance. This color change was reversible in this temperature range, as shown in the spectral change observed in a cooling process. The spectral change in **PDA-1** is accounted for by the conformation change in the intra- and intermolecular interactions of the π-systems in the main chain based on the side-chain crystallinity and mobility.

Because the PDAs obtained in the present study are soluble in various solvents, they can be readily blended with other

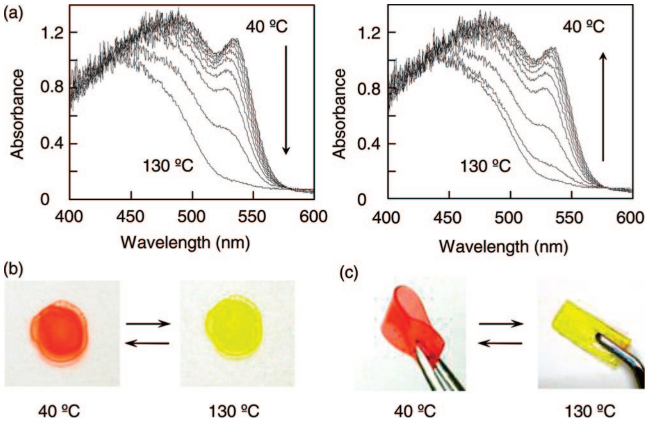

Figure 4. (a) Change in the visible spectrum of **PDA-1** in the solid state during the heating and cooling processes and (b) color change in appearance in the solid. The solid film was prepared by casting of the chloroform solution of **PDA-1** on a glass plate and dried at room temperature. The absorption spectra were determined by the transmission method. (c) Change in the color of **PDA-1** embedded in the poly(vinyl alcohol) matrix.

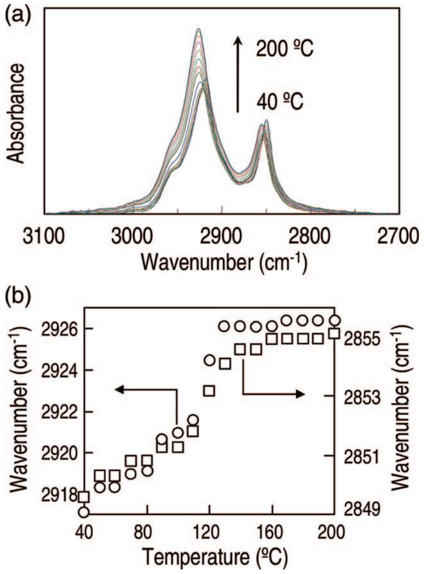

Figure 5. (a) Change in the IR spectrum (2700–3100 cm^{-1} region) of **PDA-1** in the bulk upon heating from 40 to 200 °C. The heating rate was 2 °C/min. The spectra observed with each 10 °C step are shown here. (b) Shift in the peak position of the absorption bands observed at 2850–2855 (□) and 2917–2926 cm^{-1} (○).

polymers. When **PDA-1** dissolved in THF was mixed with poly(methyl methacrylate) in THF or with an aqueous solution of poly(vinyl alcohol), transparent red films were obtained by casting and drying.[29] A reversible color change depending on the temperature was observed in the polymer matrices, as shown in Figure 4c.[22] The λ_{max} value was ca. 480 nm in the UV–vis absorption spectrum of **PDA-1** at room temperature in the polymer matrix, and it gradually shifted to 445 nm when heated. The thermochromic behavior of PDA in the polymer matrices was the same as that observed in the bulk system. The transmission electron microscopy observations confirmed the phase separation of the PDA domain from the polymer matrices.

The color change of the PDAs was expected to be related to the crystallization and melting of the long alkyl chains in the side groups.[30] Therefore, the conformational structure of the side chain alkyl group of **PDA-1** was investigated by IR spectroscopy under temperature control. Figure 5 shows the change in the absorption bands due to the C−H stretching vibration of the methylene groups in the IR spectrum of **PDA-1** in the bulk upon heating. The absorption bands observed at 2850 and 2917 cm^{-1} at room temperature linearly shifted to a higher wavenumber region according to an increase in the temperature below the T_m, at which a discontinuous change was observed. The absorption bands had constant wavenumbers (2855 and 2926 cm^{-1}) at a high temperature over the T_m. The observed IR spectrum well explains the change in the conformation of the alkyl chains from the trans zigzag structure in the crystalline state at room temperature to a random chain in the melt at a higher temperature.

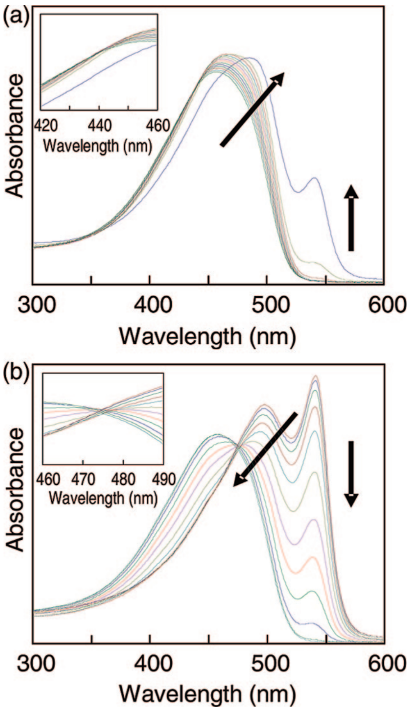

Figure 6. Change in the absorption spectrum of **PDA-1** in THF during (a) cooling and (b) heating processes with each 5 °C step in the temperature range of −10 to 50 °C. For the heating process, measurement started from −10 °C after the solution was first cooled to −78 °C.

Thermochromism in Solution. Interestingly, the thermochromism of PDA was observed not only in the solid state but also in solution. Figure 6 shows the UV–vis absorption spectra of **PDA-1** in THF. The spectrum reversibly changed depending on the temperature, similar to the thermochromism in the solid state. During the cooling process, the peak at 457 nm gradually shifted to a longer wavelength region in the temperature range between 50 and 0 °C, and then a large shift was observed that reached 485 nm at −10 °C. The peak further shifted to 498 nm by cooling in a dry ice−methanol bath. In addition, a new and sharp absorption band was observed at 540 nm below 0 °C, and its intensity increased with a decrease in the temperature. No shift was observed for the peak at 540 nm, being different from the shift in another peak in the lower wavenumber region. The sharp absorption of PDA at 540 nm is due to the organization of the polymer chains and the intermolecular interaction between the π-systems of the main chains. During the heating process, a spectral change was monitored using the solution, which was first cooled to −78 °C, as shown in Figure 6b. Clear changes in the position and the intensity of the absorption bands were observed. These spectral changes depending on the temperature were reversible, but no isosbestic point was observed during the cooling and heating processes.

In Figure 7, the λ_{max} values for the broad absorption of **PDA-1** at the lower wavelength were plotted as a function of the

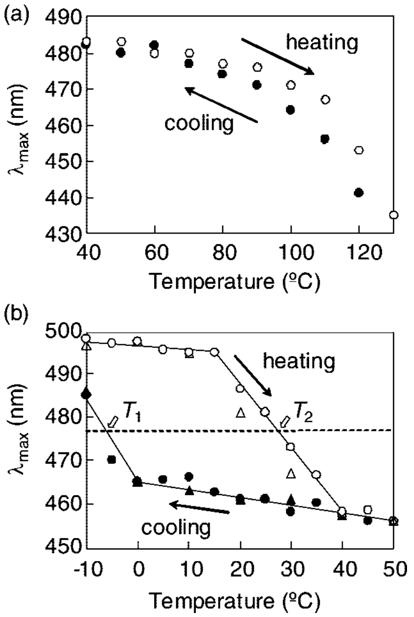

Figure 7. Change in λ_{max} value for the peak at 450–500 nm in the absorption spectra of **PDA-1** (a) in the bulk and (b) in THF during the heating and cooling processes. Circles and triangles indicate data for the first and second runs, respectively. The transition temperatures (T_1 and T_2) are defined for (b) as the temperatures at which the hysteresis curve during the heating and cooling processes is across the average of the λ_{max} values for the red and yellow solutions. The broken line shows the average of the λ_{max} values for red and yellow solutions. The data in the solution were collected at 50 °C and then cooled stepwise to −10 °C. The solution was further cooled to −40 °C for 1 h and then kept at −10 °C before the measurement during the heating process.

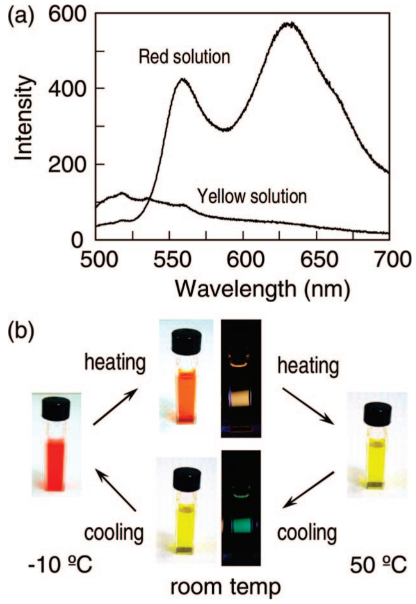

Figure 8. (a) Fluorescence spectrum of **PDA-1** in THF. The excitation wavelength was 480 nm. (b) Color change in the THF solution of **PDA-1**. Right figures at room temperature are the emission of orange and green lights from the red and yellow solutions, respectively. The excitation wavelength was 365 nm.

temperature for the bulk and solution systems. As shown in this figure, a clear hysteresis loop was observed for the THF solution of **PDA-1**, while no hysteresis was observed in the solid state. Namely, the two different solution colors were observed at room temperature, depending on the thermal history. The apparent color of the solution was yellow at 50 °C and remained around room temperature upon cooling. On the other hand, the red solution turned orange around room temperature and then changed to yellow above room temperature. These two different **PDA-1** color solutions showed different fluorescence properties as expected. The green and orange emissions were observed from the yellow and red solutions, respectively, when the excitation wavelength was 365 nm. Figure 8 shows the fluorescence spectra obtained from the yellow and red solutions. The excitation wavelength was 480 nm, at which both solutions had similar absorbances. The red solution clearly showed a high emission intensity, although the quantum yield for the red solution is low. On the other hand, very weak emission was observed from the yellow solution.

Effect of Side-Chain Structure. The effect of the polymer structure on the hysteresis loop of the absorption property in solution was investigated. The transition temperatures, T_1 and T_2, are defined as the temperatures at which the hysteresis curve during the heating and cooling processes is across the average of the λ_{max} values for the red and yellow solutions, as already shown in Figure 7, respectively. The results are summarized in Table 2. The transition temperature T_2 decreased with a decrease in the carbon number of the alkyl chain in the side chain in the order of T_2 = 34 °C for **PDA-3** (m = 15) > 28 °C for **PDA-1** (m = 11) > 26 °C for **PDA-2** (m = 9), while another transition temperatures T_1 were determined with less accuracy due to the limited temperature range for the measurement in the present study (−10 to 50 °C). The crystallinity of the PDAs probably depends on the structure of the substituents, resulting in the difference in the transition temperature. Furthermore, it was confirmed that the structure of the substituent on the benzyl group influenced the transition temperatures despite the position away from the conjugated main chain of PDA. The T_2 values decrease in the following order: T_2 = 31 °C for **PDA-7** (X = 4-Br) > 28 °C for **PDA-1** (X = 4-MeO) > 25 °C for **PDA-6** (X = 4-Cl) > 18 °C for **PDA-4** (X = H) > 4 °C for **PDA-5** (X = 3-MeO). For the system in this study, a solvent effect was also observed. The T_2 value decreased in the order of T_2 = 42 °C (1,3-dioxane) > 36 °C (2-methyltetrahydrofuran) > 34 °C (toluene) > 28 °C (THF) > below −10 °C (chloroform) for **PDA-1**. No clear relationship was observed between the dielectric constant and the T_2 value.

The solvatochromism of **PDA-1** was further investigated. In a pure chloroform solution, the color of the solution was yellow, and a single and broad absorption peak was observed at 464 nm. The temperature dependence of the spectrum in chloroform was less sensitive. The chloroform solution of **PDA-1** always showed a yellow color, which was independent of the temperature examined in the present study. **PDA-1** clearly showed solvatochromism in a mixed solvent of chloroform and hexane, as shown in Figure 9. When the ratio of hexane increased to 70%, the peak slightly shifted and the intensity of a new peak at 540 nm increased. We obtained an absorption spectrum with a maximum peak at 540 nm at the hexane ratio of 80%, similar to that observed in the THF solution at a low temperature. We concluded that the solubility and crystallinity of the PDAs are related to the transition temperatures for chromism, judging from the results of the structure and solvent dependence of the thermochromism of the PDAs.

Formation of Aggregates in the Solution. Moreover, we confirmed the formation of aggregates for the solution containing 80% hexane when the solution stood for a long time. A solution in THF with a red color was also expected to include the formation of an aggregate in solution. Therefore, we checked for the possible formation of aggregates using the NMR and DLS measurements of the red solution of **PDA-1**. In the ^{1}H NMR spectrum of **PDA-1** in THF-d_8, all the peaks due to the polymer structures were observed at room temperature, but their

Table 2. Transition Temperatures and Maximum Absorption Wavelength for UV–vis Absorption Properties of PDAs

polymer	m	X	solvent (δ, ϵ)[a]	T_1 (°C)	T_2 (°C)	λ_{max} (red) (nm)	λ_{max} (yellow) (nm)
PDA-1	11	4-MeO	chloroform (9.3, 4.81)	*b*	*b*	*b*	464
			THF (9.1, 7.58)	−8	28	498	457
			2-methyltetrahydrofuran (8.5, 6.97)	1	36	500	455
			toluene (8.9, 2.38)	−5	34	500	457
			1,4-dioxane (10.0, 2.21)	28	42	499	453
PDA-2	9	4-MeO	THF	−4	26	498	456
PDA-3	15	4-MeO	THF	9	34	495	457
PDA-4	11	H	THF	−5	18	492	450
PDA-5	11	3-MeO	THF	<−10	4[c]	*b*	448
PDA-6	11	4-Cl	THF	−3	25	495	455
PDA-7	11	4-Br	THF	−2	31	495	452

[a] δ: solubility parameter in cal$^{0.5}$/cm$^{0.5}$, ϵ: dielectric constant at 25 °C. [b] Not determined. [c] Determined with a λ_{max}(red) value assumed to be 492 nm.

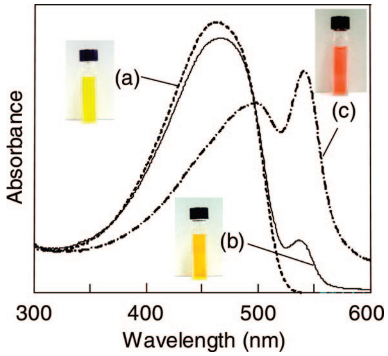

Figure 9. Solvatochromism of **PDA-1** in the mixed solvents of chloroform and hexane at room temperature. The volume ratio of chloroform/hexane = (a) 100/0, (b) 30/70, and (c) 20/80. **PDA-1** is insoluble in hexane.

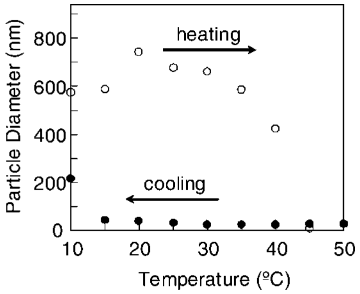

Figure 10. Change in particle diameter of **PDA-1** at various temperatures in THF determined by DLS measurement. Data were collected during the heating process (open circle) from 10 to 50 °C for each 5 °C step after keeping the solution at −40 °C for 30 min, followed by cooling (filled circle) from 50 to 10 °C.

intensity decreased when the temperature decreased. No signal due to the polymer was observed at −10 °C. This suggests the aggregation of the polymer chains at low temperature. Figure 10 shows the average particle size determined by the DLS analysis as a function of the temperature for the cooling and heating processes. This result shows that the red solution includes particles with a diameter of ca. 600 nm. On the basis of these results, it has been revealed that the conformational change in the polymer chain during the aggregation causes a change in the absorption characteristics of the PDAs. Although the aggregation of the PDA chains in a poor solvent was already pointed out for several polymer–solvent systems,[15–17] our results have direct evidence for the aggregate formation in the solution as the origin of the drastic color change of the PDAs in solution. The chromatic behavior depended on various factors, for example, temperature and solvent, as well as the polymer solubility and crystallinity. It has been reported that aggregation often induces an efficient emission by the suppression of intramolecular vibrational and rotational motions in the aggregates (aggregation-induced emission).[31] Such intramolecular motions cause a fast nonirradiative relaxation, leading to the reduction in the fluorescence quantum yield. In our system, the PDA forms aggregates in the red solution, in which the limited conformational mobility of the molecules resulted in the fluorescence emission, as was already shown in Figure 8.

In conclusion, we have revealed the thermochromism of PDA in the solid state and in solution by the fabrication of partly crystalline PDAs. The obtained PDAs showed thermochromism not only in the bulk and polymer matrices but also in solution. In the solid state, the alkyl chain of the PDA has a trans zigzag structure at room temperature, resulting in the alignment of the polymer chains. The spectral change is accounted for by the conformation change in the PDA main chains according to the side chain crystallinity and mobility. The UV–vis absorption spectrum of the PDAs in solution also changed, which depended on the temperature with a large hysteresis. We found that aggregates were formed in the solution when the temperature decreased on the basis of the results of the NMR and DLS measurements. The PDA chains start to aggregate according to the decrease in the solubility in a poor solvent and at a lower temperature, leading to the color change of the solution from yellow to red. Eventually, the thermochromism and solvatochromism are observed in solutions. The results obtained in the present study will help to control the chromism phenomena of conjugating polymers including PDAs for various applications. We are continuing study on the thermochromism of PDAs in the solid state in order to reveal the chromatic characteristics of PDAs including reversible and irreversible phase transitions between their blue and red phases.

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Supporting Information Available: Spectral data of monomers, TG/DTA curves, TEM photograph, UV–vis absorption spectra, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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