Supporting Information for Macromolecules (ma-2007-02789f)

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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Contents

Spectral Data of Monomers

4-Methoxybenzyl 10,12-pentacosadiynoate (**DA-1**): mp 41–42 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 0.88 (t, *J* = 7.2 Hz, CH_3, 3H), 1.26–1.62 (m, CH_2, 32H), 2.24 (t, *J* = 7.2 Hz, CH_2–C≡C–C≡C–CH_2, 4H), 2.32 (t, *J* = 7.2 Hz, CH_2CO_2, 2H), 3.81 (s, $C_6H_4OCH_3$, 3H), 5.04 (s, $CH_2C_6H_4$, 2H), 6.88–7.31 (m, C_6H_4, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.14 (CH_3), 19.18, 19.21 22.69, 24.91, 28.30, 28.35, 28.74, 28.87, 28.88, 29.04, 29.06, 29.10, 29.35, 29.48, 29.62, 29.63, 31.93, and 34.33 (CH_2), 55.27 (OCH_3), 65.20 and 65.29 (C≡*C*–*C*≡C), 65.89 (CO_2CH_2), 77.45 and 77.60 (*C*≡C–C≡*C*), 113.90, 128.25, 130.05, and 159.56 (phenyl), 173.73 (C=O); IR (KBr) 1721 cm^{-1} ($\nu_{C=O}$).

4-Methoxybenzyl 10,12-triacosadiynoate (**DA-2**): mp 33–34 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 0.88 (t, *J* = 7.2 Hz, CH_3, 3H), 1.26–1.63 (m, CH_2, 28H), 2.24 (t, *J* = 7.2 Hz, CH_2–C≡C–C≡C–CH_2, 4H), 2.32 (t, *J* = 7.2 Hz, CH_2CO_2, 2H), 3.81 (s, $C_6H_4OCH_3$, 3H), 5.05 (s, $CH_2C_6H_4$, 2H), 6.87–7.31 (m, C_6H_4, 4H). ^{13}C NMR (100 MHz, CD_3OD) δ 14.13 (CH_3), 19.18, 19.21 22.69, 24.91, 28.29, 28.35, 28.74, 28.86, 28.88, 29.04, 29.06, 29.10, 29.31, 29.48, 29.57, 31.90, and 34.33 (CH_2), 55.28 (OCH_3), 65.20 and 65.29 (C≡*C*–*C*≡C), 65.89 (CO_2CH_2), 77.45 and 77.61 (*C*≡C–C≡*C*), 113.90, 128.24, 130.05, and 159.56 (phenyl), 173.75 (C=O).

4-Methoxybenzyl 10,12-nonacosadiynoate (**DA-3**): mp 53–54 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 0.88 (t, *J* = 7.2 Hz, CH_3, 3H), 1.25–1.55 (m, CH_2, 40H), 2.24 (t, *J* = 7.2 Hz, CH_2–C≡C–C≡C–CH_2, 4H), 2.32 (t, *J* = 7.2 Hz, CH_2CO_2, 2H), 3.81 (s, $C_6H_4OCH_3$, 3H), 5.05 (s, $CH_2C_6H_4$, 2H), 6.88–7.31 (m, C_6H_4, 4H).

Benzyl 10,12-pentacosadiynoate (**DA-4**): Yield 82%, mp 36 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, CH_3, 3H), 1.26–1.65 (m, CH_2, 32H), 2.24 (t, *J* = 7.2 Hz, CH_2–C≡C–C≡C–CH_2, 4H), 2.35 (t, *J* = 7.2 Hz, CH_2CO_2, 2H), 5.12 (s, $CH_2C_6H_5$, 2H), 7.31–7.39 (m, C_6H_5, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.15 (CH_3), 19.19, 19.21, 22.70, 24.91, 28.29, 28.35, 28.74, 28.87, 28.89, 29.05, 29.11, 29.36, 29.49, 29.62, 29.64, 29.66, 31.93, and 34.30 (CH_2), 65.19 and 65.27 (C≡*C*–*C*≡C), 66.08 (CO_2CH_2), 77.45 and 77.63 (*C*≡C–C≡*C*) 128.19, 128.54, and 136.11 (phenyl), 173.67 (C=O); IR (KBr) 1726 cm^{-1} ($\nu_{C=O}$).

3-Methoxybenzyl 10,12-pentacosadiynoate (**DA-5**): mp 35–36 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, CH_3, 3H), 1.26–1.66 (m, CH_2, 32H), 2.24 (t, *J* = 7.2 Hz, CH_2–C≡C–C≡C–CH_2, 4H), 2.36 (t, *J* = 7.2 Hz, CH_2CO_2, 2H), 3.82 (s, $C_6H_4OCH_3$, 3H), 5.09 (s, $CH_2C_6H_4$, 2H), 6.85–7.30 (m, C_6H_4, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.15 (CH_3), 19.19, 19.21, 22.71, 24.92, 28.30, 28.35, 28.75, 28.87, 28.90, 29.07, 29.11, 29.37, 29.49, 29.62, 29.65, 29.67, 31.93, and 34.30 (CH_2), 55.24 (OCH_3), 65.20 and 65.29 (C≡*C*–*C*≡C), 65.93 (CO_2CH_2) 77.45 and 77.62 (*C*≡C–C≡*C*), 113.57, 113.64, 120.33, 129.62, 137.64, and 159.71 (phenyl), 173.63 (C=O); IR (KBr) 1727 cm^{-1} ($\nu_{C=O}$).

4-Chlorobenzyl 10,12-pentacosadiynoate (**DA-6**): Yield 86%, mp 34–35 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, CH_3, 3H), 1.26–1.64 (m, CH_2, 32H), 2.24 (t, *J* = 7.2 Hz, CH_2–C≡C–C≡C–CH_2, 4H), 2.34 (t, *J* = 7.2 Hz, CH_2CO_2, 2H), 5.07(s, $CH_2C_6H_4$, 2H), 7.28–7.35 (m, C_6H_4, 4H); IR (KBr) 1725 cm^{-1} ($\nu_{C=O}$).

4-Bromobenzyl 10,12-pentacosadiynoate (**DA-7**): Yield 85%, mp 40–41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, CH_3, 3H), 1.26–1.64 (m, CH_2, 32H), 2.24 (t, *J* = 7.2 Hz, CH_2–C≡C–C≡C–CH_2, 4H), 2.34 (t, *J* = 7.2 Hz, CH_2CO_2, 2H), 5.06 (s, $CH_2C_6H_4$, 2H), 7.22–7.50 (m, C_6H_4, 4H); IR (KBr) 1725 cm^{-1} ($\nu_{C=O}$).

4-Carboxybenzyl 10,12-pentacosadiynoate (**DA-8**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, CH_3, 3H), 1.25–1.50 (m, CH_2, 32H), 2.23 (t, *J* = 7.2 Hz, CH_2–C≡C–C≡C–CH_2, 4H), 2.37 (t, *J* = 7.2 Hz, CH_2CO_2, 2H), 5.42 (s, $CH_2C_6H_4$, 2H), 7.50–8.10 (m, C_6H_4, 4H)

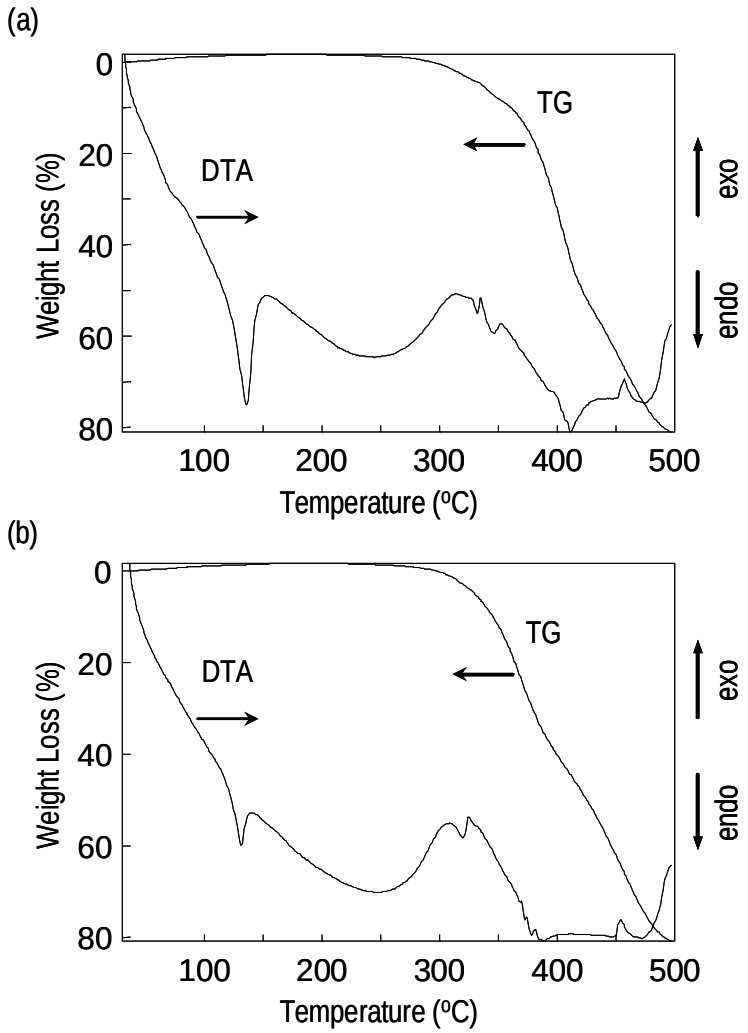

Figure S1. TG/DTA curves of (a) crystalline and (b) partly crystalline **PDA-1**s, which were obtained by solid-state polymerization and the subsequent dissolution and reprecipitation processes, respectively. Measured in a nitrogen stream at the heating rate of 10 ºC/min.

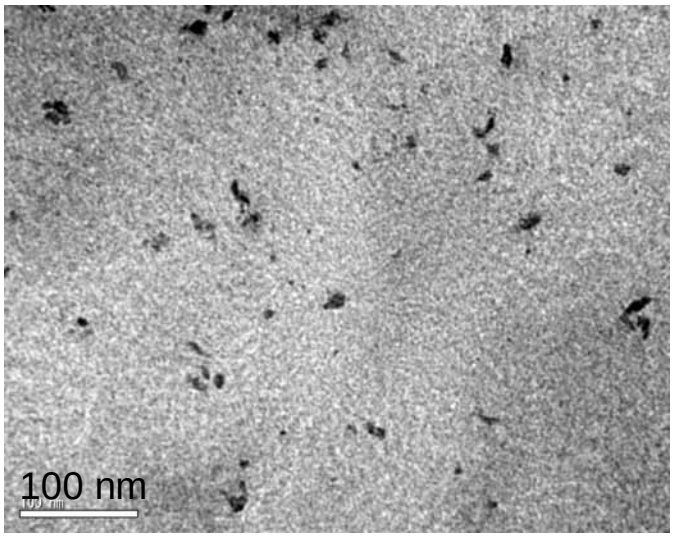

Figure S2. TEM photograph of **PDA-1** embedded poly(vinyl alcohol) film**.**

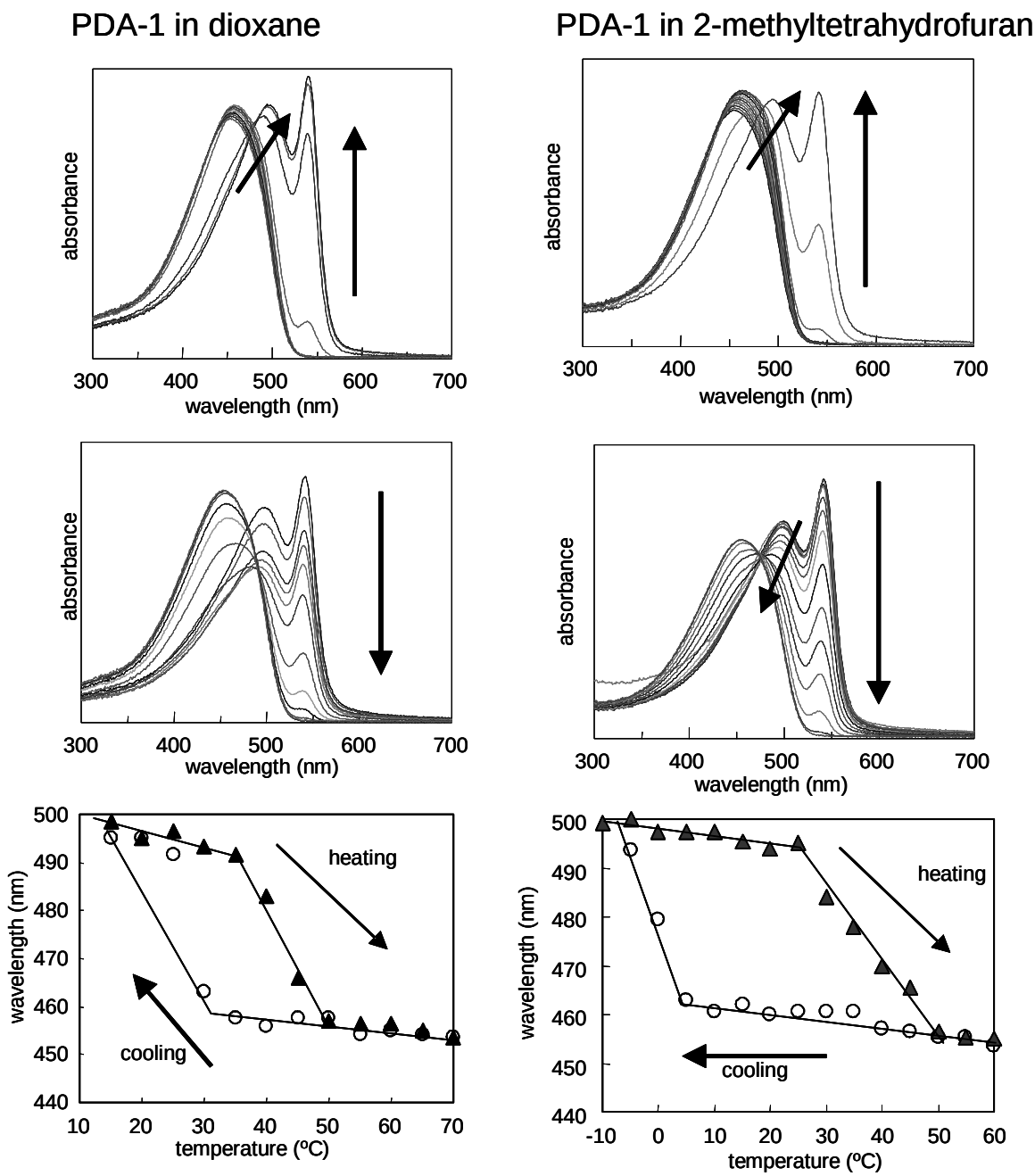

Figure S3. Change in the absorption spectra of **PDA-1** in 1,4-dioxane and 2-methyltetrahydrofuran during cooling and heating processes with each 5 °C step in the temperature range of 10 to 70 °C and –10 to 60 °C, respectively.

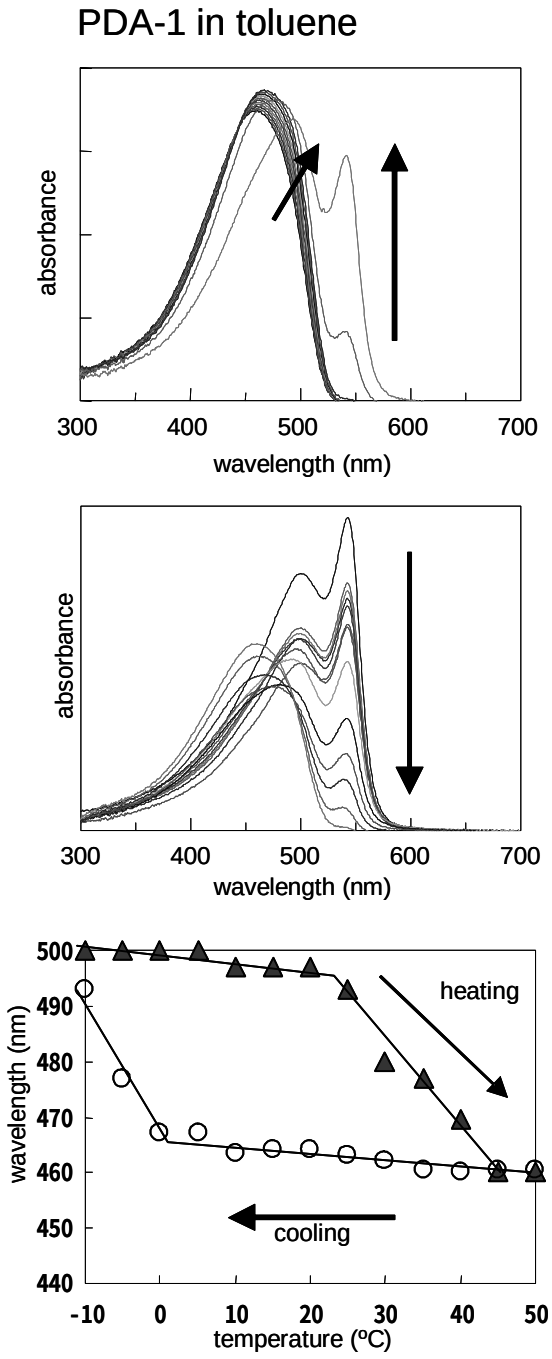

Figure S4. Change in the absorption spectrum of **PDA-1** in toluene during cooling and heating processes with each 5 °C step in the temperature range of –10 to 50 °C.

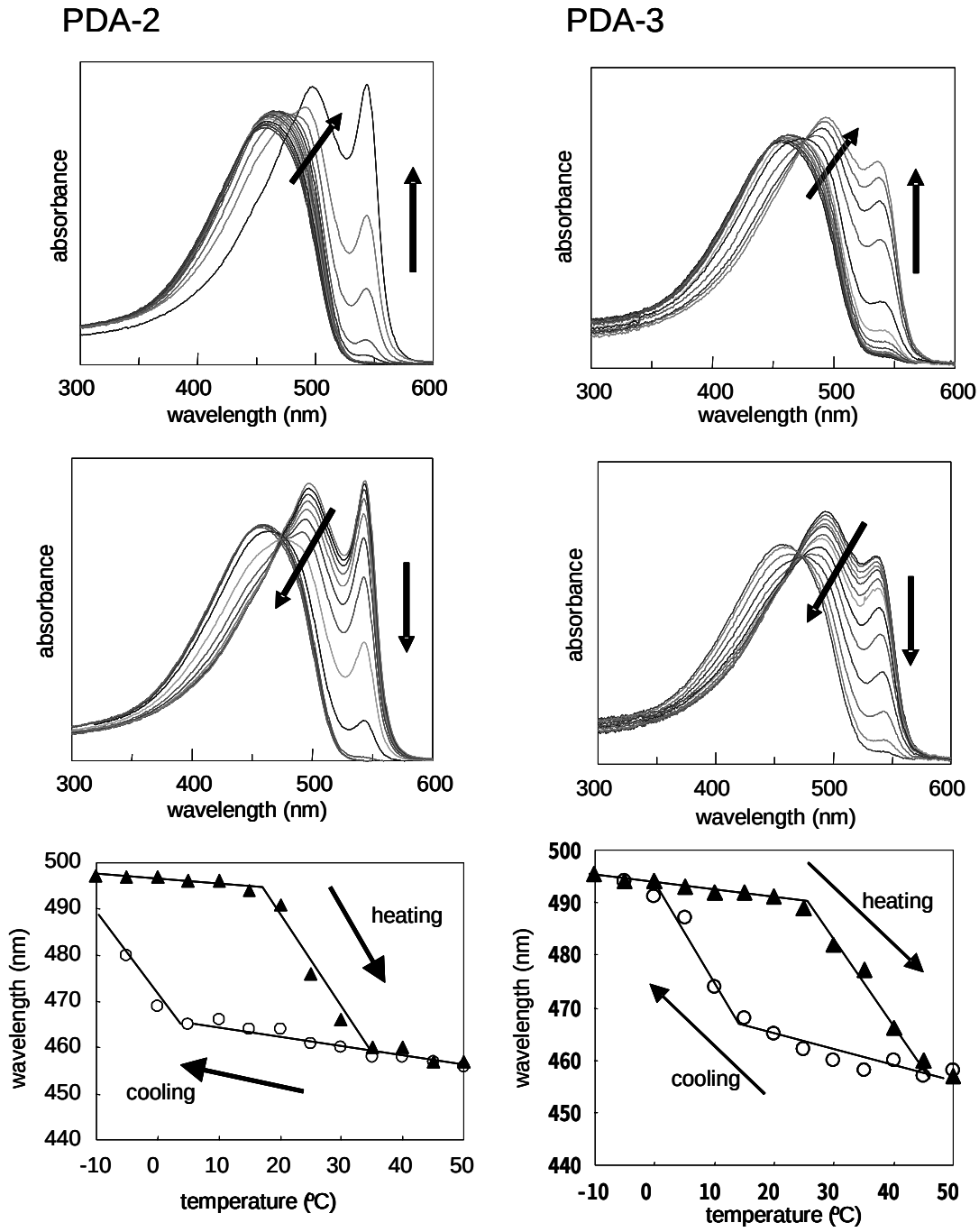

Figure S5. Change in the absorption spectra of **PDA-2** and **PDA-3** in THF during cooling and heating processes with each 5 °C step in the temperature range of –10 to 50 °C.

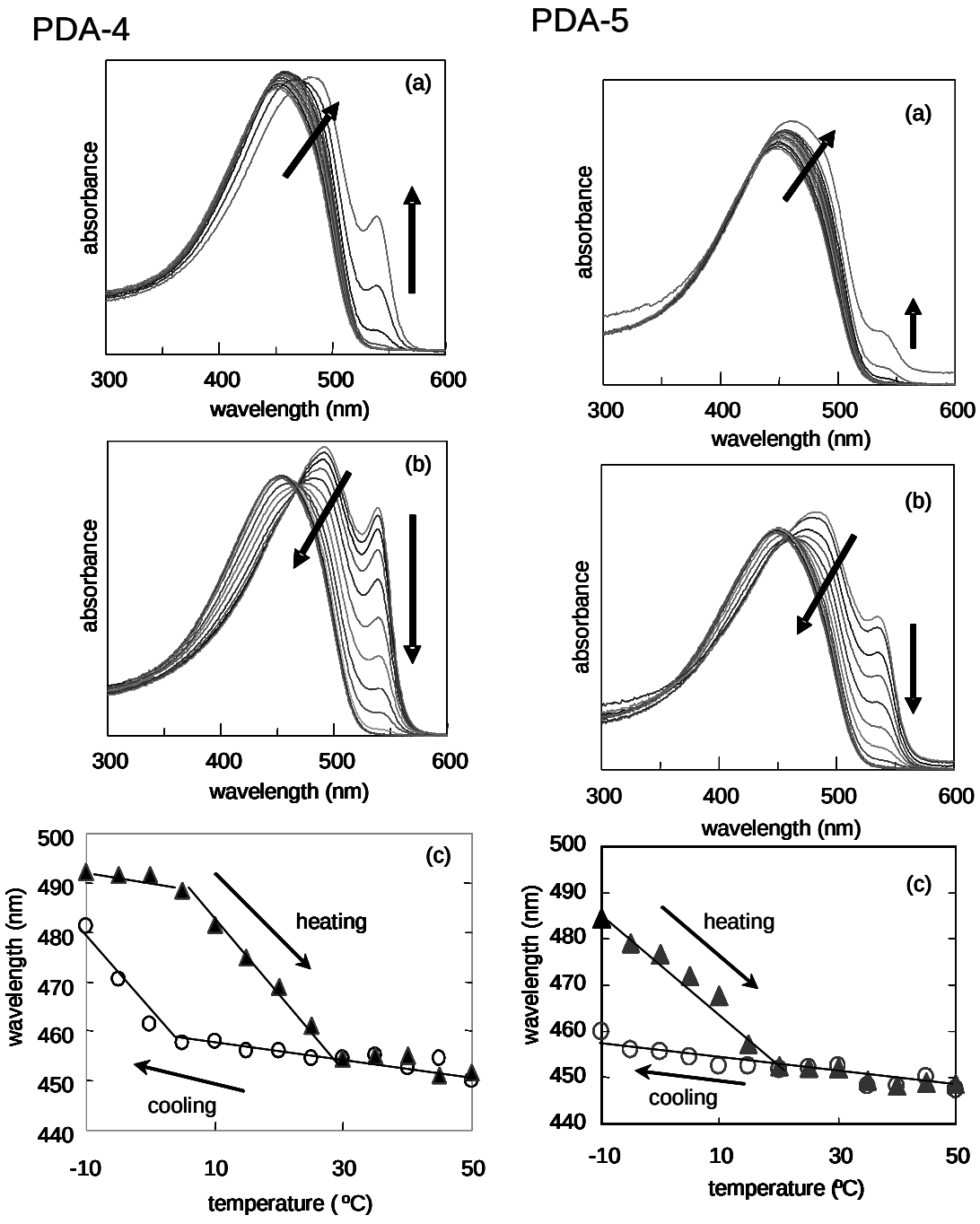

Figure S6. Change in the absorption spectra of **PDA-4** and **PDA-5** in THF during cooling and heating processes with each 5 °C step in the temperature range of –10 to 50 °C.

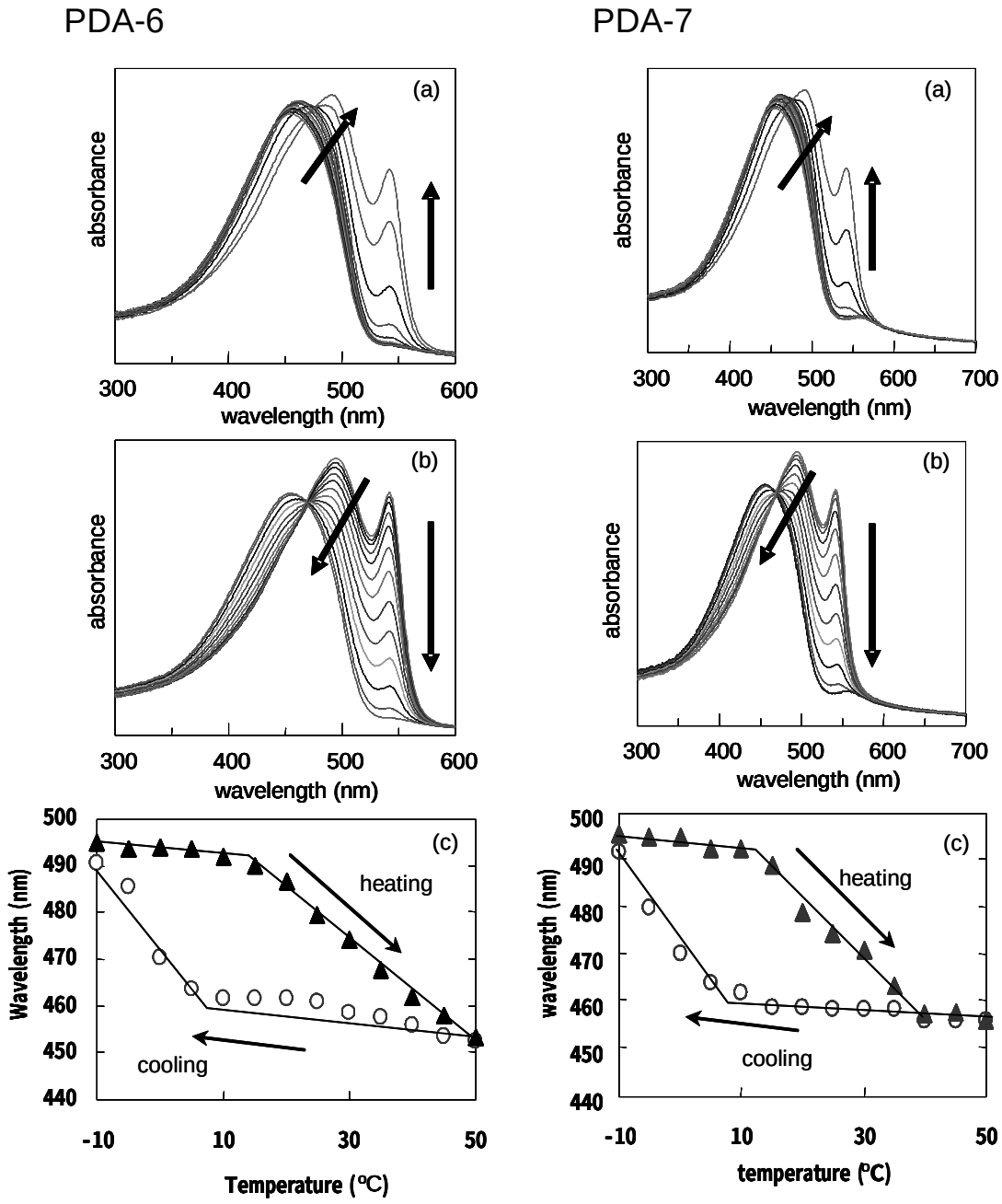

Figure S7. Change in the absorption spectra of **PDA-6** and **PDA-7** in THF during cooling and heating processes with each 5 °C step in the temperature range of –10 to 50 °C.

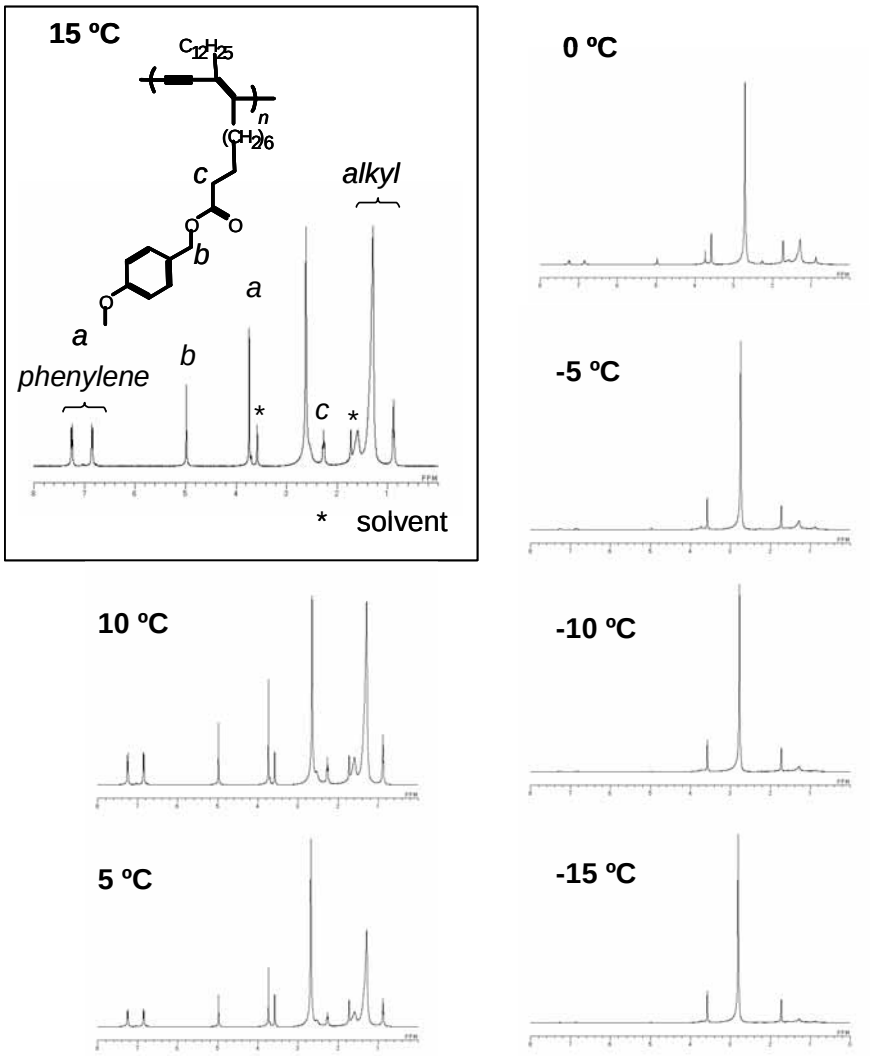

Figure S8. ^{1}H NMR spectrum of **PDA-1** in THF-d_8 at various temperatures.