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Electronic Supplementary Information (ESI)

Glass-transition-induced color-changing resin containing layered polydiacetylene

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Experimental methods

Synthesis of the PSt/PDA resin. All the reagents were used as purchased without purification. About 160 mg of 10,12-pentacosadiynoic acid (PCDA, TCI, 97.0 %) monomer was dissolved in 1.6 g of styrene (St, Kanto, 99.0 %) monomer liquid. After filtration of the solution to remove the polymerized PCDA, 0.38 cm^3 of the precursor solution was poured into a glass vessel 2 cm^3 in volume. Then, 2,2'-azobis(isobutyronitrile) (AIBN, TCI, 98.0 %) as an initiator was dissolved into the solution. The concentration of AIBN (C_{AIBN}) was changed at 0.1, 0.2, and 1.0 mol%. The St containing PCDA and AIBN, typically 0.11 cm^3, was transferred to a sample tube 2 cm^3 in volume. The polymerization of St was performed in a drying oven at 60 °C for 48 h. Then, PCDA monomer in the solid PSt matrix was polymerized with irradiation of LED-UV light (365 nm) to both sides for each 30 min. The cylindrical bulk composite of PSt/PDA about 5 mm in width and 3 mm in height was prepared by trimming. The reference PSt samples were prepared by the same procedure without addition of PCDA.

Characterization of the stimuli-responsive color-change properties. The cylindrical shape of the PSt/PDA composites was heated on a temperature-controlled stage in the range 25–80 °C. The photographs of the sample were taken after heating and keeping at certain temperature for 5 min. The R, G, and B values were estimated from the photographs using Image J software. Then, the RGB values were converted to x, y, and z values using the following (eq. S1) according to ITU-R BT. 709, an international standard.[52] The structure changes with heating were analyzed by differential scanning calorimetry (DSC, Shimadzu, DSC-60plus) under nitrogen atmosphere at the scan rate 5 °C min^{-1}. Alumina was used as the reference.

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0.4124 & 0.3576 & 0.1805 \\ 0.2126 & 0.7152 & 0.0722 \\ 0.0193 & 0.1192 & 0.9505 \end{bmatrix} \begin{bmatrix} R \\ G \\ B \end{bmatrix} \quad \ldots \text{(eq. S1)}$$

Structure characterization. The state of the carboxy group was analyzed by Fourier-transform infrared spectroscopy (FT-IR, Jasco, FT/IR-4200). The sample was prepared by mixing with KBr. UV-Vis spectra were measured by a spectrophotometer (Jasco, V-670). The SE and BSE images of PDA in PSt was observed by scanning electron microscopy (SEM, Carl-Zeiss, Merlin VP Compact) operated at 1.5 kV. The SE and BSE images were obtained. The treated color of the BSE images was prepared by a software for microscopy image (Gatan, Digital Micrograph).

FT-IR spectra of the PSt/PDA composites

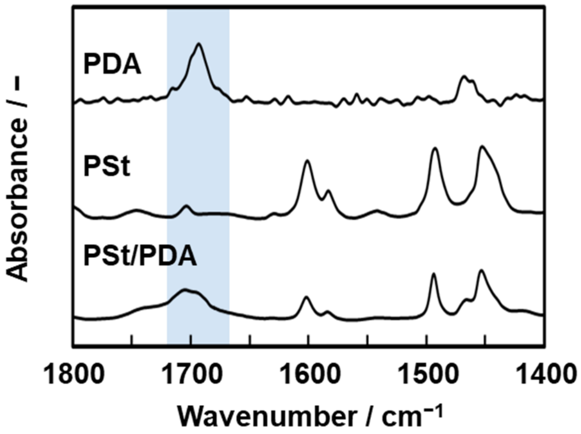

Fig. S1. FT-IR spectra of pure PDA, PSt, and PSt/PDA.

FT-IR spectrum of PSt/PDA showed the absorption around 1700 cm^{-1} corresponding to the dimerized carboxy group characteristic to the layered PDA.[50]

Summary of T_x and T_{DSC} for the eight different samples

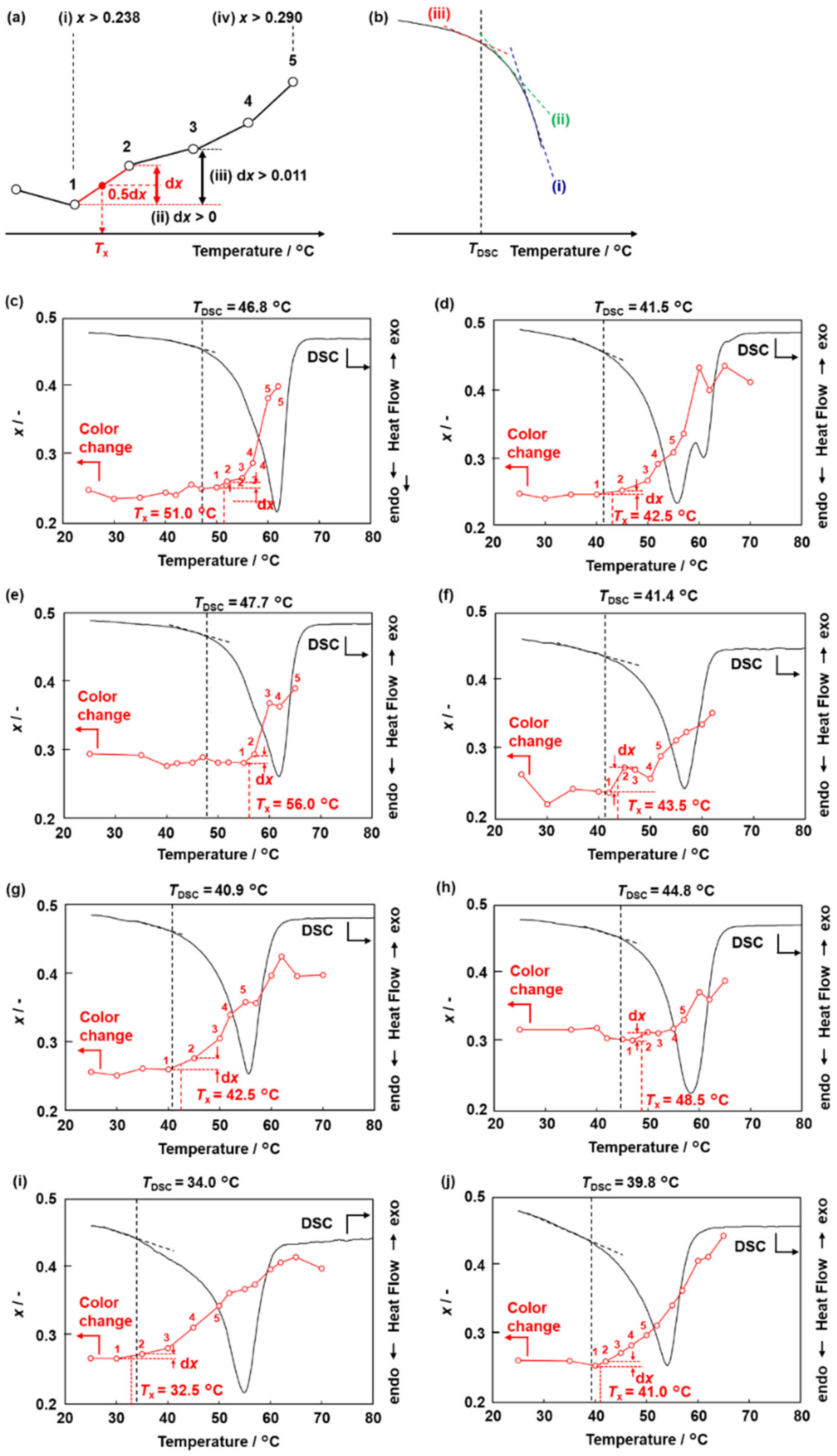

Fig. S2. Relationship between T and x (red) and DSC thermogram (black) of the eight different samples. (a,b) Definition of T_x and T_{DSC}, respectively. (c–e) C_{AIBN} = 0.1 mol%. (f–h)

C_{AIBN} = 0.2 mol%. (i,j) C_{AIBN} = 1.0 mol%.

The T_{x} and T_{DSC} were defined as follows. The five plots (1-5) were assigned by the following rules (i)-(iv) on the relationship between temperature and x (Fig. S2a). (i) The x value of the plot 1 is larger than 0.238 ($x > 0.28$). (ii) An increase in the x value from the plots 1 to 2 (dx) is positive (d$x > 0$). (iii) An increase in the x value from the plots 1 to 3 (dx) is larger than 0.011 (d$x > 0.011$). (iv) The x value of the plot 5 is larger than 0.290 ($x > 0.290$). Then, the temperature to achieve 0.5dx between the plots 1 and 2 was defined as T_x. The DSC thermograms show the large endothermic peak corresponding to the deformation of layered PDA at temperature higher than 50 °C (Fig. S2b). The slope to this large peak is defined as the slope (i). Prior to the slope (i), the two different slopes are drawn at the lower temperature side (the slopes (ii) and (iii) in Fig. S2b). The slope (iii) is used to estimate the T_{DSC}.

Table S1 Summary of T_{x} and T_{DSC} estimated from Fig. S2.

Entry	C_{AIBN} / mol%	T_{x} / °C	T_{DSC} / °C
1	0.1	51.0	46.84
2	0.1	45.5	41.50
3	0.1	56.0	47.69
4	0.2	43.5	41.43
5	0.2	42.5	40.90
6	0.2	48.5	44.79
7	1.0	32.5	33.99
8	1.0	41.0	39.75

The T_{DSC} was estimated from the DSC thermogram (the black curves in Fig. S2). The relationship between T and x provided the T_{x} (the red curves in Fig. S2). The data were summarized in Table S1. Relationship between T_{DSC} and T_{x} in Fig. 4d were prepared on the basis of Table S1. The T_{DSC} and T_{x} were not linearly varied with changes of C_{AIBN}. In the present work, the polymerization of PSt was performed in a small scale, namely 0.11 cm^3 in 2 cm^3 sample tube, to reduce consumption of PCDA monomer. The actual polymerization conditions were slightly changed in each batch because of evaporation of St, even though the initial conditions are the same. The amount of the evaporating St can be ignored in the larger-scale polymerization setup

DSC thermograms of pure PSt and PDA

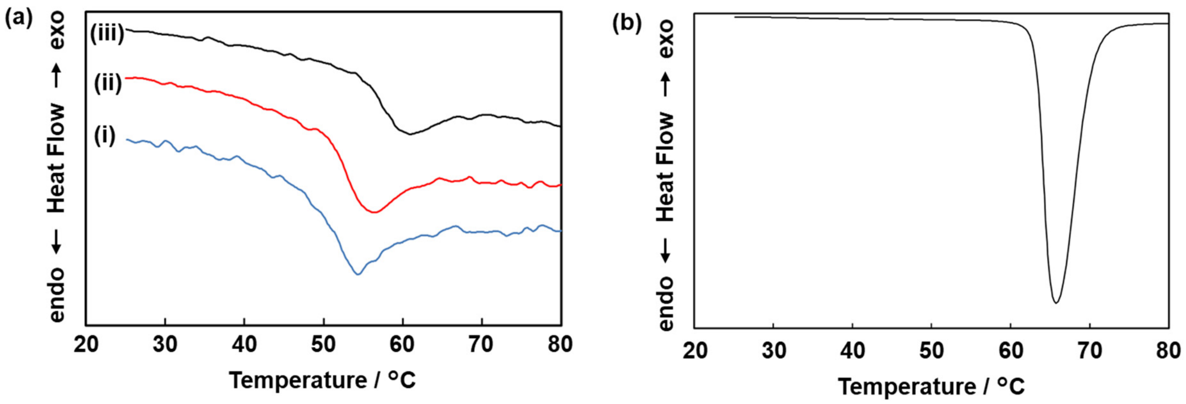

Fig. S3. DSC thermograms of pure PSt (a) with C_{AIBN} = 0.1 (i), 0.5 (ii), and 1.0 mol% (iii) and PDA (b).

Pure PSt showed the baseline shift and endothermic peak corresponding to T_g around 55 °C (Fig. S3a). Pure PDA showed the endothermic peak around 65 °C (Fig. S3b). This behavior is ascribed to deformation of the layered structure of PDA.

GPC analysis of PSt in the composite

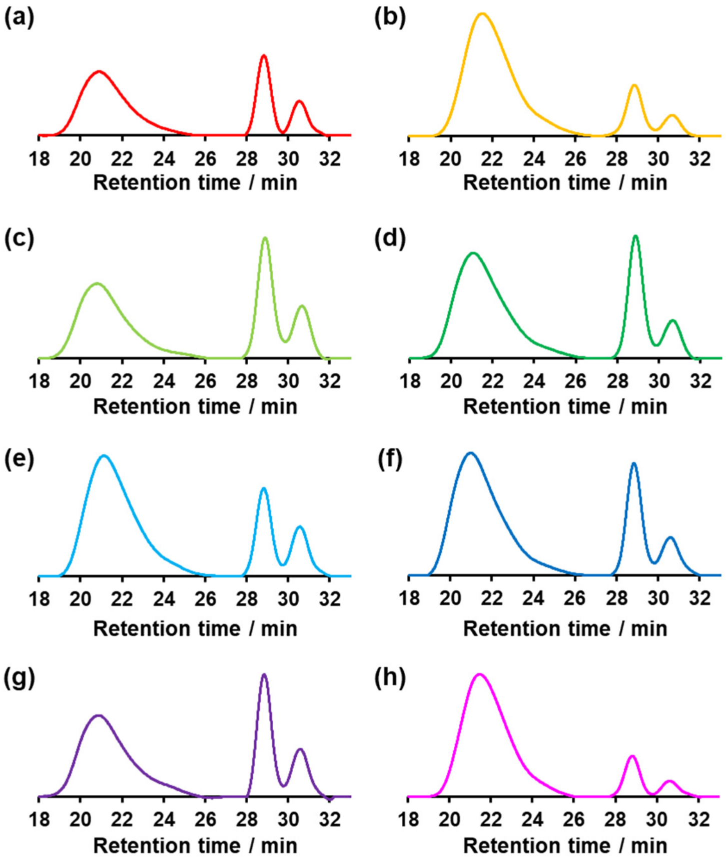

Fig. S4. GPC traces of the PSt in the composites. The panels (a)–(h) correspond to the samples listed the entries 1–8 in Table S1, respectively.

Table S2. Summary of the molecular weight (retention time) and poly dispersity index (PDI) for the 1st, 2nd, and 3rd peaks of the 8 samples estimated from GPC measurement in Fig. S4.

Entry	1st peak[a]	PDI	2nd peak[a,b]	PDI	3rd peak[a,b]	PDI
1	72805 (20.7)	1.52	835 (28.8)	1.02	408 (30.5)	1.01
2	32408 (21.5)	1.93	829 (28.9)	1.03	384 (30.7)	1.01
3	64268 (20.8)	1.79	806 (28.9)	1.02	385 (30.7)	1.01
4	38744 (21.1)	2.22	811 (28.9)	1.02	387 (30.7)	1.01
5	47836 (21.1)	1.78	840 (28.8)	1.02	398 (30.6)	1.02
6	41697 (21.0)	2.22	826 (28.8)	1.02	388 (30.6)	1.02
7	54669 (20.9)	1.95	827 (28.9)	1.02	391 (30.6)	1.02
8	34188 (21.5)	1.91	845 (28.8)	1.02	380 (30.6)	1.02

[a] The retention time is displayed in the bracket. [b] The lower limit of the calibration curve in GPC instrument is 1200. Molecular weight below 1200 may not be accurate.

The PSt/PDA was dissolved in toluene and then the incorporated PDA particles were removed by filtration. The molecular weight of all samples was measured by gel permeation chromatography (GPC), which was carried out by THF eluent using the Ultimate 3000 liquid chromatograph equipped with a 101 refractive index detector and three Shodex columns (Shodex KF-802, KF-803 and KF-804). The signal was collected by DIONEX Shodex RI-101 refractometer (RI) detector and UltiMate 3000 variable wavelength detector operated at 254 nm for the THF system. The calibration was based on narrow linear polystyrene standard ranging in molecular weight from 1.20×10^3 g mol^{-1} to 1.41×10^6 g mol^{-1} for the THF system.

The GPC traces showed three peaks for all the 8 samples (Fig. S4 and Table S2 in the ESI). The retention time and molecular weight for each sample were summarized in Table S2. The 2nd and 3rd peaks at the longer retention time indicate the presence of low-molecular-weight PSt in the composite. Since the lower limit of the calibration curve in GPC instrument is 1200, molecular weight below 1200 may not be accurate. These results indicate that the low-molecular weight of PSt in the composite contributes to induce molecular motion with glass transition at lower temperature.

PSt/PDA composites prepared by the different method

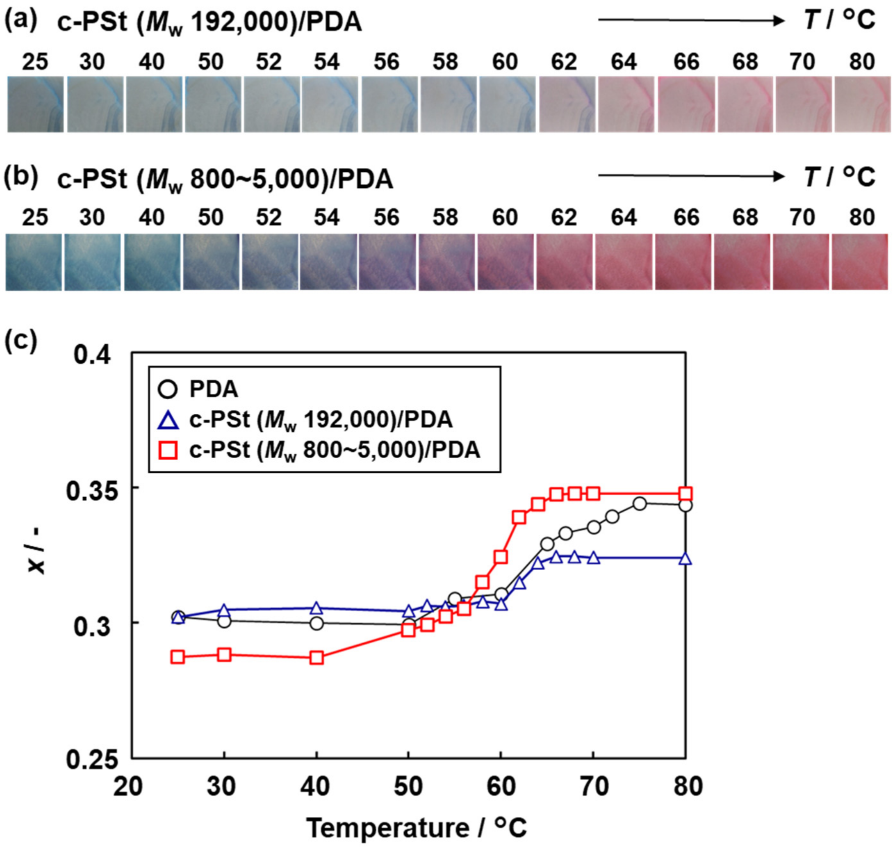

Fig. S5. Temperature-responsive color-change properties of PSt/PDA composites prepared by the different method as the reference. (a, b) Photographs of the c-PSt (M_w 192,000)/PDA (a) and c-PSt (M_w 800~5,000)/PDA (b) the samples on a glass substrate with heating. (c) Relationship between temperature and x value of the reference samples.

The reference composites were prepared using two commercial PSt (Aldrich, average M_w 192,000 and Polyscience, M_w 800~5,000) (c-PSt (M_w 192,000) and c-PSt (M_w 800~5,000)). The precursor solution containing 50 mg PCDA and 280 mg PSt was prepared with 20 cm^3 of toluene. The precursor solution, typically 0.5 cm^3, was casted on a glass substrate. After evaporation of toluene, PSt/PCDA film was covered on the glass substrate. The films of c-PSt (M_w 192,000)/PDA and c-PSt (M_w 800~5,000)/PDA were obtained by topochemical polymerization with irradiation of UV light. As the reference, the PDA deposited on the glass substrate was also prepared without addition of commercial PSt in the same procedure. This method provided not three-dimensional (3D) shape but the two-dimensional (2D) casting film on a substrate, whereas the bulk three-dimensional form of resin, as shown in Fig. 2a–c, was obtained by the simultaneous polymerization and crystallization methods.

The c-PSt (M_w 192,000)/PDA and c-PSt (M_w 800~5,000)/PDA showed the different color-change behavior (Fig. S5a,b). The c-PSt (M_w 192,000)/PDA and PDA on the glass substrate showed the similar color-change behavior with heating (the circles and triangles in Fig. S5c). An increase in the x value was started with heating after 50 °C. The c-PSt (M_w 192,000) with higher M_w and T_g has no effects on the color-change behavior of PDA. In contrast, the x value of the c-PSt (M_w 800~5,000)/PDA increased with heating after 40 °C (the circles in Fig. S5c). The color change is induced by c-PSt (M_w 800~5,000) with lower M_w and T_g. These results support the color change is induced by molecular motion of PSt with glass transition.

Effects of the heating rate on the color-change behavior

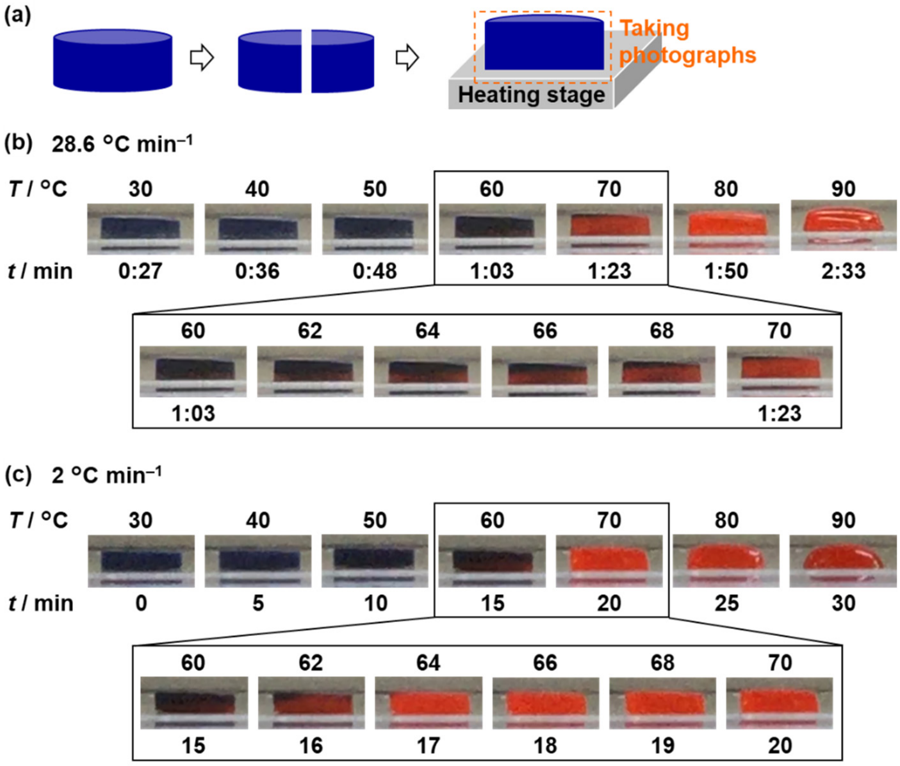

Fig. S6. Color-change behavior of the PSt/PDA sample with different heating rate. (a) Schematic illustration of the experimental setup. (b,c) Photographs of the samples with heating at 28.6 °C min^{-1} (b) and 2 °C min^{-1} (c).

The same sample was divided into two pieces to study the color-change behavior with different heating rate (Fig. S6a). The separated samples were set on a temperature-controlled stage. The sample was heated at 28.6 °C min^{-1} and 2 °C min^{-1} (Fig. S6b,c). The photographs of the cross-sectional view were taken at specific temperature. The higher heating rate showed the complete color-change to red at the higher temperature around 70 °C (Fig. S6b), whereas the complete color change was achieved around 64 °C at the lower heating rate (Fig. S6c). This difference in the color-change temperature supports that molecular motion with glass transition of PSt has effects on the color change of PDA.