Role of Gel to Fluid Transition Temperatures of Polydiacetylene Vesicles with 10,12-Pentacosadiynoic Acid and Cholesterol in Their Thermochromisms

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This study demonstrates gel-to-fluid transition temperatures of polydiacetylene bilayer vesicles could play important roles in their colorimetric transition temperatures. We prepared five types of polydiaceylene vesicles with 10,12-pentacosadiynoic acid (PCDA) and cholesterol (0–40 mol % of total content). From temperature-dependent observations of the optical signals (colors and UV-vis spectra), the blue-to-red colorimetric transition temperatures of polydiacetylene vesicles were decreased with the cholesterol contents. A further study with microcalorimetry and dynamic light scattering revealed that the polydiacetylene vesicles first underwent gel-to-fluid transitions, which were followed by event(s) responsible for the colorimetric transitions. Energies required for each event were quantified from analysis of the peaks in the microcalorimetry thermograms. The inclusion of cholesterol in the vesicles decreased both the gel-to-fluid and the colorimetric transition temperatures, suggesting that the colorimetric transition of the polydiacetylene vesicles was mediated by the former event although the event was not the direct reason for the color change.

Key Words : Gel to fluid transition, Polydiacetylene vesicles, Colorimetric transition, Microcalorimetry thermograms

Introduction

Polydiacetylenes have been used as conducting materials[1] but they have also been recently considered for use as sensing materials for many applications.[2-14] In the latter case, the applications rely on their ability to change colors in response to temperature,[15] pH,[16] receptors,[17-21] and other molecules[22] in a system. In addition, the flexibility of the precursors of polydiacetylenes to construct a variety of micro- or nanostructures (depending on the preparation methods) makes it possible to use them for the desired purposes.[23-29] Moreover, recent advances in synthetic methods enable the polydiacetylenes to reversibly respond to external stimuli, thereby expanding their versatility.[30-35]

Along with the technical advances, some researchers have been studying reasons for the color change of polydiacetylenes. It was suggested that the change in the conformation of the conjugated ene-yne backbone or the conjugated *p*-orbital arrays (from planar to partially distorted) varied the conjugation length, which was primarily responsible for the color change of the polydiacetylenes.[36-39] Regarding factors affecting conformation change in the π-bond, head group interactions, arising from hydrogen bonds/lateral stacking between aromatic rings or the flexibility of head groups, were suggested to play important roles.[30,33-35,40] Meanwhile, melting of the unreacted monomers was also suggested to be a factor for the conformation change of the backbone.[41] On the other hand, it is little known how deeply the characteristics of self-assembled bilayers (in case of vesicles) or films of the polydiacetylenes connected with the conformation change of the backbone, affecting the colorimetric transitions. If any, this might be also important because the colorimetric transition temperatures of polydiacetylene vesicles and films could be manipulated by altering the self-assembled structures.

Here we investigated the effect of gel-to-fluid transition temperatures on colorimetric transition temperatures of polydiacetylene bilayer vesicles. We prepared five types of polydiaceylene vesicles based on 10,12-pentacosadiynoic acid (PCDA) and cholesterol. PCDA bilayer vesicles were constructed in an aqueous system and were polymerized with an ultraviolet light by breaking a triple bond in the PCDA (Figure 1). The polymerized vesicles showed a color change (blue to red). We modified the vesicle properties the polymerized PCDA by inclusion of cholesterol (0–40 mol %), thereby varying their colorimetric transition temperatures. By comparing the temperature-dependent changes in color, spectra, hydrodynamic sizes, and thermograms of the polymerized PCDA-based vesicles, processes involving the color changes were quantitatively discussed. Lastly, we discussed how the gel-to-fluid transitions were associated with the colorimetric transitions of the polymerized vesicles.

Experimental

Materials. PCDA (98%, GFS Chemicals) was purified before use by first solubilizing it in chloroform (HPLC, Burdick & Jackson) followed by filtration. Then, PCDA was dried in a rotary evaporator (R-200, BÜCHI, Switzerland) at 35 ºC. Cholesterol (99%, Aldrich) and ethanol (HPLC, Fischer

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Before polymerization   After polymerization
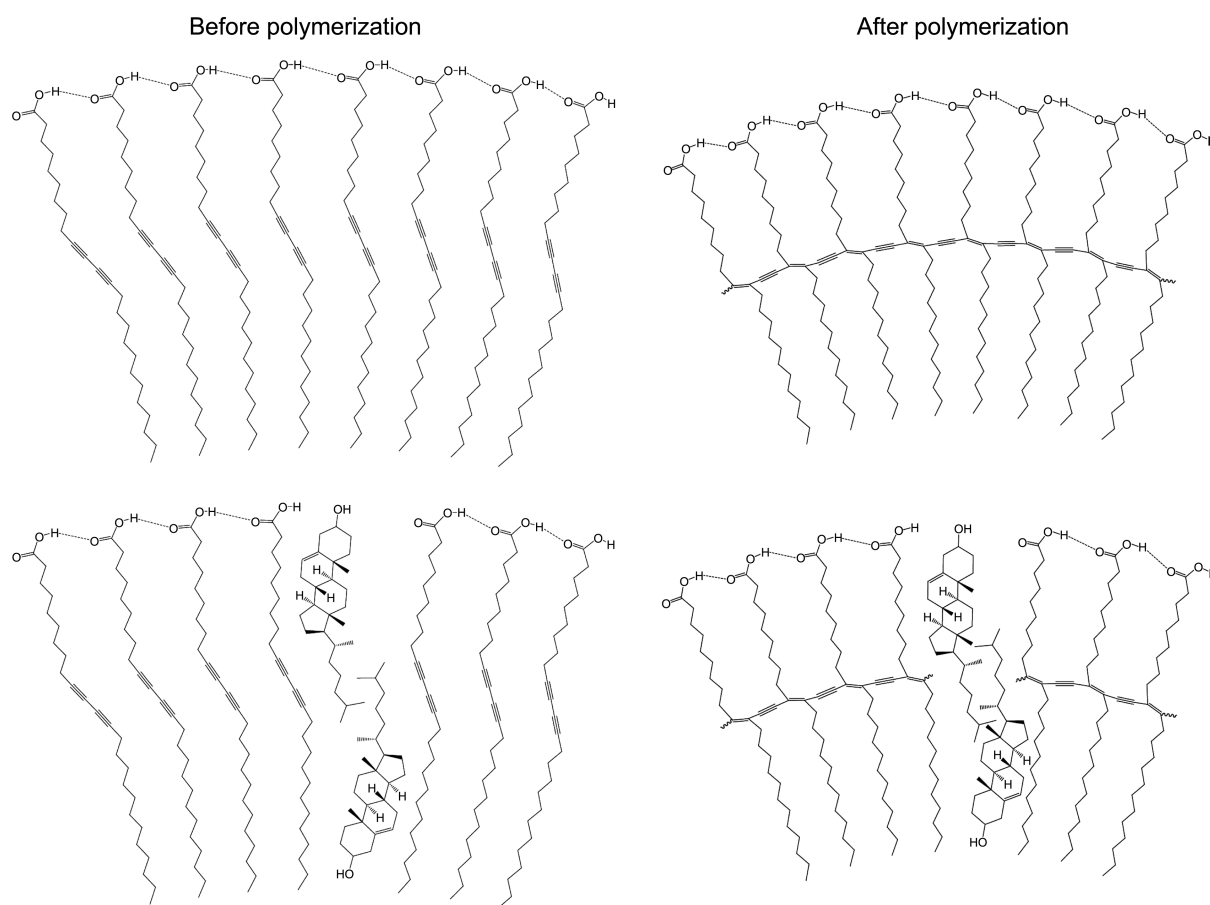
Figure 1. Molecular structures for the bilayer vesicles of PCDA (top) and PCDA-cholesterol (bottom) before (left) and after (right) the photopolymerization. For short, only monolayers of the vesicles are shown.

Scientific) were purchased and used as received.

Synthesis of the Polymerized PCDA-based Bilayer Vesicles. As a standard method, 19 mL of deionized water was heated and equilibrated at 80 °C. Then, 1 mL of a preheated 0.2 mM PCDA ethanolic solution was added to deionized water under sonication with a probe sonicator (Sonic dismembrator model 550, Fisher Scientific, USA). We kept mixing the aqueous PCDA vesicle dispersion under sonication for 10 min. After the mixing, the mixture was wrapped with aluminum foil and stored at 4 °C for 3 h. Then, the ethanol in the mixture was removed using the rotary evaporator at 35 °C. The PCDA dispersion in deionized water was stored at 4 °C for a while, and the dispersion was polymerized using an UV lamp (VL-4.LC, Vilber Lourmat, France) for 3 min at room temperature. Polymerized PCDA vesicles were stored at 4 °C before the analysis. There were essentially no differences in the procedures for the preparation of the polymerized vesicles bearing cholesterols except that a certain amount of PCDA was replaced by the equivalent amount of cholesterol while the concentration of the PCDA and cholesterol was kept constant (0.2 mM) in ethanol. We prepared five types of PCDA-based polymerized vesicles where the concentrations of the cholesterol were 0, 10, 20, 30, and 40 mol %.

Characterizations of the Polymerized PCDA-based

Vesicles. The hydrodynamic diameters of the five polymerized PCDA-based vesicles, before and after the photopolymerization, were measured at room temperature by using dynamic light scattering (Nano-ZS, Malvern Instrument, United Kingdom). UV-vis spectroscopy (Cary 50, Agilent, USA) was used to investigate the optical signals of the polymerized PCDA-based vesicles. Fourier transform infrared spectroscopy (FT-IR, FTLA2000-100, ABB, Switzerland) was used to predict the conformation of the polymerized vesicles.

Monitoring the Processes of the Color Change of the Polymerized PCDA-based Vesicles. The colors of the polymerized PCDA-based vesicles were monitored with the following experimental procedures. After the equilibrium at room temperature, the aqueous dispersion containing the vesicles was heated to a certain temperature at which the vesicles were equilibrated for 2 h. After recording the color of the vesicle dispersions by taking a photograph, 100 μL of aqueous vesicle dispersion was diluted in 0.9 mL of deionized water in a quartz cuvette, and an UV-vis spectrum was recorded. Then the dispersion was heated again to another temperature for equilibrium, and the optical signals were also recorded after the equilibrium. The monitoring temperatures were from room temperature to 75 °C. Hydrodynamic diameters of the polymerized PCDA-based vesicle disper-

sions were also measured as a function of temperature by using dynamic light spectroscopy. The polymerized vesicles were equilibrated in a quartz cuvette at a certain temperature for 30 min, and the diameters were measured. We investigated thermal behaviors of the PCDA and PCDA-cholesterol (40 mol %) vesicles, before and after the polymerization, by using microcalorimetry (VP-DSC, MicroCal, United Kingdom). Typically, 0.6 mL of aqueous vesicle dispersion was filled into a sample chamber, and a reference chamber was filled with deionized water. The dispersion was scanned from 15 °C to 80 °C with a scan rate of 1 °C/min.

We used MagicPlot Pro software to deconvolute the micro-calorimetry thermograms of the vesicles. The peaks in the thermograms were constructed with the program by setting the total enthalpies obtained from integration of constructed peaks to be the same as the heats integrated from each thermogram.

Results and Discussion

Characterizations of the Polymerized PCDA and PCDA-cholesterol Vesicles. The PCDA-based bilayer vesicles were
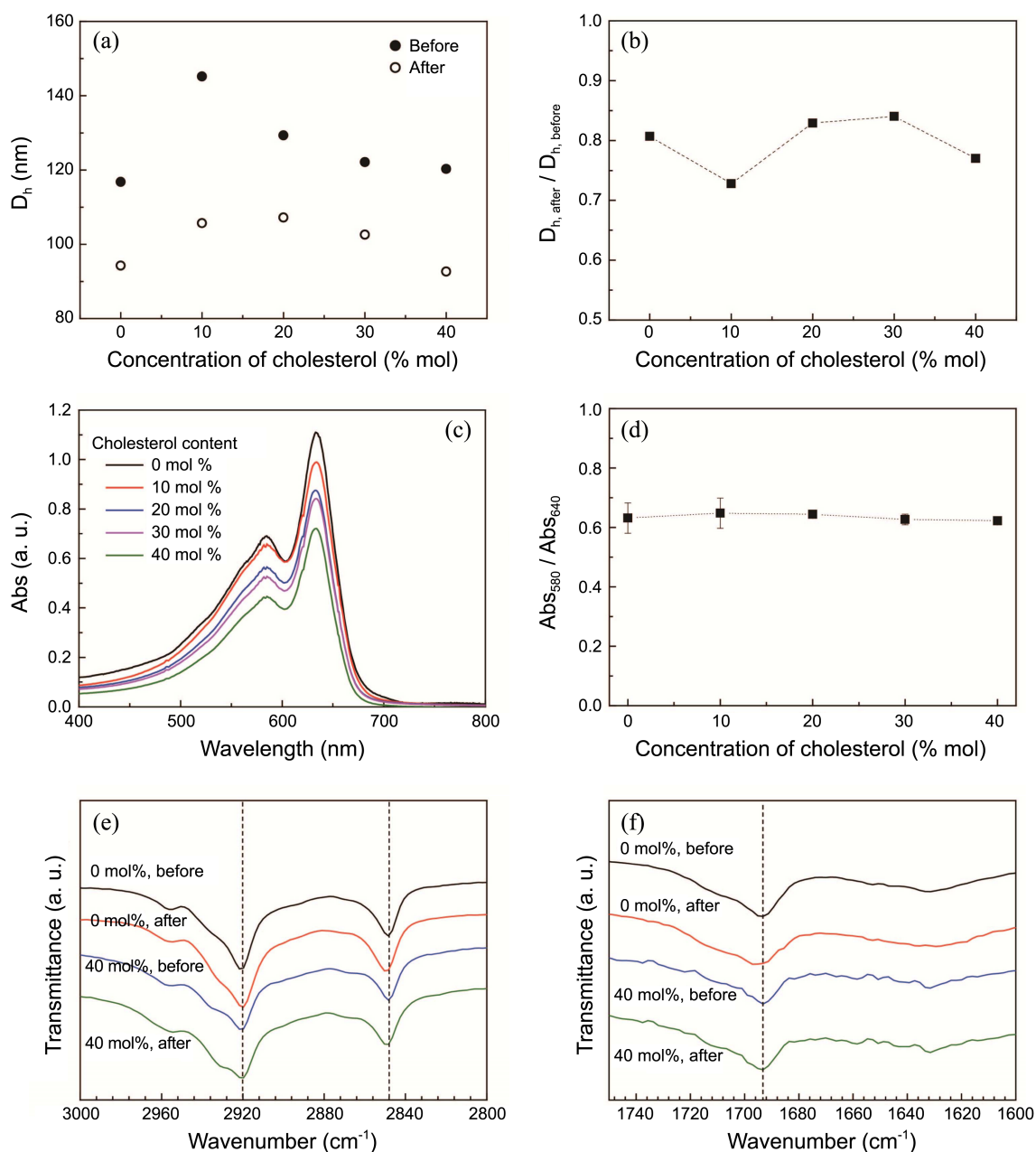
Figure 2. (a) Hydrodynamic diameters of the PCDA-based vesicles before (filled circles) and after (empty circles) the photopolymerization. (b) Ratios of the hydrodynamic sizes of the vesicles measured after to before the photopolymerization. (c) UV-vis spectra for the polymerized PCDA-based vesicles having different cholesterol contents. (d) Ratios of the peaks at 585 nm to 637 nm of the polymerized PCDA-based vesicles as a function of cholesterol contents. (e and f) FT-IR spectra in the (e) 3000–2800 cm^{-1} and (f) 1750–1600 cm^{-1} regions of the polymerized vesicles having different cholesterol contents.

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formed while adding an ethanolic solution of PCDA or mixtures of PCDA and cholesterol to deionized water under sonication. The storage of the aqueous vesicle dispersions at 4 °C for 3 h was necessary to induce an ordered packing of the vesicles, thereby facilitating a rapid photopolymerization reaction between PCDA molecules in the vesicles. After the removal of the ethanol from the dispersion, the exposure of the vesicles to UV turned their colors from white to blue, indicative of the formation of π-conjugation between the PCDA molecules by breaking their triple bonds.

Figure 2(a) shows the hydrodynamic diameters of the five polymerized PCDA-based vesicles. The five vesicles had similar hydrodynamic diameters (90–110 nm) in deionized water. Across the board, the vesicle sizes after the photo-polymerization were reduced by approximately 20%, probably due to the shrinkage of the vesicles during the poly-merization reaction (Figure 2(b)). From UV-vis spectra (Figure 2(c)), the polymerized PCDA-based vesicles typical-ly displayed two maximum peaks at 637 and 585 nm, respectively. The peaks at 637 and 585 nm originated from an exciton band due to the π-π* electronic transition to the first allowed excited state and a vibronic band due to the coupling of the main transition to the stretching modes of the backbone, respectively.[42] Regardless of the concentrations of cholesterol in the polymerized vesicles, the positions of the two peaks and the ratios of the intensities at 585 nm to 637
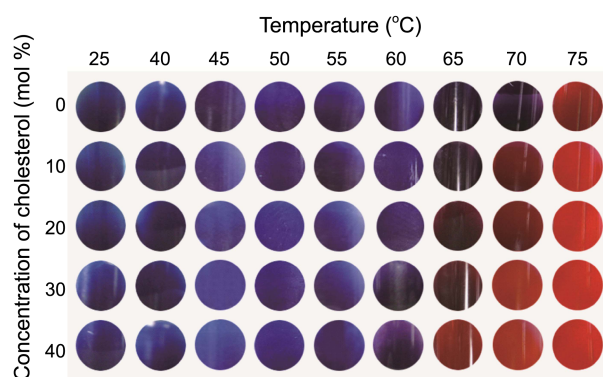
Figure 3. A photograph showing the colors of the polymerized PCDA-based vesicles with various contents of cholesterol at various temperatures.

nm were essentially the same (Figure 2(d)). Meanwhile, the ratios of the peak intensity at 637 nm of the polymerized vesicles bearing the cholesterol to that of polymerized PCDA vesicle decreased quite linearly to 0.65 (40 mol %) with the concentration of cholesterol, due to a decrease in the amount of PCDA in the vesicles. The constant peak position and the linear decrease in the intensities of the polymerized vesicles might suggest that the inclusion of the cholesterol did not greatly affect the conjugation length: the cholesterol was thought not to be homogenously mixed, but to be mostly
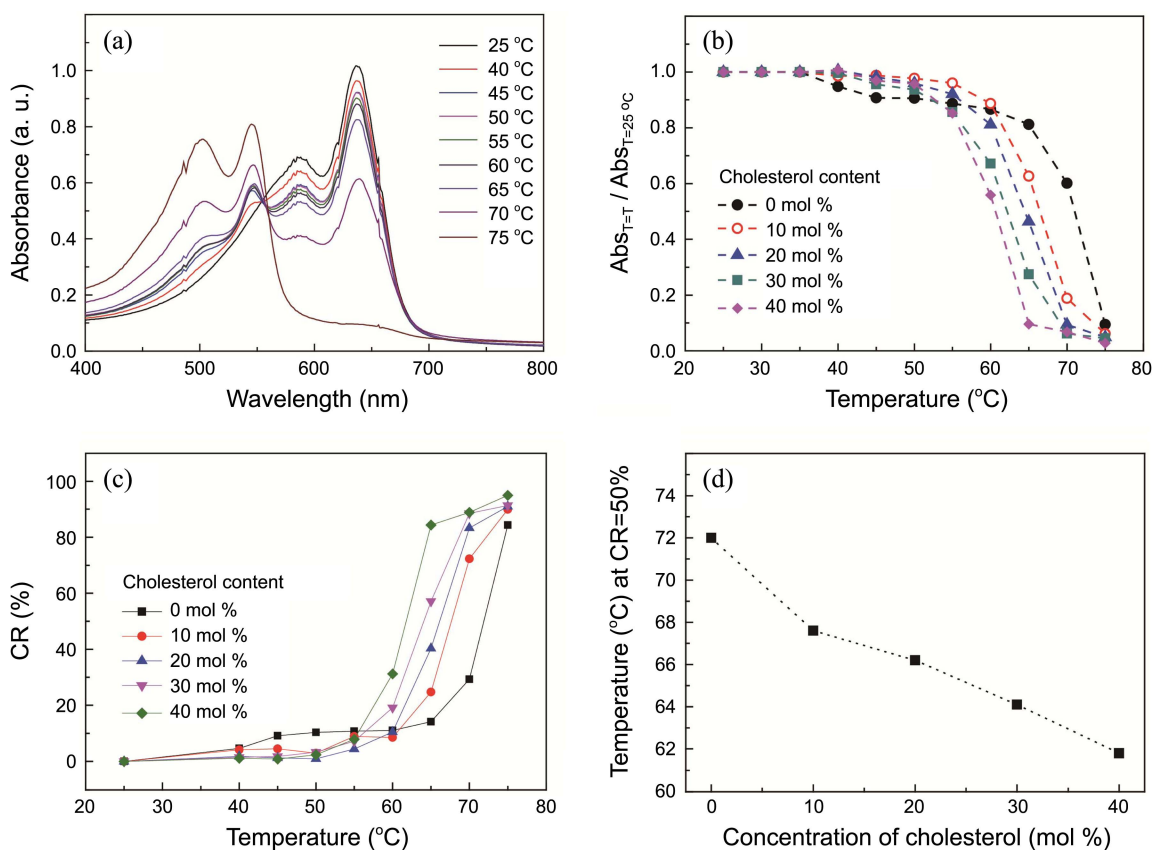
Figure 4. (a) UV-vis spectra of the polymerized PCDA vesicles for various temperatures. (b) A plot showing the ratios of the absorbance at 637 nm and at test temperature to that at room temperature. (c) A plot showing CR values as a function of test temperatures. (d) Temperatures at CR = 50% of the polymerized PCDA-based vesicles.

From a FT-IR analysis (Figure 2(e)), all the vesicles generally displayed peaks at 2850 and 2920 cm^{-1}, which corresponded to the symmetric and assymetric stretching peaks of CH$_2$ in the aliphatic chain. The two peaks less than those values were indicative of the formation of crystalline phases of alkyl chains.[43-47] In addition, all the vesicles had in common a peak around 1690 cm^{-1}, which was due to the carbonyl groups involving hydrogen bonds.[30] The results suggested that the five polymerized vesicles had enough cohesiveness among the PCDA molecules to form hydrogen bonds between headgroups and self-assemblies between alkyl groups.

Temperature-dependent Color Changes of the Polymerized PCDA and PCDA-cholesterol Vesicles. We next monitored the temperature dependent change in colors of the five polymerized PCDA-based vesicles (Figure 3). The colors of the samples were recorded at each test temperature. The polymerized PCDA vesicle (no cholesterol) started changing color from blue to purple at 65–70 °C, and to a mixture of purple and red at 75 °C. For the polymerized vesicles bearing the cholesterol, such changes occurred at lower temperatures than in the polymerized PCDA vesicles, and the temperatures decreased with increasing cholesterol content. At 40 mol % cholesterol, the temperature was decreased by approximately 10 °C when compared with the temperature of polymerized PCDA vesicle.

UV-vis spectroscopy was used to record the spectra of the vesicles at each test temperature (Figure 4(a) for the polymerized PCDA vesicle; also see Figure S1 in the Supplementary Materials for the spectra of other vesicles). At 60–75 °C, the polymerized PCDA-based vesicles showed sharp decreases in the intensities of the peaks at 637 and 585 nm, and new peaks around 546 and 503 nm evolved. The results clearly suggested that the effective conjugation lengths of the polymerized PCDA-based vesicles became shorter with increasing temperatures.

To determine the colorimetric transition temperature of the five polymerized PCDA vesicles from the UV-vis spectra, we obtained the ratios of peak intensity at 637 nm for a certain temperature to that for room temperature (Figure 4(b)). The ratios sharply decreased at the transition regions. In addition, the colorimetric response (CR) values of the vesicles were also estimated based on the formula:[17]

$$CR = \left(\frac{\left(\frac{A_{blue}}{A_{blue}+A_{red}} \right)_{RT} - \left(\frac{A_{blue}}{A_{blue}+A_{red}} \right)_{T}}{\left(\frac{A_{blue}}{A_{blue}+A_{red}} \right)_{RT}} \right) \times 100 \quad (1)$$

where A is the absorbance of blue (637 nm) and red components (546 nm) obtained by UV-vis spectroscopy, and the subscripts "RT" and "T" represent the ratios of the blue components at room temperature and at a test temperature, respectively. CR values were plotted in Figure 4(c) as a function of temperature. The values also sharply increased in the vicinity of the temperatures of the color changes, and the increase in the cholesterol contents displayed such a change at lower temperatures. Temperatures reaching the value of CR = 50%, used as the transition temperatures for color change,[17] were also decreasing with increasing concentrations (Figure 4(d)). At 40 mol % cholesterol, the transition temperature of the polymerized vesicle was decreased by 10 °C when compared with the value of polymerized PCDA vesicles.

Quantitative Analysis for the Color Change of the Polymerized PCDA and PCDA-cholesterol Vesicles. To better understand the processes of thermally-induced color change, we obtained the microcalorimetry thermograms of the PCDA vesicles and PCDA vesicles having 40 mol % cholesterol before and after the photopolymerization. Before the photopolymerization reaction (Figure 5(a)), the vesicle formed with only PCDA displayed a tiny peak at 46.0 °C and large peak at 59.1 °C. Peak analysis (see Table 1) revealed that the enthalpies of the tiny and large peaks were estimated to be 0.18 and 10.79 kcal/mol, respectively. On the other hand, the vesicle bearing 40 mol % cholesterol had one peak with a shoulder at 52.6 °C, and the peak temperature of was 4.4 °C lower than the main peak of the vesicle with only PCDA. The enthalpy of fusion of the peak corresponded to 7.10 kcal/mol. The phase change of the vesicles from a gel to a fluid phase was responsible for the peaks before the polymerization:[48-50] Below the transition temperatures, PCDA-based vesicles formed a gel-like phase through self-assembly among PCDA molecules or PCDA and cholesterol. After the transition, the vesicles became mobile due to the melting of the self-assembled bilayers in the vesicles.

After the polymerization, the PCDA-based vesicles had quite different thermograms (Figure 5(b)). For the polymerized PCDA vesicles, the contribution of a small peak around 46 °C became meaningful, occupying 25% of the total heat (2.59 kcal/mol). However, the major peak at 59.2 °C was still prominent even after the polymerization, having 3.76 kcal/mol. More interestingly, a new peak at 74 °C was observed with an enthalpy of 4.06 kcal/mol. For the polymerized vesicles containing 40 mol % cholesterol, the main peak seen before the polymerization was also found at 55.3 °C after the polymerization. In addition, as in the case of the polymerized PCDA vesicles, a new peak around 66.0

Table 1. Analysis of thermograms obtained with PCDA-based vesicles before and after photopolymerization

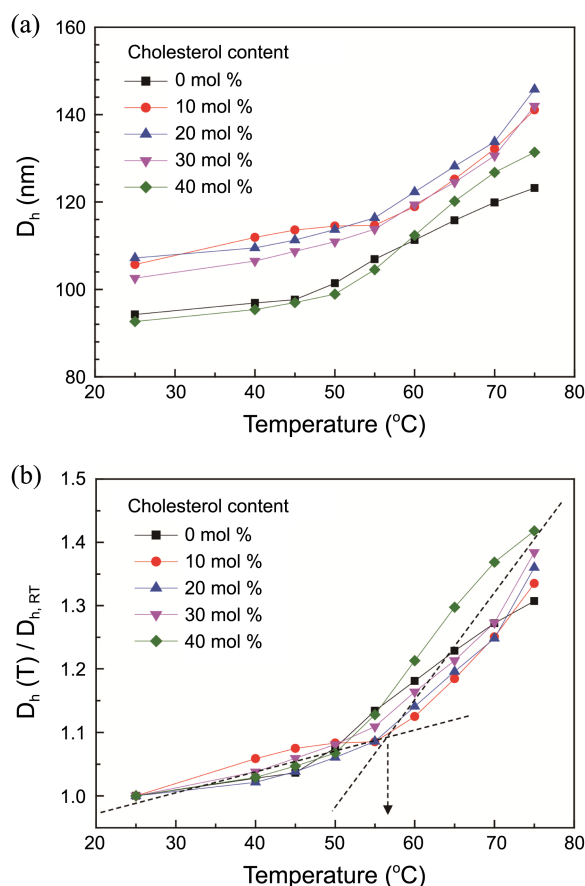| Cholesterol contents	Before polymerization		After polymerization	
	0 mol %	40 mol %	0 mol %	40 mol %
Peak Temperatures (°C)	46.0/59.1	54.7/52.6	48.3/59.2/74.0	55.3/66.0
Enthalpy (kcal/mol)	0.18/10.79	7.10	2.59/3.76/4.06	3.49/4.48

(a)

(b)
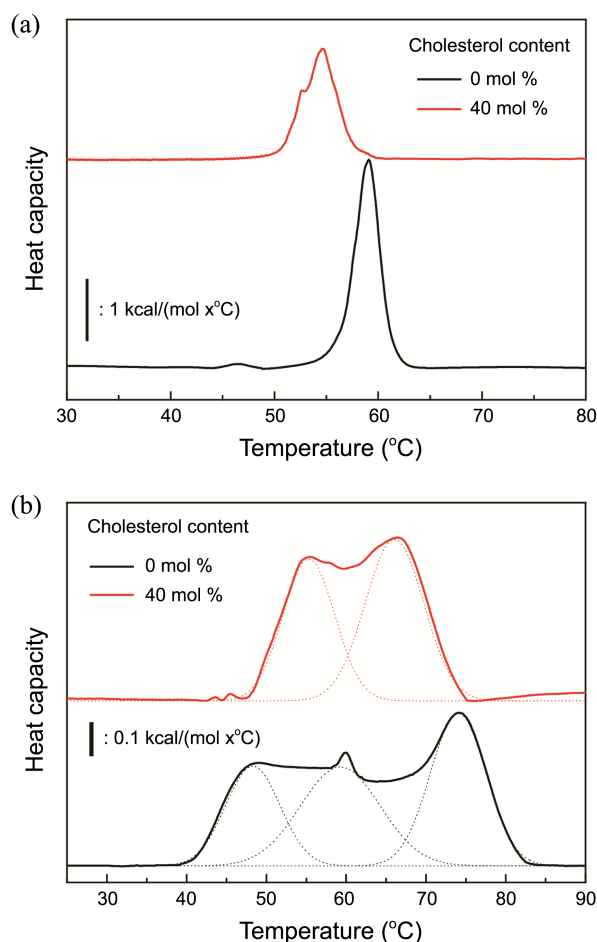
Figure 5. Microcalorimetry thermograms of the PCDA vesicles (black lines) and PCDA vesicles having 40 mol % of cholesterol (red lines) before (a) and after (b) the photopolymerization.

(a)

(b)

Figure 6. (a) Hydrodynamic diameters of the polymerized PCDA-based vesicles as a function of test temperatures. (b) A plot showing $D_h(T)/D_{h,RT}$ as a function of test temperature, where $D_h(T)$ is the hydrodynamic diameter at a test temperature and $D_{h,RT}$ is the diameter at room temperature.

°C was found. The enthalpies of the two peaks were 3.49 and 4.48 kcal/mol, respectively. It was worth noting that the last peaks found at 74 °C and 66 °C of the two types of polymerized vesicles were very close to the temperatures measured at CR = 50%, suggesting that the color change of the vesicles were closely associated with these peaks.

It was expected that the structural reorganization of the vesicles during the polymerization resulted in the splits of the main peaks found before the polymerization. The polymerization took place in the middle of the PCDA molecule by breaking a triple bond (see Figure 1). As such, the upper part of the polymerized PCDA (where the hydrogen bonds and double bonds were involved) could have different structures from the lower part of the PCDA (where the hydrophobic groups were assembled).

To seek for the origin of the peaks in the thermograms of the polymerized vesicles, we next monitored the change in the hydrodynamic diameters of the vesicles with temperature (Figure 6). The sizes of all the vesicles were increasing with temperature due to the thermal expansion of the vesicles (Figure 6(a)). Figure 6(a) was replotted in the form of $D_h(T)$/$D_{h,RT}$, where $D_h(T)$ was the size at a certain temperature and $D_{h,RT}$ was the size at room temperature. From this figure, the

slope, indicative of the degree of thermal expansion per unit temperature, were mostly changed at 55–60 °C. It was generally known that the slopes of materials altered when there were phase changes (*e.g.*, glass transition and melting).[51] Therefore, the gel to fluid phase change of the polymerized vesicles was responsible for the observed temperatures,[52] and the peaks below 60 °C in our thermograms might be mostly due to the phase change of the polymerized vesicles. However, from the size data, it was hard to find the effect of cholesterol on the transition temperatures.

Provided that the gel-to-fluid phase change of the polymerized vesicles was mostly due to the melting of the self-assembled alkyl chains in the polymerized vesicles,[53] either the first two peaks (for PCDA vesicles) or the first peak (for PCDA-cholesterol vesicles) in the thermograms were/was primarily attributable to the hydrophobic dissociation of the polymerized vesicles. As such, the heats roughly corresponded to 3–5 kcal/mol (see Table 1). The values were very close to the melting enthalpies of self-assembled alkanethiol monolayers on gold surface or gold nanoparticles.[54-56]

Since the temperatures of the last peaks (74 °C and 66 °C) were very close to the those of color changes and at CR = 50%, the peaks were expected to contain energies for the

conformation changes of the π-conjugation[57,58] and for the structural changes inducing the conformation changes in the polymerized vesicles. Based on the literatures and our experimental results, the conformation change of the current system could be induced by the dissociation of hydrogen bonds (see Figure S2 in the Supplementary Materials).[30] While dissociation of the unreacted monomers could also be responsible,[41] we thought this contribution, if any, had been already considered in the peaks below 60 °C because the unreacted PCDA was also assembled with the polymerized vesicles. It was known that the strength of hydrogen bonds and strain energies for the conformation change were in the range of 3–10 kcal/mol[59] and ~5 kcal/mol,[57] respectively. These heats were close to the values of the reaming heats of the polymerized vesicles. However, from the present study, it was hard to know how much of each parameter contributed to the heats of the last peaks of the polymerized vesicles.

We suggested that the color change of the polymerized PCDA-based vesicles was a result of complex events. The vesicles underwent thermal expansion during heating, and the expansion was even significant after the gel-to-fluid phase transition (55–60 °C), mainly due to the dissociation of self-assembled hydrophobic groups. The gel-to-fluid transitions of the polydiacetylene vesicles shown below 60 °C would not be directly associated with the color change. Instead, after the event, the mobility of vesicles and the distances between the PCDA molecules could be much increased, and thus the intermolecular forces were decreased, enabling the distortion of planar conformation sufficient for the color changes.[34-37]

The role of gel-to-fluid transition on the colorimetric transition of the polydiacetylene vesicles can be confirmed by discussing the effect of cholesterol. The gel-to-fluid phase transition temperature of the PCDA vesicles having 40 mol % cholesterol was lower than the vesicle with only PCDA, regardless of polymerization reaction. In addition, the temperatures of color changes of the polymerized vesicles were lower, too. Very recent simulation work by Kuo and Chang suggested that inclusion of cholesterol in the bilayers having ionic interactions increased the disorder of the bilayers by either weakening polar interactions between head-groups or creating voids in nonpolar regions.[60] Likewise, the addition of cholesterol into the vesicle membrane could also increase defects in the lateral packing of amphiphilies (especially in the hydrophobic parts), increasing the disorder of the bilayers. As a result, the vesicles bearing cholesterol became mobile from lower temperatures than the PCDA-based vesicle. From Table 1, the total enthalpies of the polymerized PCDA vesicles were lowered when cholesterol was embedded in the vesicles, implying that the inclusion of cholesterol weakened the intermolecular forces between the components of bilayers. Such changes in the bilayer characteristics could influence following events (hydrogen bonds dissociation and conformation change of π-conjugation) of the polymerized vesicles, thereby decreasing the temperatures of color changes. From a further microcalorimetry study with PCDA vesicles having 20 mol % of cholesterol (un-

polymerized, see Figure S3 in the Supplementary Materials), the gel-to-fluid transition temperatures (55.9 °C) were between those of PCDA and PCDA-cholesterol (40 mol %) vesicles. The results were in line with the effect of cholesterol on the temperatures of color changes, as seen in Figure 4(d).

Conclusions

This study shows experimentally that gel-to-fluid transition temperatures of polydiacetylene bilayer vesicles could affect their colorimetric transition temperatures. From a number of qualitative and quantitative studies, we found that the color change of the vesicles was a result of consecutive changes in the structures. The gel-to-fluid transition of the polymerized vesicles was found to be the first process. The event increased the mobility of the vesicles and thus weakened the intermolecular forces (*e.g.* hydrogen bonds in the head group) to induce a partial movement of p bonds for the color change. Inclusion of cholesterol in the PCDA vesicles decreased the gel-to-fluid transition temperatures, thereby decreasing the colorimetric temperatures. Although the present studies manipulated the gel-to-fluid transition with small temperature ranges (~10 °C), our recent following works succeeded in regulating the temperatures of color changes by 35 °C from introduction of various amphiphilic compounds in the polymerized PCDA vesicles (data not shown). Practically, such a control over the thermochromism could extend the applications of the polydiacetylenes. For example, polydiacetylene vesicles whose colorimetric transition temperatures are tuned at 35−45 °C are useful for bio-sensing/detection systems. The present study also provided a quantitative description of the processes of thermally-induced color change of polydiacetylene vesicles. Therefore, the study may not only offer a fundamental basis for the transition of polydiacetylenes but also help design polydiacetylenes for various applications.

Supplementary Materials. Temperature-dependent UV-vis spectra of the polymerized PCDA-based vesicle having cholesterol, FT-IR spectra at 1750–1600 cm^{-1} region of the polymerized PCDA vesicles before/after the photopolymerization and after the color change (blue to red), and a microcalorimetry thermogram of PCDA-cholesterol vesicle (20 mol %) before the polymerization were shown in the Supplementary Materials.

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