Rational Design and in-Situ FTIR Analyses of Colorimetrically Reversibe Polydiacetylene Supramolecules

Jong-Man Kim,*,† Ji-Seok Lee,⊥,† Hyun Choi,⊥,§ Daewon Sohn,‡ and Dong June Ahn*,§

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea; Department of Chemistry, Hanyang University, Seoul 133-791, Korea; and Department of Chemical and Biological Engineering, and Institute for Nano Science, Korea University, Seoul 136-701, Korea

Received July 16, 2005; Revised Manuscript Received September 1, 2005

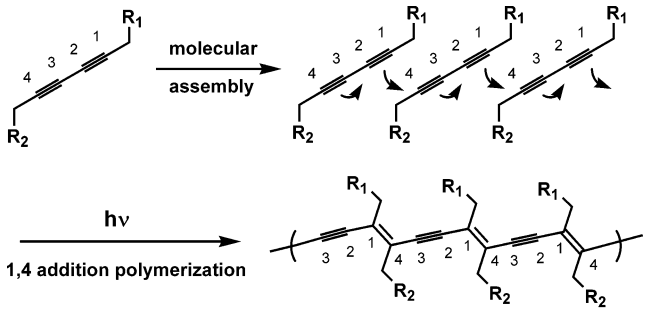
ABSTRACT: The colorimetric reversibility of polydiacetylene supramolecules, derived from a variety of functionalized diacetylenic lipids, has been subjected to detailed investigation. In an earlier effort, it was shown that polydiacetylene vesicles prepared from PCDA-*m*BzA **1**, bearing terminal *m*-carboxyphenylamido groups, display complete reversibility upon thermal stimulation [*J. Am. Chem. Soc.* **2003**, *125*, 8976]. The origin and nature of reversible thermochromism in these systems have been elucidated in-situ in the current studies by using polydiacetylene supramolecules, prepared from analogues of PCDA-*m*BzA **1**. Issues related to the effects of (1) internal amide groups, (2) headgroup aromatic interactions, (3) lengths of the hydrophobic alkyl chains, and (4) terminal carboxylic groups on the colorimetric reversibility of the polydiacetylene supramolecules have been probed. The results demonstrate that well-developed hydrogen-bonding and aromatic interactions between headgroups are essential for complete recovery of the length of the conjugated π-electron chain following thermal stimulus. The results of this comprehensive investigation allow for the first time the rational design of reversible colorimetric sensors based on polydiacetylene supramolecules.

Introduction

The development of efficient chemosensors based on conjugated polymers continues to be topic of great interest in both fundamental and applied research areas.[1] Conjugated polymer systems are highly attractive because changes in their absorption, emission, and redox properties are sensitive functions of environmental perturbations. A major advantage of using conjugated polymer-based chemosensors, in comparison to conventional sensors based on small molecules, is found in the potential for signal amplification when subjected to external stimuli. As a result, a wide variety of conjugated polymers, including polythiophenes,[2−5] polyanilines,[6−8] polypyrroles,[9] polyphenylenes,[10] and poly(phenylene ethynylenes),[11−14] polyacetylenes,[15] and polydiacetylenes,[16−37] have been investigated as sensing matrices.

Among the conjugated polymers reported to date, polydiacetylene (PDA)-based chemosensors are unique in terms of method of preparation, molecular structure, and output signal. Unlike other conjugated polymers, functionalized polydiacetylenes are prepared by using photopolymerization of self-assembled diacetylene monomers (Scheme 1). Closely packed and properly ordered diacetylene lipids undergo polymerization via 1,4-addition reaction to form alternating ene−yne polymer chains upon irradiation with 254 nm light (in the case of thin films/vesicle solutions) or with γ-irradiation (in the case of solid powders). Polydiacetylenes, generated

Scheme 1. Schematic Representation of Polymerization of Assembled Functional Diacetylenes by Irradiation with UV Light



(R_1 = functionalized alkyl chain, R_2 = alkyl chain)

under optimized photochemical conditions, color intense blue. In general, nanostructured polydiacetylenes investigated for use as potential chemosensors are prepared as vesicles in aqueous solutions,[25] Langmuir−Blodgett (LB)/Langmuir−Schaefer (LS) films,[28] or immobilized vesicles[38−40] on solid supports.

The unique property of nanostructured polydiacetylenes that leads to their application as sensing elements is the occurrence of a color change from blue to red that takes place in response to a variety of environmental perturbations such as temperature, pH, and ligand−receptor interactions.[16−33] Polydiacetylene films and vesicles, functionalized with carbohydrates, have proven to be effective biosensors for the detection of the influenza virus,[28] cholera toxin,[22] and *E. coli.*[33] Colorimetric detection of glucose, based on ligand-induced conformational changes of hexokinase immobilized on a polydiacetylene monolayer, stands as another elegant application of polydiacetylenes biosensing.[18] A system for selective detection of metal ions, formed by embedding an ionophore into the polydiacetylene liposome,

* To whom the correspondence should be addressed. Jong-Man Kim: Tel +82-2-2220-0522, Fax +82-2-2298-4101, e-mail jmk@hanyang.ac.kr. Dong June Ahn: Tel +82-2-3290-3301, Fax +82-2-926-6102, e-mail ahn@korea.ac.kr.

† Department of Chemical Engineering, Hanyang University.

‡ Department of Chemistry, Hanyang University.

§ Korea University.

⊥ Equally contributed to this work.

10.1021/ma051551i CCC: $30.25 © 2005 American Chemical Society
Published on Web 10/07/2005

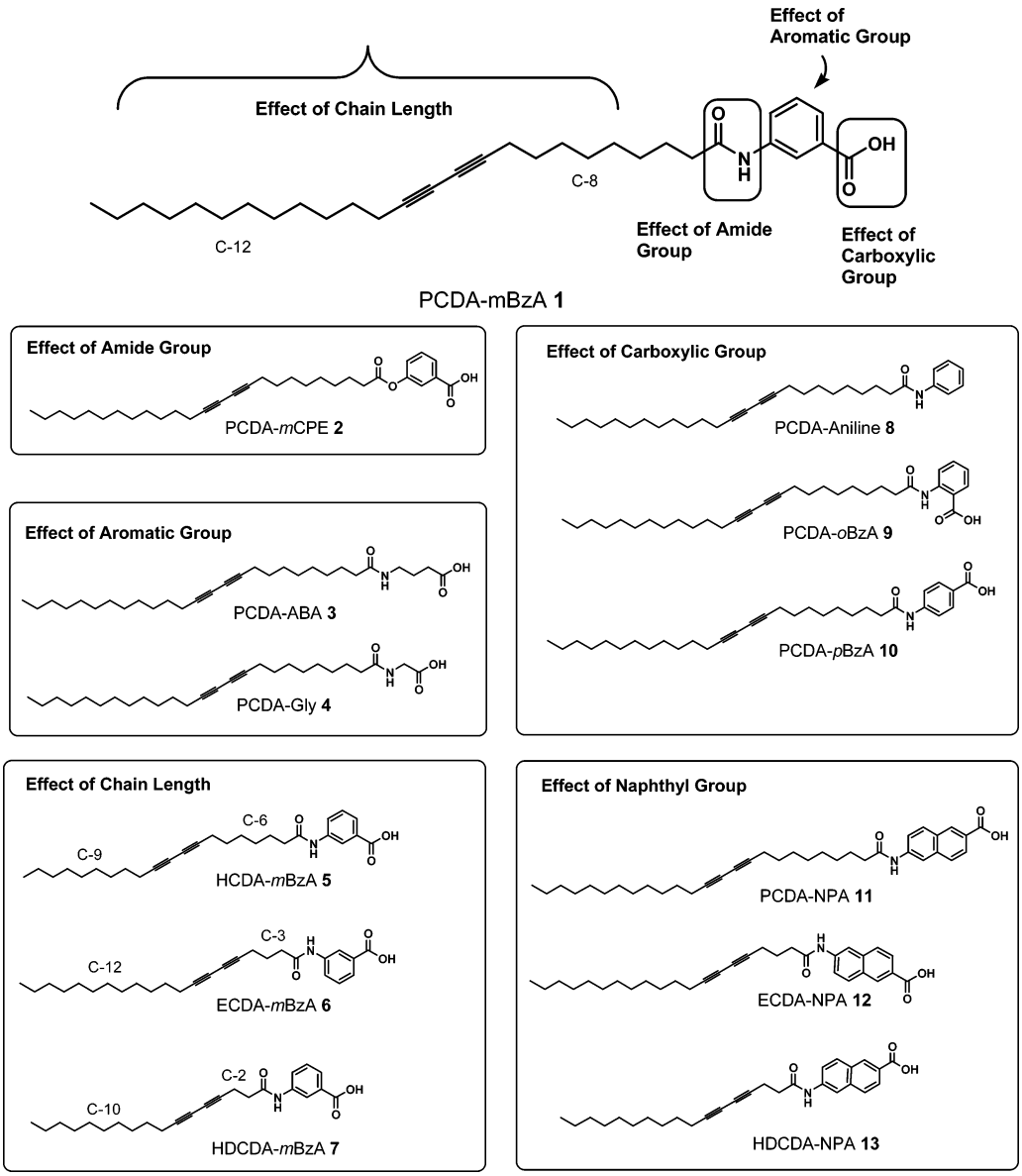


Figure 1. Structures of diacetylene lipids investigated for thermochromism.

also has been reported.[21] Very recently, a polydiacetylene sensor system, based on specific antibody−antigen interaction, has been developed.[25] Finally, we have observed cyclodextrin-induced color changes in a polymerized diacetylene Langmuir−Schaefer film.[41]

The polydiacetylene-based chemosensors reported thus far function in an irreversible fashion. Accordingly, the blue-to-red color change that takes place when an external stimulus is applied is not reversed when the external stimulus is removed. To the best of our knowledge, only a few examples of reversible chromism of the polydiacetylenes have been reported to date. Included in this short list are diacetylenic phospholipids vesicles in aqueous solution,[42] PDA/silica nanocomposites,[43] spin-coated PDA films,[44] a polydiacetylene crystal,[37] and urethane-substituted polydiacetylene powders.[45] Recently, colorimetric reversibility in ion binding to a hydrazide-modified, single-chain diacetylene lipid was described.[20]

Importantly, a comprehensive analysis of the structure-related origin of colorimetric reversibility in polydiacetylene-based supramolecules has not been carried out. Pertinent to this issue is our recent observation that carboxy-substituted anilido diacetylene PCDA-*m*BzA **1** derived, polydiacetylene supramolecules undergo completely reversible color transitions upon thermal and pH stimuli.[46] In the effort described below, we have executed a detailed investigation of the origin of colorimetric reversibility in these polydiacetylene supramolecules. In addition, the influence of structural changes on thermochromism of these supramolecules has been explored mainly by using in-situ FTIR spectroscopic analyses revealing detailed headgroup interactions. Specifically, we have studied the effects of (1) amide hydrogen bonding, (2) aromatic interactions, (3) alkyl chain lengths, and (4) carboxylic groups on the reversibility thermochromism. For these purposes, a variety of diacetylene lipids (Figure 1) have been prepared. Included in this list is the ester group containing diacetylene monomer PCDA-*m*CPE **2**, which was used to gain information about the role played by amide hydrogen-bonding interactions. Effects of aromatic interaction on reversible thermochromism were probed with the aminobutyric acid- and glycine-derived diacetylene lipids PCDA-ABA **3** and PCDA-Gly **4**. The diacetylenes, HCDA-*m*BzA **5**, ECDA-*m*BzA **6**, and

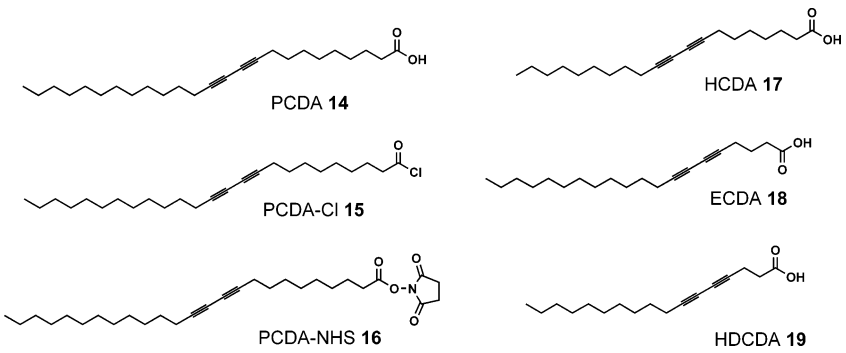


Figure 2. Structures of diacetylene derivatives used for the synthesis of lipid monomers.

HDCDA-*m*BzA **7**, having different numbers of methylene groups in their alkyl chains, were employed to study the effects of the chain length on colorimetric transitions. The influence of carboxylic groups on the polymerization process and thermochromism was examined by using the aniline-derived diacetylene lipid PCDA-aniline **8** and the *ortho*- and *para*-carboxy-substituted diacetylenes, PCDA-*o*BzA **9** and PCDA-*p*BzA **10**. Finally, the naphthoic acid-derived diacetylene lipids PCDA-NPA **11**, ECDA-NPA **12**, and HDCDA-NPA **13** were studied to gain information about how extended aromatic interactions govern thermochromism.

Results

Preparation of Diacetylene Lipid Monomers. The diacetylenic lipid monomers used in this study were prepared from the diacetylene derivatives shown in Figure 2. Commercially available 10,12-pentacosadiynoic acid (PCDA, **14**) was converted either to the acid chloride PCDA-Cl **15** or to the *N*-hydroxysuccinic ester PCDA-NHS **16**. Treatment of the acid chloride PCDA-Cl **15** with the appropriate aniline derivatives gave the diacetylene lipids PCDA-*m*BzA **1**, PCDA-aniline **8**, PCDA-*o*BzA **9**, PCDA-*p*BzA **10**, and PCDA-NPA **11**. The acid chloride PCDA-Cl **15** was coupled with 3-hydroxybenzoic acid to give the desired ester derivative PCDA-*m*CPE **2**. The activated ester PCDA-NHS **16** was employed in the preparation of the aminobutyric acid derivative PCDA-ABA **3** and the glycine-derived diacetylene lipid PCDA-Gly **4**. Using similar approaches, the diacetylene derivatives HCDA-*m*BzA **5**, ECDA-*m*BzA **6**, HDCDA-*m*BzA **7**, ECDA-NPA **12**, and HDCDA-NPA **13** were generated starting with 8,10-heneicosadiynoic acid (HCDA **17**), 5,7-eicosadiynoic acid (ECDA **18**), and 4,6-heptadecadiynoic acid (HDCDA **19**).

Preparation of Polydiacetylene Vesicles. Routine procedures were used to transform the diacetylene lipid monomers to polydiacetylene vesicles in aqueous solution and Langmuir−Schaefer (LS) film on OTE glass. The polydiacetylene vesicles were prepared by probe sonication of the diacetylene derivatives in HEPES buffer or in deionized water, followed by irradiation with 254 nm light. The diacetylene lipid monomers **1**−**7** undergo polymerization to form stable blue vesicles. In contrast, the aniline-derived diacetylene monomer PCDA-aniline **8** does not form vesicles under these conditions, owing to the hydrophobic nature of the headgroup. The *ortho*-positioned carboxylic group containing diacetylene lipid PCDA-*o*BzA **9** rapidly generates aggregates. This phenomenon is likely due to intramolecular hydrogen bonding between the amide hydrogen and the carbonyl group of the carboxylic moiet which prevents intermolecular interaction between the neighboring headgroups.

Table 1. Properties of Polymerized Diacetylenes

diacetylene lipid	vesicle formation (λ_{max}, nm)	vesicle size (nm)[a]	color of solution	stability of vesicles
PCDA-*m*BzA **1**	Y (648)	224	blue	stable
PCDA-*m*CPE **2**	Y (647)	88	blue	stable
PCDA-ABA **3**	Y (647)	174	blue	stable
PCDA-Gly **4**	Y (648)	ND	blue	stable
HCDA-*m*BzA **5**	Y (648)	236	blue	stable
ECDA-*m*BzA **6**	Y (659)	ND	blue	stable
HDCDA-*m*BzA **7**	Y (611)	ND	blue	stable
PCDA-aniline **8**	N	ND	ND	ND
PCDA-*o*BzA **9**	Y	aggregate	purple	unstable
PCDA-*p*BzA **10**	Y (638)	138	blue	stable
PCDA-NPA**11**	Y (636)	128	blue	stable
ECDA-NPA **12**	Y (638)	130	blue	stable
HDCDA-NPA **13**	Y (638)	164	blue	stable
PCDA **14**	Y (638)	232	blue	stable
HCDA **17**	Y	aggregate	blue	unstable
ECDA **18**	Y	aggregate	blue	unstable
HDCDA **19**	Y	aggregate	blue	unstable

[a] Determined by dynamic light scattering; ND = not determined.

Irradiation of these aggregates produces blue aggregates. In contrast, stable polydiacetylene vesicles are formed from the *para*-substituted diacetylene monomer PCDA-*p*BzA **10** and thenaphthoic acid-containing diacetylene lipids **11**−**13**. The properties of the polydiacetylene vesicles are summarized in Table 1.

Scanning electron microscope (SEM) images of the polydiacetylene vesicles, prepared with PCDA-*m*BzA **1**, ECDA-NPA **12**, and PCDA **14**, are shown in Figure 3. Independent of the nature of headgroup and the chain length, the polymerized diacetylene vesicles are nearly spherically shaped with sub-100 nm diameters. These shape/size characteristics are seen with the other vesicles prepared in this study (see Supporting Information). The deviation in these diameters from those of polydiacetylene vesicles in aqueous solution (ca. 100−250 nm, by dynamic light scattering) suggests that significant shrinkage of the vesicles occur in the dehydrating process associated with sample preparation for the SEM images.

Preparation of Polydiacetylene LS Films. Monomeric diacetylene derivatives were assembled into ordered multilayers on Langmuir troughs. After irradiation with 254 nm UV light, the polymerized diacetylene layers were transferred by using the horizontal touch method (Langmuir−Schaefer method) to the hydrophobized glass substrate. All the diacetylene monomers except the one derived from diacetylene derivative **9** were formed stable blue LS films.

The transmission and near-normal external reflection FTIR spectra of the LS films, arising by polymerization

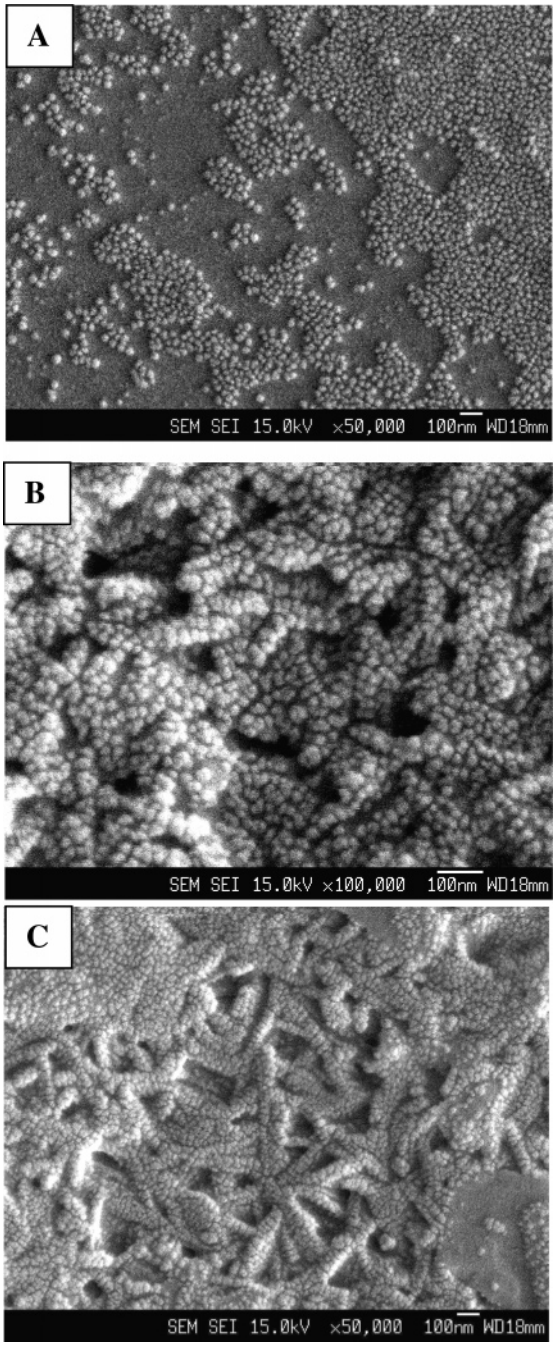


Figure 3. SEM images of polydiacetylene vesicles prepared from PCDA-mBzA **1** (A), ECDA-NPA **12** (B), and PCDA **14** (C).

of the diacetylene derivatives, are displayed in Figure 4, and the peak assignments are listed in Table 2. These data show that the degree and nature of hydrogen bonding between the headgroups are dependent on the structures of the starting diacetylene monomers. Polydiacetylene LS films arising from PCDA **14**, HCDA **17**, ECDA **18**, and HDCDA **19**, monomers with terminal carboxylic moieties that are commonly used for further derivatization, showed hydrogen-bonded carbonyl stretching bands around 1694−1690 cm^{-1}. The film from terminal phenyl ring containing PCDA-aniline **8** showed hydrogen-bonded amide and carbonyl stretching bands at 3292 and 1659 cm^{-1}, respectively, along with a ring stretching band at 1600 cm^{-1}. In contrast, three bands attributed to hydrogen bonding are observed for the PCDA-*m*BzA **1** (3281, 1690, 1657 cm^{-1}), PCDA-*o*BzA **9**

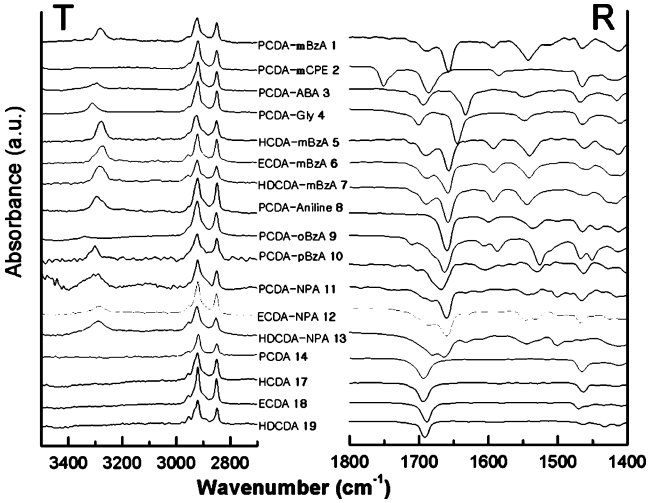


Figure 4. Transmission (T) and near-normal external reflection (R) FTIR spectra of LS films of polymerized diacetylene derivatives deposited on glass.

(3340, 1710, 1663 cm^{-1}), and PCDA-*p*BzA **10** (3302, 1702, 1669 cm^{-1}) derived polydiacetylenes. In this series, the lower positions of the three bands for the film from PCDA-*m*BzA **1** show that hydrogen-bonding interactions are relatively strong. The comparison of data for PCDA **14**, PCDA-aniline **8**, and PCDA-*m*BzA **1** shows that the latter polydiacteylene film has the stronger or comparable terminal carbonyl hydrogen bond (1690 cm^{-1}) and amide−carbonyl hydrogen bond (3281 and 1657 cm^{-1}). Replacement of the ester for an amide group (PCDA-*m*CPE **2**) results in deletion of amide related hydrogen bonding, as seen by a shift in the carbonyl band to 1751 cm^{-1}. When the *m*-carboxyphenylamido group is replaced by either aminobutric acid (PCDA-ABA **3**) or glycine (PCDA-Gly **4**), the three hydrogen-bonding related bands remain unchanged, although the aromatic phenyl group is absent. Interestingly, variations in the alkyl chain length (HCDA-*m*BzA **5**, ECDA-*m*BzA **6**, and HDCDA-*m*BzA **7**) have no effect on the hydrogen-bonding interactions (compared to PCDA-mBzA **1**). Finally, introduction of naphthoic acid moieties (as in films from PCDA-NPA **11**, ECDA-NPA **12**, and HDCDA-NPA **13**) results in a moderate enhancement of the strength of terminal carboxyl group hydrogen bonds but a decreased amide hydrogen bonding in comparison to the respective phenyl analogues (PCDA-*m*BzA **5**, ECDA-*m*BzA **6**, and HDCDA-*m*BzA **7**).

Thermochromism of Polydiacetylene Vesicles in Solution. To investigate the reversibility of colorimetric transitions, PDA solutions of the polydiacetylene vesicles were gradually heated to 90 °C while monitoring color changes by using UV−vis spectroscopy. The spectral data obtained with liposome solutions prepared from representative diacetylene monomers are given in Figure 5 (see Supporting Information for the complete UV−vis spectroscopic profiles).

At room temperature, a solution of the PDA vesicle, prepared from the PCDA-*m*BzA **1**, shows the typical blue color corresponding to a visible absorption maximum wavelength at 640 nm (Figure 5A). When the temperature is raised from 25 to 90 °C, the absorption maximum of the solution undergoes a gradual blue shift which plateaus at 580 nm. Upon cooling to 25 °C, the absorption maximum shifts back to 640 nm, and the original intensity is recovered. The complete thermally promoted colorimetric reversibility of this system was

Table 2. Peak Assignments of LS Films of Polydiacetylene Derivatives

derivatives	νNH (cm^{-1})	$\nu_a CH_2$ (cm^{-1})	$\nu_s CH_2$ (cm^{-1})	νC=Oⓐ[a] (cm^{-1})	νC=Oⓑ[b] (cm^{-1})	phenyl or naphthyl bands (cm^{-1})	CNH (cm^{-1})
PCDA-*m*BzA **1**	3281	2921	2849	1690	1657	1594	1543
PCDA-*m*CPE **2**		2919	2849	1686	1751	1585	
PCDA-ABA **3**	3297	2920	2850	1694	1633		1549
PCDA-Gly **4**	3312	2920	2850	1700	1645		1549
HCDA-*m*BzA **5**	3280	2922	2848	1689	1656	1593	1544
ECDA-*m*BzA **6**	3273	2923	2850	1688	1658	1593	1541
HDCDA-*m*BzA **7**	3286	2922	2851	1689	1658	1593	1544
PCDA-aniline **8**	3292	2919	2848		1659	1600	1537
PCDA-*o*BzA **9**	3340	2922	2852	1710	1663	1606, 1587	1526
PCDA-*p*BzA **10**	3302	2920	2849	1702	1669	1605	1530
PCDA-NPA **11**	3291	2921	2850	1686	1660	1633, 1614, 1574	1544, 1534
ECDA-NPA **12**	3283	2921	2851	1687	1660	1632, 1606, 1581	1546, 1533
HDCDA-NPA **13**	3290	2923	2853	1681	1664	1632, 1612, 1582	1544
PCDA **14**		2919	2848	1694			
HCDA **17**		2921	2850	1694			
ECDA **18**		2920	2851	1690			
HDCDA **19**		2920	2849	1692			

[a] Carbonyl stretching at terminal carboxylic group. [b] Carbonyl stretching at amide group.

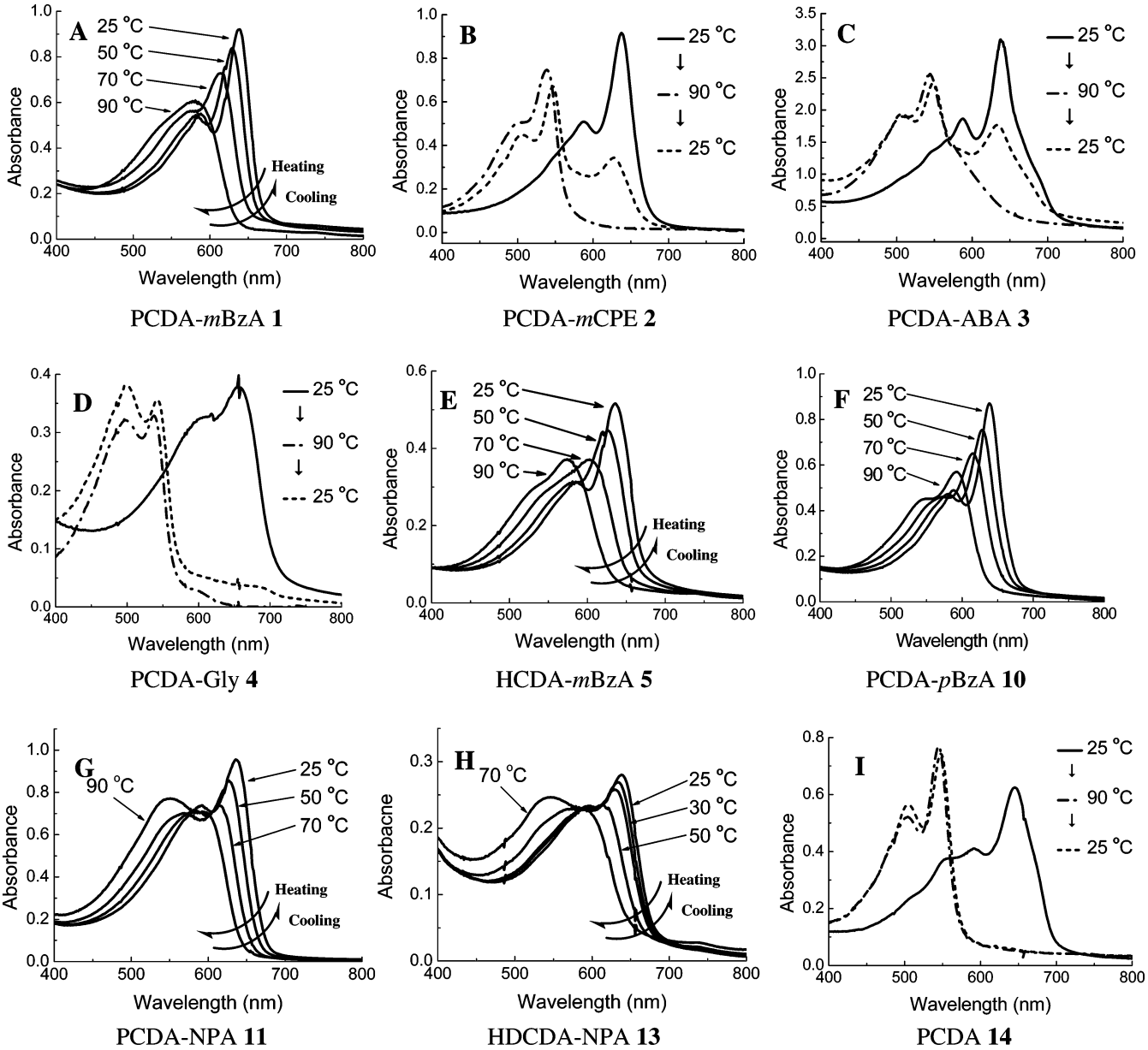


Figure 5. Visible spectroscopic monitoring of PDA derivatives liposome solution upon heating and cooling process.

demonstrated by repeating the thermal cycle without losing the initial and final respective intensities at 640 and 580 nm. In addition, when the vesicle solution is subjected to prolonged heating at the reflux tempera-

ture, the color of the solution became pink, and the original blue color returned when the solution is cooled to room temperature.

In contrast, a solution of polymer vesicles prepared from PCDA-*m*CPE **2**, an ester analogue of PCDA-*m*BzA **1**, does not display thermally stimulated colorimetric reversibility. Heating the solution from room temperature to 90 °C produced a color change from blue to orange-red, and the original blue color did not return completely when the solution is cooled to 25 °C. As can be seen by monitoring absorption spectrum of the solution (Figure 5B), heating the solution from room temperature to 90 °C resulted in a shift in the absorption maximum from 640 to 550 nm where it remained almost unchanged (only partial recovery of the peak at 640 nm) upon cooling the solution back to 25 °C.

The next systems studied enabled us to probe the effects of the aromatic interactions on colorimetric reversibility. Compared with PCDA-*m*BzA **1**, the aminobutyric acid-derived PCDA-ABA **3** has a similar distance between the amide group and the terminal carboxylic group except that it does not contain a phenyl ring. A solution of polymerized vesicles prepared from **3** was subjected to the heating−cooling processes. As shown in Figure 5C, spectroscopic monitoring demonstrates that these vesicles display partial colorimetric reversibility.

To gain more information about the role of the phenyl group, polymerized vesicles prepared from PCDA-Gly **4**, which has a shorter alkyl chain connecting the headgroup than in PCDA-ABA **3**, were investigated. The color of a solution of these vesicles changed from blue to orange-red upon heating, and the orange-red color remained unchanged when the solution was cooled to 25 °C. No peak recovery at 650 nm was observed during the cooling process (Figure 5D).

The effect of hydrophobic carbon chain lengths on the reversible thermochromism was investigated with HCDA-*m*BzA **5**, EDCA-*m*BzA **6**, and HDCDA-*m*BzA **7**. These three lipids have the same headgroups but shorter length alkyl tails than PCDA-*m*BzA **1**. Interestingly, the length of the alkyl chain was found to have a negligible effect on the colorimetric reversibility of the resulting polymerized vesicles. Thus, complete reversibility was observed with solutions containing the polymer vesicles made of **5**, **6**, and **7**. The reversible visible spectral changes promoted by thermal stimulation of a solution of polymerized vesicles prepared from HCDA-*m*BzA **5** are shown in Figure 5E. It is intriguing that HDCDA-*m*BzA **7**, which has only two methylene units between the diacetylene group and the amide headgroup, forms stable blue polydiacetylene vesicles. The HDCDA **19** which has the same number of methylene units as HDCDA-*m*BzA **7** was found to form highly unstable polymer vesicles that eventually generated significant amounts of aggregates.

The effect of the terminal carboxylic groups on the nature of colorimetric reversibility was probed by using polydiacetylene vesicles made from lipid monomers PCDA-aniline **8**, PCDA-*o*BzA **9**, and PCDA-*p*BzA **10**. Among the three, PCDA-*p*BzA **10** produces stable blue polymer vesicles which in solution display complete colorimetric reversibility (Figure 5F).

The effect of naphthyl groups on colorimetric reversibility was investigated by using solutions of polymer vescicles generated from PCDA-NPA **11**, ECDA-NPA **12**, and HDCDA-NPA **13**. The three monomers have

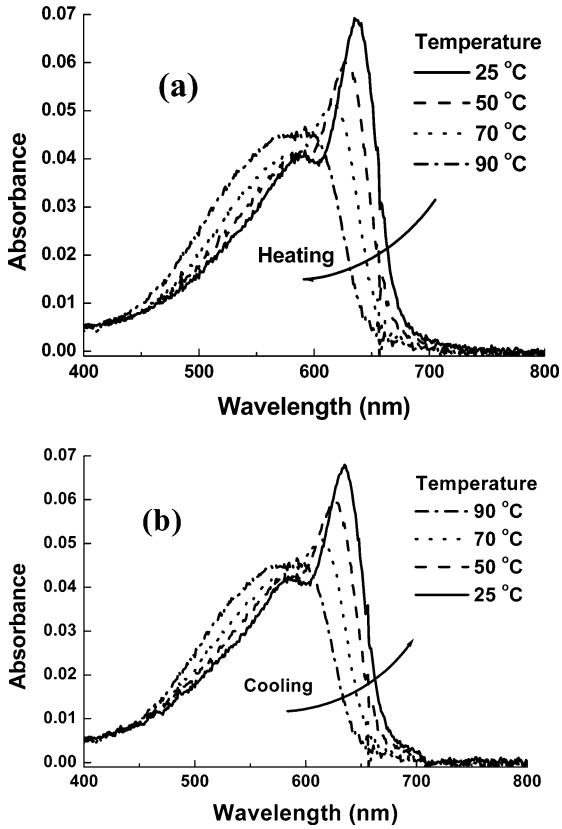


Figure 6. Visible spectroscopic monitoring of PDA LS films prepared with PCDA-*m*BzA **1** upon heating (a) and cooling (b) process.

naphthalene moieties, and as a result, the degree of aromatic interactions is expected to be larger than in polymers made from PCDA-*m*BzA **1**, ECDA-*m*BzA **6**, and HDCDA-*m*BzA **7**. In fact, solutions of polymer vesicles derived **11**, **12**, and **13** all display complete colorimetric reversibility upon thermal stimulation. In addition, it was found that polymer vesicles prepared from these monomers are much more stable than those derived from the corresponding phenyl analogues, PCDA-*m*BzA **1**, ECDA-*m*BzA **6**, and HDCDA-*m*BzA **7**, respectively. Comparison of visible spectroscopic monitoring of polymerized PCDA-NPA **11** (Figure 5G) and HDCDA-NPA **13** (Figure 5H) indicates that the latter having a shorter length in side alkyl chain is more sensitive in changing color against thermal stimulus.

Figure 5I shows visible spectroscopic monitoring of PDA vesicles prepared with PCDA **14**. As well-known, irreversible color transition was observed upon heating and cooling cycles.

Thermochromism of Polydiacetylene LS Films. Visible spectroscopic monitoring of the thermal perturbation of a polymerized diacetylene LS film derived from PCDA-mBzA **1** is shown in Figure 6. The qualitative spectral changes are nearly identical to those observed with the solution of polymer vesicles (Figure 5A). Basically, no significant differences are observed between the spectral changes caused by heating solutions of polydiacetylene vesicles or LS films derived from other lipid monomers (see Supporting Information). Interestingly, the lipid monomer from PCDA-aniline **8**, which does not form stable polymer vesicles in solution, generates blue LS films. The LS film from **8**, however, is colorimetrically irreversible when the thermal stimulus is removed following the initial color transition from

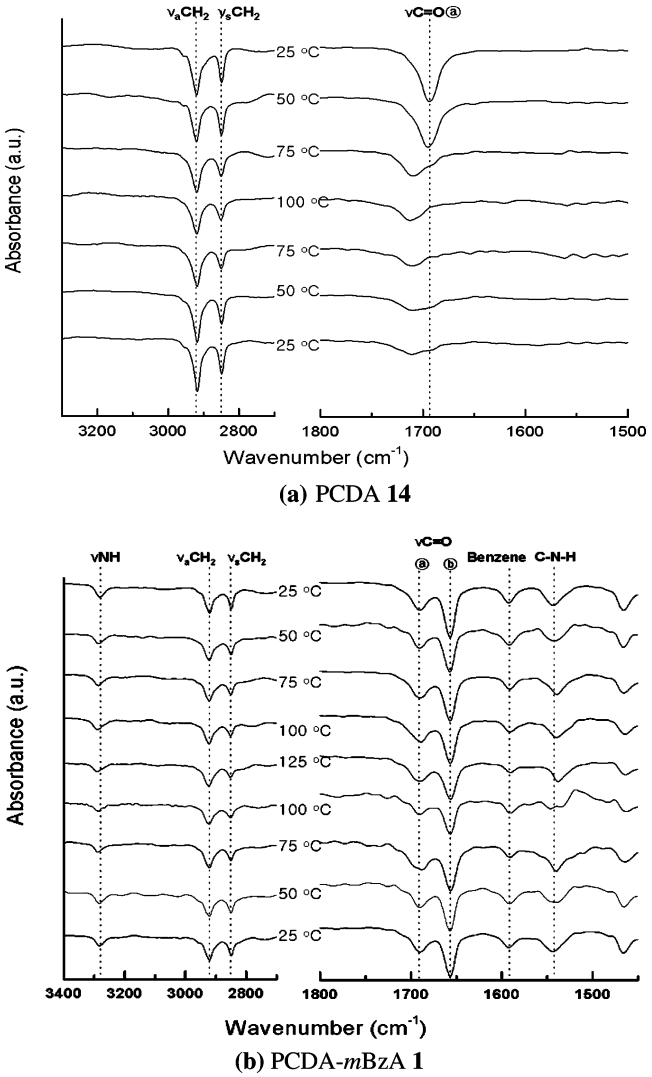


Figure 7. In-situ near-normal external reflection FTIR spectra of LS films of PCDA **15** (a) and PCDA-*m*BzA **1** (b) on hydrophobized glasses: νC=O ⓐ and ⓑ stand for carbonyl stretching bands in terminal carboxyl and amide positions, respectively.

blue to red. The purple LS film arising from lipid monomer PCDA-*o*BzA **9** displays us irreversible color changing properties. The *para*-substituted lipid PCDA-*p*BzA **10**, which forms a stable blue solution of polymerized vesicles, also forms a faint blue LS film whose color is thermally and completely reversible.

To gain more insight into the thermally promoted colorimetric reversibility of polymerized diacetylenes, in-situ FTIR analysis of the LS films was carried out in the 10° near-normal external reflection mode (Figures 7 and 8, Table 3). Common to all the derivatives studied, peaks associated with methylene stretching modes shift to higher wavenumbers when the film is heated but return to their initial positions when the sample is cooled, which has been reported for fatty acid Langmuir−Blodgett films and has been described in terms of "order-to-disorder" transition mechanism.[47] In Figure 7 are recorded the in-situ FTIR analyses of PCDA **14** (Figure 7a), a typical monomer which displays irreversible thermochromism, and PCDA-*m*BzA **1** (Figure 7b), one that typifies reversible thermochromism. When heated to >75 °C, the hydrogen-bonded carbonyl stretching band of the film from PCDA **14** shifts from an initial value of 1694 cm^{-1} to 1712 cm^{-1}, indicating that the strength of the hydrogen bond decreases. However, upon cooling the sample to 25 °C, the carbonyl stretching band remains at ca. 1711 cm^{-1}, showing that the strength of hydrogen bonding is not recovered. In contrast, the LS film derived from PCDA-*m*BzA **1** retains the strength of its hydrogen bond throughout the heating and cooling cycle as indicated by the absence of a change in the position of the carbonyl stretching band.

The FTIR method described above was used to determine whether parallels exist between reversible thermochromism properties of other LS films and thermally promoted changes in hydrogen bond strengths (Figure 8). The LS film, derived from PCDA-*m*CPE **2**, that does not display complete colorometric reversibility shows a decreased peak intensity in the terminal carbonyl band upon heating. The other thermochromically irreversible films show similar behavior. For example, the one from PCDA-ABA **3** that lacks an aromatic group shows terminal carbonyls of which hydrogen bonding is disrupted as in the case of PCDA **14**, along with amide hydrogen-bonded carbonyls recoverable. Also, for the PCDA-aniline **8** film in which a terminal carboxylic group is absent, a recoverable hydrogen-bonded carbonyl in the amide group is observed. In contrast, when the colorimetrically reversible film from PCDA-NPA **11** is subjected to the thermal cycle, the peak position and intensity for the hydrogen-bonded carbonyl bands remain nearly constant. It is noted that the same behavior is observed for thermochromically reversible films from PCDA-*m*BzA **1**, HCDA-*m*BzA **5**, and PCDA-*p*BzA **10** (see Supporting Information). The trends noted in the FTIR studies demonstrate that strong hydrogen-bonding and aromatic interactions which are retained at high temperature is an essential requirement for the reversibility of thermochromism in polydiacetylene LS films. These interactions enable the length of the conjugated π-electron system to be regenerated after the thermal stimulus is removed.

Discussion

Several significant issues have been addressed in the effort described above, which focused on elucidating the effects of (1) amide groups, (2) aromatic headgroups, (3) hydrophobic chain length, and (4) terminal carboxylic groups on the thermocolorimetric reversibility of the polymerized diacetylene vesicles. The observations made in experiments, in which thermally promoted changes in color and hydrogen-bonding interactions were measured and correlated (summarized in Table 4), strongly suggest that cooperative and integrated interactions between amide, aromatic, and carboxylic acid headgroups are a necessary condition for achieving color reversibility of polymerized diacetylenes. Accordingly, complete thermochromic reversibility takes place in polymers (e.g., those from PCDA-*m*BzA **1**, HCDA-*m*BzA **5**, PCDA-*p*BzA **10**, and PCDA-NPA **11)** where hydrogen-bonding interactions remain unchanged throughout the thermal cycle. When the cooperative interactions between the headgroups are insufficiently strong (e.g., in ploymers from PCDA-*m*CPE **2**, PCDA-ABA **3**, and PCDA-aniline **8**) only partial reversibility is observed. Finally, in the extreme case where hydrogen-bonding interactions are absent or irreversibly disrupted, as in the polymer from PCDA **14** and most of those studied previously, the color change is completely irreversible. Observations made in studies with polymer vesicles

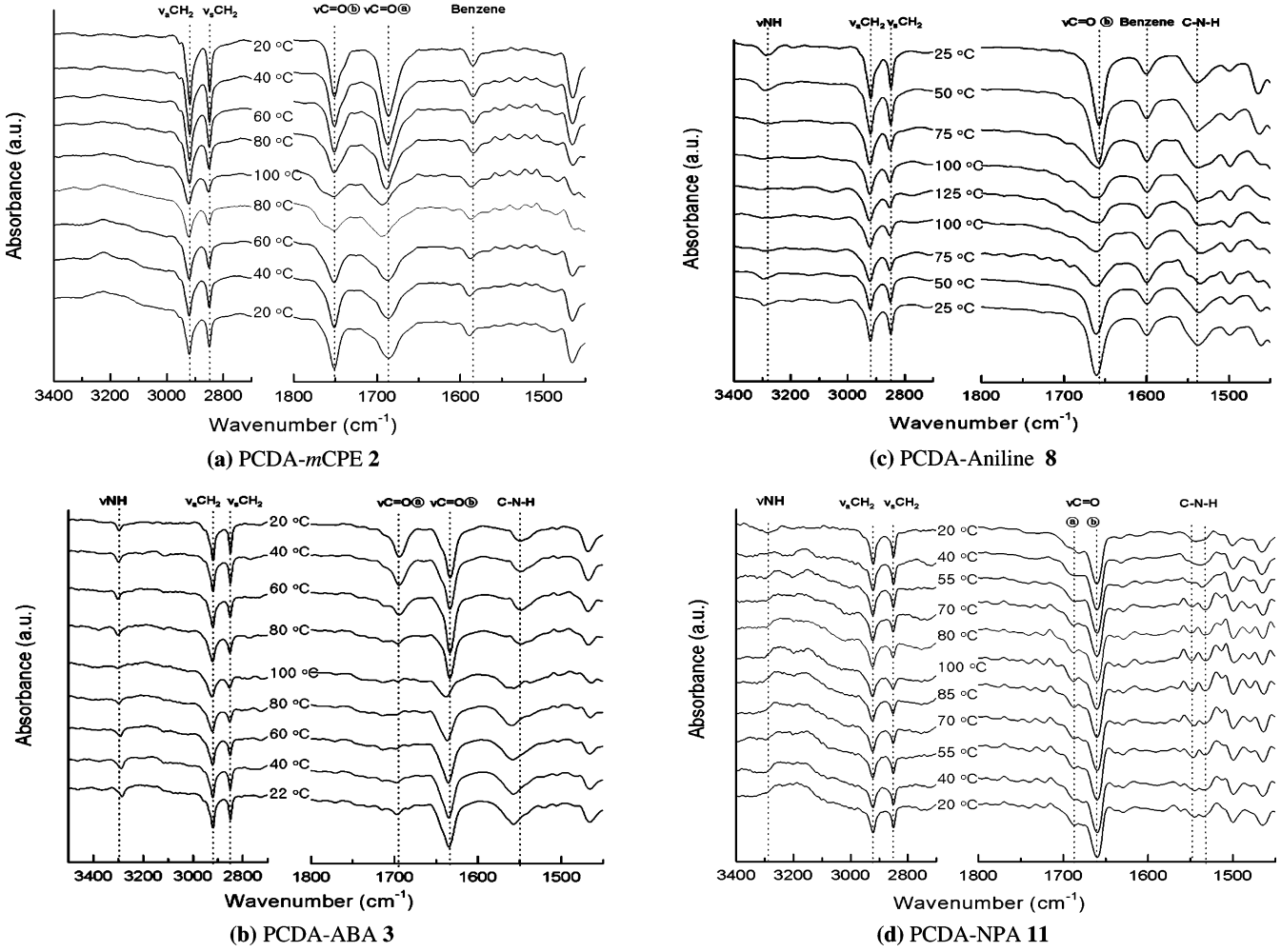


Figure 8. In-situ near-normal external reflection FTIR spectra of LS films of PCDA-*m*CPE **2** (a), PCDA-ABA **3** (b), PCDA-aniline **8** (c), and PCDA-NPA **11** (d) on hydrophobized glasses: νC=O ⓐ and ⓑ stand for carbonyl stretching bands in terminal carboxyl and amide positions, respectively.

prepared from PCDA-*m*CPE **2** clearly indicate that internal hydrogen-bondable amide groups are required in order to obtain a reversible color change upon thermal stimulation. A similar observation was made in solid-state ^{13}C NMR studies of urethane-substituted polydiacetylene powders.[41]

Another important factor governing the reversibility of thermochromism in these systems is aromatic interactions between headgroups. Structural effects on the colorimetric reversibility in polymers derived from PCDA-*m*BzA **1** and PCDA-ABA **3** give useful information on this effect. Since the distances between the headgroups in each of these polymers should be nearly identical, their different thermochromic properties must be a consequence of the phenyl group in the material arising from **1**. Thus, the colorimetric irreversibility observed with polydiacetylenes made from PCDA-ABA **3** demonstrates the importance of aromatic headgroups. Interestingly, the presence of aromatic headgroups not only influences colorimetric reversibility but also has a pronounced effect on the stability of polydiacetylenes. For example, the diacetylene lipid HDCDA **19** (Figure 2) does not form stable polymer vesicles in aqueous solution presumably as a result of the fact that it contains too short of a methylene chain (only two methylenes) between the diacetylene and terminal carboxylic moieties. Addition of an aminobenzoic acid unit to HDCDA **19**, as is the case in diacetylene lipid HDCDA-*m*BzA **7**, allows formation of a solution of stable blue polymer vesicles that display thermochromic reversibility. Even more stable polymer vesicles with enhanced colorimetric reversibility are generated from naphthalene-derived lipid HDCDA-NPA **13**.

Investigations of the effect of the hydrophobic chain length on the colorimetric reversibility have led to the important conclusion that recovery of the conjugation length of the π-electron chromophore after thermal stimualtion of polydiacetylene polymers is possible when strong interactions between headgroups are present.

In addition, the results of this effort show that polydiacetylene polymers containing terminal carboxylic acid groups are optimal for further applications. Two important reasons exist for this conclusion. First, the hydrophilic nature of carboxylic groups allows efficient formation of lipid bilayers in aqueous solution. Second, carboxylic acid groups form strong hydrogen bonds with neighboring carboxylic groups as indicated by analysis of the FTIR spectra shown in Figure 4. Accordingly, the diacetylene derivative PCDA-aniline **8**, which lacks a carboxylic acid group, does not form polymerized vesicles in aqueous solution. In addition, the *ortho*-substituted lipid monomer PCDA-*o*BzA **9** undergoes photopolymerization to afford unstable purple polymer vesicles that immediately aggregate. This result is presumably caused by the preference for intramolecular hydrogen bonding between the amide and *ortho*-positioned carboxylic

Table 3. Changes in Peak Positions Measured in-Situ during Thermal Cycles

derivatives	temp (°C)	NH stretching (ν NH, cm^{-1})	asymmetric methylene stretching ($\nu_a CH_2$, cm^{-1})	symmetric methylene stretching ($\nu_s CH_2$, cm^{-1})	carbonyl stretching in carboxyl group (νC=O ⓐ, cm^{-1})	carbonyl stretching in amide group (νC=O ⓑ, cm^{-1})
PCDA-*m*BzA **1**	25	3281	2920	2849	1690	1657
	75	3287	2921	2851	1690	1657
	100	3289	2922	2852	1689	1657
	75	3288	2921	2852	1690	1656
	25	3282	2920	2850	1690	1657
PCDA-*m*CPE **2**	20		2919	2849	1686	1751
	60		2921	2851	1688	1752
	100		2923	2853	1694	1752
	60		2921	2851	1687	1752
	20		2920	2850	1686	1751
PCDA-ABA**3**	20	3297	2920	2850	1694	1633
	60	3302	2921	2851	1695	1634
	100	3302	2924	2853	1696	1638
	60	3299	2921	2851	1699	1635
	22	3285	2920	2850	1698	1634
HCDA-*m*BzA **5**	30	3280	2922	2848	1689	1656
	75	3289	2922	2850	1688	1657
	98	3290	2923	2850	1688	1657
	77	3286	2921	2850	1688	1657
	30	3282	2922	2849	1689	1657
PCDA-aniline**8**	25	3292	2919	2848		1659
	75		2922	2852		1659
	125		2923	2853		1660
	75		2922	2852		1660
	25	3293	2921	2849		1659
PCDA-*p*BzA **10**	30	3302	2920	2849	1702 (shoulder)	1669
	58	3307	2921	2851	1702 (shoulder)	1669
	80	3311	2922	2852	1702 (shoulder)	1670
	60	3306	2922	2851	1702 (shoulder)	1669
	30	3305	2920	2850	1702 (shoulder)	1668
PCDA-NPA**11**	20	3291	2921	2850	1686	1660
	70		2923	2852	1688	1660
	100		2924	2852	1688	1660
	70		2923	2851	1685	1660
	20		2922	2851	1686	1660
PCDA**14**	25		2919	2848	1694	
	75		2922	2852	1709	
	100		2923	2853	1712	
	75		2922	2852	1711	
	25		2921	2849	1711	

Table 4. Summary of in-Situ FTIR Observations of Molecular Interactions Influencing Colorimetric Reversibility of Polydiacetylene Supramolecules (I: Peak Intensity; Δ: Peak Shift)

derivatives	observed reversibility	H-bonding at the terminal carbonyl group	H-bonding at the amide carbonyl group	aromatic interaction
PCDA-*m*BzA **1**	yes	maintained	maintained	yes
PCDA-*m*CPE **2**	partial	weakened (I: decreased; Δ: little but recovered)	not H-bonded	yes
PCDA-ABA **3**	partial	weakened (I: decreased a lot;Δ: yes)	recovered (I: decreased but recovered; Δ: little but recovered)	none
HCDA-*m*BzA **5**	yes	maintained	maintained	yes
PCDA-aniline **8**	partial	none	recovered (I: decreased but recovered; Δ: no)	yes
PCDA-*p*BzA **10**	yes	maintained	maintained	yes
PCDA-NPA **11**	yes	maintained	maintained	yes
PCDA**14**	no	weakened (I: decreased a lot; Δ: yes)	none	none

groups which blocks interchain hydrogen bonding. Supporting this proposal is the finding that the *para*-substituted diacetylene lipid PCDA-*p*BzA **10** generates blue stable polymer vesicles in aqueous solution that display complete colorimetric reversibility.

Conclusions

The observations made in the investigations described above have led to a greater fundamental understanding of how structural changes effect the thermochromic reversibility of polydiacetylene supramolecules. A significant conclusion drawn from this effort is that strong, integrated double hydrogen-bonding networks and aromatic interactions in headgroups provide supramolecular assemblies (vesicles and films) with the capability of recovering their initial molecular structures and average π-electron conjugation length following external stimulation. This conclusion is relevant to numerous studies in which irreversible polydiacetylene supramolecular assemblies have been used to detect various molecular recognition events. The findings summarized in this report should lay the foundation for the development of new and versatile reversible sensors based on polydiacetylenes.

Experimental Section

Materials. 10,12-Pentacosadiynoic acid (PCDA, **14**), HCDA **17**, ECDA **18**, and HDCDA **19** were purchased from GFS chemicals. 10,12-Pentacosadiynoic acid chloride (PCDA-Cl **15**)

and the *N*-hydroxysuccinimide ester of 10,12-pentacosadiynoic acid (PCDA-NHS **16**) were prepared as described in the literature.[48] The diacetylenic monomers PCDA-*m*BzA **1**, PCDA-aniline **8**, PCDA-*o*BzA **9**, and PCDA-*p*BzA **10** were previously reported.[46]

Preparation of Diacetylene Monomers. The diacetylene monomers investigated in this study were prepared by coupling either the acid chlorides (for the preparation of **2**, **5**, **6**, **7**, **11**, **12**, and **13**) or *N*-hydroxysuccininic esters (for the preparation of **3** and **4**) of PCDA **14**, HCDA **17**, ECDA **18**, or HDCDA **19** with corresponding amines or alcohol. A typical procedure for the preparation of PCDA-*m*CPE **2** is as follows. To a solution containing 1.39 g (3.70 mmol) of 10,12-pentacosadiynoic acid in 20 mL of methylene chloride was added dropwise 0.94 g (7.4 mmol) of oxalyl chloride at room temperature. The resulting solution was stirred at room temperature for 1 h. To the solution was added a catalytic amount (one drop) of DMF and stirred for an additional hour. After concentrating in vacuo, the residue was redissolved in 15 mL of methylene chloride. The resulting solution was added dropwise to the solution containing 0.66 g (4.81 mmol) of 3-aminobenzoic acid in 15 mL of THF. The resuting mixture was allowed to stir for overnight at room temperature. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (4:1 chloroform: methanol) to give 0.48 g (26%) of the desired diacetylene monomer PCDA-*m*CPE **2** as a white solid. Other diacetylene monomers were also prepared by employing similar procedures. Spectroscopic data for the monomers are as follows:

PCDA-*m*CPE **2**: mp 71 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3H), 1.20−1.80 (m, 36H), 2.22 (t, 4H), 2.35 (t, 2H), 7.07−7.55 (m, 5H), 7.18 (brs, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 13.86, 18.39, 22.21, 24.27, 27.86, 28.30, 28.44, 28.87, 29.16, 31.43, 33.45, 65.38, 77.495, 122.60, 126.19, 126.59, 129.68, 132.34, 150.46, 166.49, 171.55.

PCDA-ABA **3**: mp 80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, 3H), 1.20−1.62 (m, 36H), 1.86 (q, 1H), 2.18 (t, 1H), 2.21−2.38 (m, 6H), 2.24 (t, 1H), 2.42 (t, 1H), 3.35 (q, 1H), 5.72 (s, 1H), 7.50 (t, 1H), 7.82 (s, 1H), 7.98 (d, 1H), 7.18 (brs, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.02, 18.29, 22.14, 24.65, 27.72, 28.41, 29.04, 31.05, 31.34, 35.38, 40.33, 65.35, 77.92, 172.02, 174.27.

PCDA-Gly **4**: mp 96 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.86 (t, 3H), 1.20−1.62 (m, 28H), 2.11 (t, 2H), 2.28 (t, 4H), 3.69 (t, 3H), 8.08 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 18.35, 22.20, 25.22, 27.85, 28.29, 28.52, 28.65, 28.83. 29.13, 31.41, 35.07, 40.53, 65.39, 77.82, 171.52, 172.54.

HCDA-mBzA **5**: mp 164 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.83 (t, 3H), 1.20−1.65 (m, 36H), 2.31 (t, 6H), 7.41 (t, 1H), 7.60 (d, 1H), 7.81 (d, 1H), 8.23 (s, 1H), 10.07 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.67, 19.02, 22.85, 25.64, 28.46, 28.84, 29.19, 29.45, 29.67, 32.05, 37.06, 66.09, 78.52, 78.60, 120.49, 123.71, 124.44, 129.55, 132.08, 140.25, 167.98, 172.13.

ECDA-*m*BzA **6:** mp 202 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.85 (t, 3H), 1.24−1.45 (m, 22H), 1.77 (m, 2H), 2.25−2.42 (m, 6H), 7.38 (t, 1H), 7.57 (d, 1H), 7.78 (d, 1H), 8.20 (s, 1H), 10.09 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 13.95, 18.04, 18.30, 22.15, 23.65, 27.75, 28.25, 28.48, 28.78, 29.07, 31.35, 35.10, 65.32, 65.79, 77.28, 78.17, 119.84, 123.10, 123.82, 128.88, 131.24, 139.45, 167.21, 170.66.

HDCDA-*m*BzA **7**: mp 71 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.85 (t, 3H), 1.23−1.44 (m, 17H), 2.26 (t, 2H), 2.50−2.60 (m, 4H), 7.40 (t, 1H), 7.59 (d, 1H), 7.78 (d, 1H), 8.20 (s, 1H), 10.15 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 13.95, 14.65, 18.30, 22.16, 27.72, 28.25, 28.48, 28.74, 28.99, 31.35, 34.78, 65.25, 65.49, 76.90, 78.39, 119.81, 123.11, 124.01, 129.00, 131.30, 139.29, 167.18, 169.35.

PCDA-NPA **11**: mp 215 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.84 (t, 3H), 1.22−1.42 (m, 37H), 2.26 (t, 4H), 2.37 (d, 2H), 7.60 (d, 1H), 7.90 (q, 1H), 8.04 (d, 1H), 8.40 (s, 1H), 8.49 (s, 1H), 10.22 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 13.89, 18.07, 18.98, 22.76−37.25, 66.09, 78.72, 114.50, 121.09, 123.31, 125.45, 128.51, 129.53, 130.84, 135.70, 139.76, 168.84, 172.34.

ECDA-NPA **12**: mp 231 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.81 (t, 3H), 1.22−1.40 (m, 22H), 1.81 (t, 2H), 2.08 (s, 1H), 2.24 (t, 2H), 2.39 (t, 2H), 7.65 (d, 2H), 7.87(q, 2H), 8.03 (d, 1H), 8.39 (s, 1H), 8.49 (s, 1H), 10.29 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 13.89, 14.06, 18.09, 18.33, 22.18, 23.67, 27.77, 28.30, 28.52, 28.83, 29.13, 31.38, 35.24, 65.34, 65.85, 77.27, 78.14, 114.42, 120.09, 125.35, 126.46, 127.52, 128.63, 130.23, 135.79, 139.00, 167.54, 171.01.

HDCDA-NPA **13**: mp 242 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.82 (t, 3H), 1.21−1.42 (m, 17H), 2.26 (t, 2H), 2.63 (s, 4H), 7.66 (d, 1H), 7.89 (q, 2H), 8.04 (d,1H), 8.39 (s, 1H), 8.51 (s, 1H), 10.35 (s, 1H). ^{13}C NMR (300 MHz, DMSO-d_6): δ = 13.95, 14.69, 18.29, 22.16, 27.69, 28.01, 28.45, 28.69, 28.96, 31.33, 34.88, 65.28, 65.53, 77.00, 78.47, 114.54, 119.00, 123.17, 126.56, 127.62, 128.71, 130.27, 135.76, 138.79, 167.53, 169.75.

General Procedures for Liposome Formation. 10,12-Pentacosadiynoic acid (PCDA) was dissolved in chloroform, and the organic solvent was removed by purging with N_2 to generate a thin lipid film on the glass surface. A buffer solution (HEPES, 5 mM, pH = 8.0) or deionized water was added to yield a total PCDA lipid concentration of 1 mM. The samples were then heated at 80 °C for 15 min and sonicated for 15 min. The resulting solution was filtered through a 0.8 μm filter, and the filtrate was cooled at 4 °C for 12 h. Polymerization was carried out at room temperature by irradiating the solutions with 254 nm UV light (1 mW/cm^2).

Preparation of Langmuir−Schaefer (LS) Films. An aliquot of the solution containing 1 mM of a PCDA derivative in organic solvent ($CHCl_3$ or DMSO for chloroform-insoluble diacetylenes) was spread onto the air/water interface of a KSV Langmuir trough containing deionized (DI) water (the initial resistivity = 18 MΩ·cm, Milli-Q water purifier) as the subphase. The substances were equilibrated at 25 °C for 20 min to allow solvent to be removed from the interface. The lipid film was overcompressed at a surface pressure of 30 mN/m to form multilayers and polymerized by irradiation with the 254 nm UV light (1 mW/cm^2) for 45 s to give blue films. By the horizontal-touch Langmuir−Schaefer (LS) method, the prepared films were then transferred to glass slides previously hydrophobized with self-assembled octadecanoic triethoxysilane molecules and to CaF_2 substrates for further FTIR analyses.

Colorimetric Responses upon Thermal Stimuli. For experiments imposing thermal stimulus, heating from and cooling to room temperature were done with a heating cell. The instrument (HP 8453) was temperature-controlled, and the actual sample temperature was monitored. The visible spectra of the polymer vesicle solutions and LS films at different temperatures were acquired with a UV−vis spectrophotometer.

FTIR Analyses. An FTIR spectrometer (Perkin-Elmer Spectrum GX1) was used to acquire transmission and 10° near-normal external reflection spectra for the LS films deposited on glass slides. The MCT detector was cooled with liquid nitrogen, and 256 scans with a resolution of 4 cm^{-1} were accumulated to give reasonable signal-to-noise ratios. Nonpolarized infrared beam was used. The in-situ external reflection spectra at 10° from the surface normal were obtained after the samples maintained at desired temperatures for 30 min by using a house-built temperature-controlled heating element designed to fit in the sample chamber of the spectrometer.

Light Scattering Measurement. A Spectra-Physics argon ion laser producing vertically polarized light of λ_0 = 488 nm was used. The detector optics employed optical fibers coupled to an ALV/SO-SIPD/DUAL detection unit that employed an EMI PM-28B power supply and ALV/PM-PD preamplifier/discriminator. The correlator was an ALV-5000/E/WIN multiple tau correlator with 288 exponentially spaced channels. The sampling time of the correlator ranged from 10^{-6} to 130 s. The cylindrical scattering cell was located in a bath of index matching solvent (decalin) that was maintained at room temperature. The band-pass filter for 488 nm was used. Each correlation function was gathered at five different angles from θ = 30° to 90°.

Scanning Electron Microscopy (SEM). SEM images of polydiacetylene vesicles studied here were obtained on a JEOL (JSM-6330F). Samples were freshly made and deposited dropwise on gold coated silicon wafers with a 10 μL microsyringe. Pure Au (99.99%, KISTAR) was evaporated on silicon wafer. All Au−silicon wafers deposited with polydiacetylene vesicles were dried for at least 5 h in an incubator, which was followed by coating with Pt for 15 min.

Acknowledgment. Financial support for this research was provided by KOSEF (Basic Research Program, Center for Ultramicrochemical Process Systems) and by KRF.

Supporting Information Available: SEM images of PDA vesicles, UV−vis spectra of PDA solutions and LS films upon heating and cooling processes, and in-situ near-normal external reflection FTIR spectra of PDA LS films. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Recent reviews on conjugated polymer-based sensors: (a) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537. (b) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201. (c) Okada, S.; Peng, S.; Spevak, W.; Charych, D. *Acc. Chem. Res.* **1998**, *31*, 229. (d) Jelinek, R.; Kolusheva, S. *Biotechnol. Adv*. **2001**, *19*, 109. (e) Leclerc, M. *Adv. Mater.* **1999**, *11*, 1491. (f) Goldenberg, L. M.; Bryce, M. R.; Petty, M. C. *J. Mater. Chem.* **1999**, *9*, 1957.
(2) Ho, H.-A.; Boissinot, M.; Bergeron, M. G.; Corbeil, G.; Doré, K.; Boudreau, D.; Leclerc, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1548.
(3) Cassagneau, T.; Caruso, F. *Adv. Mater.* **2002**, *14*, 1629.
(4) Bäuerle, P.; Emge, A. *Adv. Mater.* **1998**, *3*, 324.
(5) Zhu, S. S.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1996**, *118*, 8713.
(6) Shoji, E.; Freund, M. S. *J. Am. Chem. Soc.* **2002**, *124*, 12486.
(7) Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 314.
(8) Pringsheim, E.; Terpetschnig, E.; Piletsky, S. A.; Wolfbeis, O. S. *Adv. Mater.* **1999**, *11*, 865.
(9) Korri-Youssoufi, H.; Yassar, A. *Biomacromolecules* **2001**, *2*, 58.
(10) Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 896.
(11) Wosnick, J. H.; Mello, C. M.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 3400.
(12) Pinto, M. R.; Kristal, B. M.; Schanze, K. S. *Langmuir* **2003**, *19*, 6523.
(13) Chen, L.; McBranch, D. W.; Wang, H.-L.; Helgelson, R.; Wudl, F.; Whitten, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 12287.
(14) Wang, B.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1997**, *119*, 12.
(15) Liu, Y.; Mills, R. C.; Boncella, J. M.; Schanze, K. S. *Langmuir* **2001**, *17*, 7452.
(16) Okada, S. Y.; Jelinek, R.; Charych, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 655.
(17) Charych, D. H.; Cheng, Q.; Reichert, A.; Kuziemko, G.; Stroh, M.; Nagy, J. O.; Spevak, W.; Stevens, R. C. *Chem. Biol.* **1996**, *3*, 113.
(18) Cheng, Q.; Stevens, R. C. *Adv. Mater.* **1997**, *9*, 481.
(19) Berman, A.; Ahn, D. J.; Lio, A.; Salmeron, M.; Reichert, A.; Charych, D. *Science* **1995**, *269*, 515.
(20) Jonas, U.; Shah, K.; Norvez, S.; Charych, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 4580.
(21) Kolusheva, S.; Shahal, T.; Jelinek, R. *J. Am. Chem. Soc.* **2000**, *122*, 776.
(22) Pan, J. J.; Charych, D. *Langmuir* **1997**, *13*, 1365.
(23) Huo, Q.; Russell, K. C.; Leblanc, R. M. *Langmuir* **1999**, *15*, 3972.
(24) Ma, Z.; Li, J.; Liu, M.; Cao, J.; Zou, Z.; Tu, J.; Jiang, L. *J. Am. Chem. Soc.* **1998**, *120*, 12678.
(25) Kolusheva, S.; Kafri, R.; Katz, M.; Jelinek, R. *J. Am. Chem. Soc.* **2001**, *123*, 417.
(26) Jelinek, R. *Drug. Dev. Res.* **2000**, *50*, 497.
(27) Kolusheva, S.; Shahal, T.; Jelinek, R. *Biochemistry* **2000**, *39*, 15851.
(28) Charych, D. H.; Nagy, J. O.; Spevak, W.; Bednarski, M. D. *Science* **1993**, *261*, 585.
(29) Song, J.; Cisar, J. S.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2004**, *126*, 8459.
(30) Rangin, M.; Basu, A. *J. Am. Chem. Soc.* **2004**, *126*, 5038.
(31) Huo, Q.; Wang, S.; Pisseloup, A.; Verma, D.; Leblanc, R. M. *Chem. Commun.* **1999**, 1601.
(32) Kim, T.; Chan, K. C.; Crooks, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 189.
(33) Li, Y.; Ma, B.; Fan, Y.; Kong, X.; Li, J. *Anal. Chem.* **2002**, *74*, 6349.
(34) Day, D.; Ringsdorf, H. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 205.
(35) Wegner, G. *Z. Naturforsch. B* **1969**, *24*, 824.
(36) Tieke, B.; Lieser, G.; Wegner, G. *J. Polym. Sci., Polym. Chem.* **1979**, *17*, 1631.
(37) Chance, R. R.; Baughman, R. H.; Mûller, H.; Eckhardt, C. J. *J. Chem. Phys.* **1977**, *67*, 3616.
(38) Kim, J.-M.; Ji, E.-K.; Woo, S.-M.; Lee, H.; Ahn, D. J. *Adv. Mater.* **2003**, *15*, 1118.
(39) Shim, H. Y.; Lee, S. H.; Ahn, D. J.; Ahn, K.-D.; Kim, J.-M. *Mater. Sci. Eng., C* **2004**, *24*, 157.
(40) Stanish, I.; Santos, J. P.; Singh, A. *J. Am. Chem. Soc.* **2001**, *123*, 1008.
(41) Cho, J.-T.; Woo, S.-M.; Ahn, D. J.; Ahn, K.-D.; Lee, H.; Kim, J.-M. *Chem. Lett.* **2003**, *32*, 282.
(42) Singh, A.; Thompson, R. B.; Schnur, J. *J. Am. Chem. Soc.* **1986**, *108*, 2785.
(43) Yang, Y.; Lu, Y.; Lu, M.; Huang, J.; Haddad, R.; Xomeritakis, G.; Liu, N.; Malanoski, A. P.; Sturmayr, D.; Fan, H.; Sasaki, D. Y.; Assink, R. A.; Shelnutt, J. A.; Swol, F.v.; Lopez, G. P.; Burns, A. R.; Brinker, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 1269.
(44) Yuan, Z.; Lee, C.-W.; Lee, S.-H. *Angew. Chem., Int. Ed.* **2004**, *43*, 4179.
(45) Lee, D.-C.; Sahoo, S. K.; Cholli, A. L.; Sandman, D. J. *Macromolecules* **2002**, *35*, 4347.
(46) Ahn, D. J.; Chae, E.-H.; Lee, K. S.; Shim, H.-Y.; Chang, T.-E.; Ahn, K.-D.; Kim, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 8976.
(47) Ahn, D. J.; Franses, E. I. *J. Phys. Chem.* **1992**, *96*, 9952 and references therein.
(48) Cheng, Q.; Yamamoto, M.; Stevens, R. C. *Langmuir* **2000**, *16*, 5333.

MA051551I