

Polydiacetylene/Silica Nanocomposites with Tunable Mesostructure and Thermochromatism from Diacetylenic Assembling Molecules

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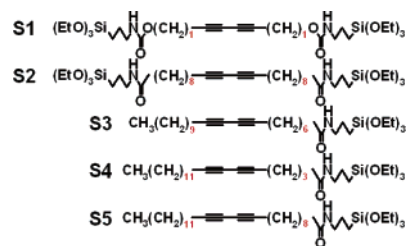
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Polydiacetylene (PDA) exhibits an intense chromatic switch from blue to red in response to external stimuli.¹ This colorimetric change can be easily perceived by the naked eye, making PDA an ideal candidate for sensing materials. To date, PDA materials in the forms of vesicles,² liposomes,¹ Langmuir–Blodgett films,³ casting films,⁴ and nanocomposites⁵ have been synthesized, and their chromatic responses to various stimuli, including temperature,⁵ pH,⁶ ions,⁷ solvent,⁸ stress,⁹ or ligand interactions, have been demonstrated.¹⁰ However, most of the chromatic responses are irreversible, limiting their application in colorimetric sensing.² By enhancing hydrogen-bonding interactions among the headgroups of PDA side chains, reversible chromatic transitions were recently observed in the PDA vesicles and Langmuir–Schaefer films.^{2,11} Robust PDA nanocomposite thin films that can be easily processed and that exhibit true colorimetric reversibility, however, have not yet been realized.

Herein, we report the synthesis of PDA/silica nanocomposite thin films with tunable mesostructure and reversible chromatic transition using a simple sol–gel assembling process. Beginning with a series of predesigned diacetylenic organosilanes, R'Si(OR)₃ or (RO)₃Si–R'–Si(OR)₃, where OR is a hydrolyzable alkoxy group (e.g., OC₂H₅) and R' is a polymerizable diacetylenic ligand, the hydrolysis reactions create amphiphilic diacetylenic silicate species. Collective noncovalent interactions direct their assembly during the coating process, resulting in the formation of nanocomposites with ordered mesostructures. Subsequent topochemical polymerization of the diacetylenic moieties produces robust PDA/silica nanocomposites (Schemes 1 and 2 in Supporting Information). In contrast to the previous studies, where the PDA side chains interacted weakly through noncovalent interactions (e.g., hydrogen bonding), the side chains in the present nanocomposites are covalently connected to the inorganic silica frameworks, providing control over the molecular alignment, stability, and electronic properties. Furthermore, the adjustable molecular architecture (e.g., the shape and side-chain length) allows control over the mesostructure (e.g., cubic and lamellar) and chromatic response of the nanocomposites. This work not only provides responsive robust chromatic materials toward practically reusable PDA sensors but also is of great fundamental value for the design of supramolecular assembly and the understanding of the chromatic mechanism of PDA.

Five diacetylenic silanes, S1, S2, S3, S4, and S5, were synthesized by reacting γ -isocyanatopropyltriethoxysilane with 2,4-hexadiyne-1,6-diol, 10,12-docosadiyndioic acid, 5,7-eicosadiynoic acid, 8,10-heneicosadiynoic acid, and 10,12-pentacosadiynoic acid, respectively, in tetrahydrofuran (THF).¹² S1 and S2 contain two ethoxysilane (Si(OEt)₃) end groups bridged by a diacetylenic chain,



while S3, S4, and S5 contain only one ethoxysilane group connecting with a diacetylenic chain. The diacetylenic nanocomposite thin films were coated on glass slides using the precursor sols that were prepared by mixing 0.17 mmol of diacetylenic precursor, 1.5 mL of THF, and 1.0 mL of HCl (0.1 N) at room temperature for ~1 day. Subsequent UV radiation converted the transparent colorless thin films into blue PDA/silica nanocomposites films. Figure 1 shows X-ray diffraction (XRD) of the nanocomposite thin films, indicating the formation of highly ordered mesostructures. S1 and S2 are symmetric, favoring the formation of a lamellar mesostructure with intense (100) reflections at a *d* spacing of 2.5 nm (Figure 1a) and 3.8 nm (Figure 1b), respectively. For comparison, S3, S4, and S5 are asymmetric, similar to traditional surfactants.

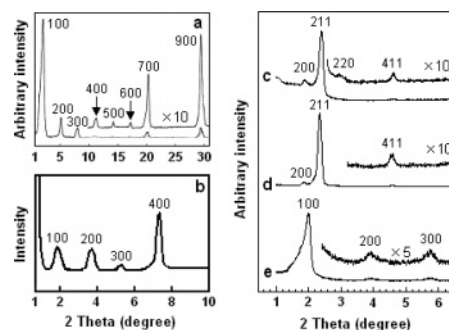


Figure 1. XRD patterns of the nanocomposites derived from S1 (a), S2 (b), S3 (c), S4 (d), and S5 (e).

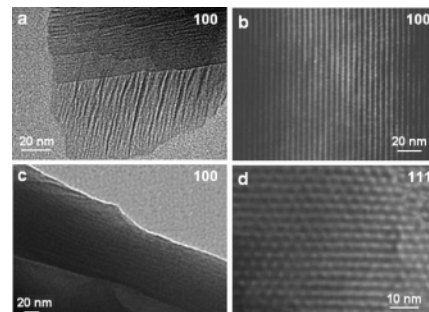


Figure 2. Representative TEM images of the nanocomposites derived from S1 (a), S2 (b), S5 (c), and S3 (d).

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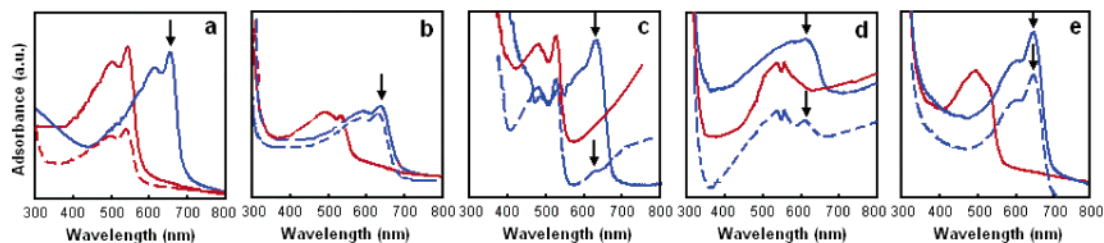


Figure 3. UV-vis spectra of the nanocomposite films subjected to a thermal cycle showing tunable chromatic reversibility. (a) S1, irreversible; (b) S2, reversible; (c) S3, partially reversible; (d) S4, partially reversible; (e) S5, reversible. The solid blue line, solid red line, and dashed line represent the spectra of the nanocomposites at room temperature prior to the thermal cycle, at 90 °C, and at room temperature after the thermal cycle, respectively.

Altering the length of the diacetylenic tails allows control over the molecular shape and the resulting mesophase. For example, S3 and S4, containing shorter diacetylenic chains (24 and 23 carbon atoms, respectively), favor the formation of a cubic mesophase with a unit cell parameter of 9.3 nm (Figure 1c and d). S5, possessing a longer diacetylenic chain (28 carbon atoms), self-organizes into a lamellar mesostructure with an intense (100) reflection at 4.4 nm (Figure 1e). These structural assignments were confirmed by transmission electron microscopy (TEM) (Figure 2). The nanocomposites assembled from S1 (2a), S2 (2b), and S5 (2c) show lamellar mesostructure with d spacings consistent with those obtained from XRD. *The periodic distance (5.2 nm) (Figure 2d, the nanocomposite from S3) is consistent with the (111) orientation of the cubic phase shown in Figure 1c.* The structural evolution of S3, S4, and S5 can be rationalized using the traditional surfactant packing parameter, $g = v/a_0l$, where v is the surfactant volume, a_0 is the area of the headgroup, and l is the tail length.² A shorter chain increases the packing parameter, favoring the formation of a higher curvature mesophase, such as a cubic phase; a longer chain reduces the packing parameter, favoring a lamellar mesophase.

The tunable molecular architecture provides the nanocomposites with adjustable thermochromic properties. Figure 3 shows UV-vis absorption spectra of the nanocomposites subjected to a temperature heating-cooling cycle. Typically, the main excitonic peak of the blue form occurs at ~640 nm with a vibronic maximum at ~590 nm, while for the red form, the excitonic peak appears at ~540 nm associated with a broad vibronic peak at ~490 nm. Once heated from room temperature to 90 °C, all of the nanocomposites demonstrate a chromatic transition from blue to red. Cooling the nanocomposites back to room temperature distinguishes the nanocomposites in terms of their colorimetric reversibility, from irreversible (S1) to partially reversible (S3, S4) and completely reversible (S2, S5). It is widely accepted that the color transition from blue to red is caused by a reduction of effective conjugation length resulting from distortions imposed by the backbone conformation.⁵ The distortions can be induced by the fluctuations within the side-chain layers activated by external stimuli.¹³ In fact, all successful colorimetric reversibilities reported, so far, are based on the enhanced hydrogen bonding among the headgroups of the side chains.^{2,11} In contrast, the present PDA assemblies are produced by covalent bonds formed through the hydrolysis and condensation reactions of the ethoxysilane groups. The complete thermochromic reversibility demonstrated by the S2 and S5 assemblies suggests that the stable covalent interactions between the PDA side chains and the inorganic silica network help restore the original chain conformations upon removal of the thermal stimuli. We noted that the flexibility of these side chains is also important for the chromatic reversibility. For example, S1, S4, S3, S2, and S5, which contain increasing numbers of carbon atoms (1, 3, 6, 8, and 8, respectively) between the diacetylenic ($-C\equiv C-C\equiv C-$) and the amide groups ($-CONH-$), provide the nanocomposites with increasing side-chain flexibility. As a result, the nanocomposites show systematically

chromatic responses from irreversible (S1) to partially reversible (S3, S4) and completely reversible (S2, S5).

The covalently bonded hybrid structure also provides the nanocomposites with better thermal stability. As reported,^{2,11} PDA may show reversible chromatic blue to red transition below a certain temperature (e.g., 77 °C for the noncovalent interactions based PDA assemblies^{11c}). Subjecting the PDA assemblies to a higher temperature results in an irreversible chromatic transition to yellow or orange.^{11c} However, because of the covalent interactions, the nanocomposite assembled from S5 shows a reversible chromatic transition at a much higher temperature of 96 °C. Furthermore, increasing the covalent interaction by using the bridging S2 building molecules raises the reversible temperature to 113 °C. Thermogravimetric analysis (TGA) also confirms the improved thermal stability. For example, the nanocomposites assembled from S2 and S5 decompose at 640 and 620 °C, respectively; these temperatures are significantly higher than the decomposition temperatures for PDA assembled from the corresponding diacetylenic acids (350 and 340 °C, respectively) (see Supporting Information).

In conclusion, we have demonstrated the design and synthesis of PDA organic/inorganic nanocomposites with adjustable mesostructure, controllable chromatic properties, and enhanced thermal stability using diacetylenic building molecules, providing novel platforms for sensing or other applications.

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Supporting Information Available: Detailed synthesis and thermochromic characterizations of PDA/silica materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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