

Letters

Supramolecular Assemblies with Tunable Morphologies from Homopolymeric and Small Organic Molecular Building Blocks

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This work demonstrates the formation of micrometer-sized supramolecular assemblies with tunable morphologies using a homopolymer, poly(4-vinylpyridine), and a small organic acid, 5,7-dodecadiynedioic acid, as the building molecules. Three different morphologies (hollow spheres, solid spheres, and rods) were obtained, depending on the molar ratio of the building molecules. It is proposed that hydrogen bonding between P4VP and DCDA and the π - π stacking of the diacetylenic moieties are responsible for the formation of these assemblies. Interestingly, ordered hexagonal and lamellar mesostructures were also formed within the microstructure during the co-assembly process. As a result, UV irradiation of the supramolecular assemblies polymerized the diacetylenic moieties, resulting in cross-linked and responsive blue polydiacetylenic assemblies that can change color to red upon external stimuli (e.g., thermal stimuli). This work provides a novel concept of the synthesis of responsive supramolecular assemblies from a homopolymer and small organic molecules.

Introduction

Micrometer-sized polymeric materials are of great interest for applications in biology, medicine, and photonic and electronic sensors.¹⁻⁵ Current synthesis methods often involve the self-organization of block or graft copolymers in selective solvents.⁶⁻⁹ The morphologies of such self-organized aggregates are controlled by tuning the intermolecular interactions among polymer chains or between copolymers and solvents.¹⁰ However, the synthesis of copolymers is lengthy and complicated, which may limit their practical applications. Herein, we demonstrate a novel route to produce micrometer-sized polymeric aggregates with controlled

morphologies (e.g. hollow spheres, solid spheres and rods) through the cooperative assembly of a homopolymer, poly(4-vinylpyridine) (P4VP), and an organic acid, 5,7-dodecadiynedioic acid (DCDA, $\text{HOOC}-(\text{CH}_2)_3\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_3-\text{COOH}$) in their common solvent, which is a mixture of THF and CHCl_3 . Hydrogen bonding between P4VP and DCDA and the π - π stacking of the diacetylenic moieties are believed to be responsible for the supramolecular assembly. In addition, the assemblies demonstrate ordered hexagonal and lamellar mesostructures. Ready polymerization of diacetylenic components upon UV irradiation further cross links the aggregate structure, producing blue responsive polydiacetylenic assemblies that switch to red under external stimuli (such as heating).

Experimental Section

5,7-Dodecadiynedioic acid (DCDA) and poly(4-vinylpyridine) (P4VP, $M_n = 65\,000$) were dissolved in a THF/ CHCl_3 mixed solvent (53/47 v/v). The DCDA solution was filtered to remove any polymerized impurity prior to use. The aggregates, with molar ratios (MR) of the carboxylic acid group (from DCDA) to the pyridine group (from P4VP) of 1/10, 1/2, and 1/1, were prepared by adding DCDA solution (10 mg/mL) to the P4VP solution (10 mg/mL)

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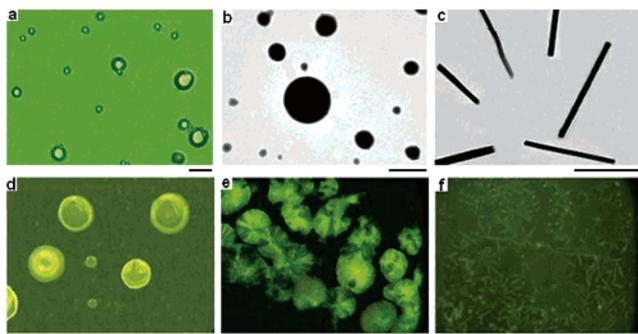


Figure 1. Optical (a), TEM (b, c), and fluorescence (d–f) micrographs of micrometer-sized polymeric aggregates prepared by the co-assembly of DCDA and P4VP in their common solvent at MRs of 1/10 (a, d), 1/2 (b, e), and 1/1 (c, f). Scale bars are 10 μm .

dropwise under ultrasound at room temperature. As-synthesized aggregate solutions were immediately dropped on glass slides for fluorescence and optical microscope observations. The microscopic studies were conducted on an Olympus IMT-2 inverted microscope connected to a high-resolution monitor (SONY) and an S-VHS VCR through a COHU CCD camera with $\lambda_{\text{ex}} = 508 \text{ nm}$. The samples for transmission electron microscopy (TEM, JEOL 2010 operated at 200 kV) were prepared by dropping aggregate solutions on copper grids in the open air. Dynamic laser light scattering (Brookhaven 90Plus) was used to measure the average hydrodynamic diameter of the aggregates. The measurements were performed at a fixed scattering angle (θ) of 90° . The aggregates were also characterized using X-ray diffraction (XRD, Phillips Xpert X-ray diffractometer, Cu K α radiation at $\lambda = 0.1542 \text{ nm}$) and UV–vis spectroscopy (BeckmanTM DU 640B UV–vis spectrophotometer).

Results and Discussion

Figure 1 shows the optical (a), TEM (b, c), and fluorescence (e–f) micrographs of the DCDA/P4VP aggregates prepared at MRs of 1/10 (a, d), 1/2 (b, e), and 1/1 (c, f), indicating the formation of three different morphologies: hollow spheres (a, d), solid spheres (b, e), and rods (c, f). The low MR of 1/10 results in the formation of hollow spheres with diameters ranging from 1 to 10 μm and with a shell thickness ranging from 0.2 to 1 μm (Figure 1a, d). Increasing the MR to 1/2 leads to the formation of solid spheres with similar sphere-size distributions (Figure 1b, e). Further increasing the MR to 1/1 mainly yields rod-shaped aggregates with diameters ranging from 200 to 400 nm and with lengths ranging from 4 to 20 μm (Figure 1c, f). Note that a small population of spherical particles was also found from the fluorescence micrograph (Figure 1f) and the TEM observation (not shown). The relative population of spheres to rods was determined by the rate of DCDA addition to the P4VP solution. For example, a slow addition of DCDA solution to the P4VP solution (e.g., 2 to 3 drops/s) led to a rod-dominating morphology, whereas a quick addition of DCDA solution to the P4VP solution increased the population of spheres.

Figure 2 shows X-ray diffraction (XRD) patterns of the assemblies prepared at MRs of 1/10 (a), 1/2 (b), and 1/1 (c), respectively. The presence of diffraction peaks at small angles suggests the formation of ordered mesostructures within these assemblies. The hollow spherical assemblies prepared at an MR of 1/10 show diffractions at 7.1 and 4.1 nm, which can be indexed as the (100) and (110) diffractions of a close-packed hexagonal mesostructure. The solid spherical assemblies prepared at an MR of 1/2 and the rod-shape assemblies prepared at an MR of 1/1 show multiordered lamellar diffractions with (100) at 7.0 and 6.8 nm, respectively. Consistent with the XRD results, the cross-sectional TEM image of the hollow spheres (Figure 2d)

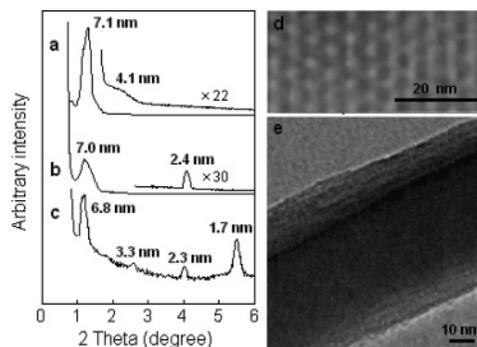


Figure 2. XRD patterns (a–c) and TEM images (d–e) of the DCDA/P4VP assemblies prepared at MRs of 1/10 (a, d), 1/2 (b), and 1/1 (c, e) showing the formation of ordered hexagonal and lamellar mesostructures within the assemblies.

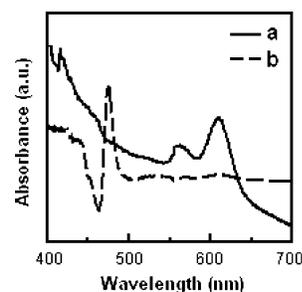


Figure 3. UV–vis spectra of polymerized aggregate solutions (MR = 1/1) showing a chromatic transition from blue (a, solid line) to red (b, dashed line) upon heating the solution from room temperature to a higher temperature (e.g., 60°C).

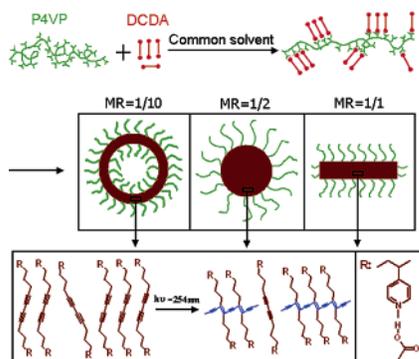
indicates an ordered hexagonal mesostructure with a repeating distance of 8.2 nm. A representative TEM image of the rod-shaped aggregates is shown in Figure 2e. Ordered lamellar structure with an interlamellar distance of $\sim 7 \text{ nm}$ is observed, agreeing well with the XRD result (diffraction pattern c).

The above-mentioned XRD and TEM studies suggest that the cooperative assembly of the DCDA and P4VP molecular building blocks spontaneously organizes them into ordered mesoscale assemblies. Exposing the colorless DCDA/P4VP aggregates to UV light (wavelength 254 nm) polymerizes the diacetylenic moieties, resulting in the formation of blue polydiacetylenic assemblies. It is known that diacetylenic derivatives undergo such topochemical polymerization only when the diacetylenic units are properly packed on the molecular scale.^{11,12} Therefore, the formation of such blue assemblies (polydiacetylene units) in turn evidences the formation of polymerizable molecular packing of the diacetylenic components within the as-synthesized assemblies. Heating the aggregates (e.g., from room temperature to 60°C) converted the blue assemblies into red assemblies. Figure 3 demonstrates UV–vis spectra of the blue and red assemblies prepared at an MR of 1/1. The absorption maximum at 607 nm for the blue assemblies shifts to 470 nm after being heated to 60°C . Note that the baseline of curve b does not go to zero at long wavelengths, indicating strong light scattering in the solution. The thermochromic transition is attributed to the reduced effective conjugation length of delocalized, π -conjugated polymer backbones due to the external stimuli.¹¹ As previously

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Scheme 1. Illustration of the Assembly Process between P4VP and DCDA Building Molecules that Leads to the Formation of Supramolecular Assemblies with Hollow Sphere, Solid Sphere, and Rod-Shaped Morphologies as Well as Topochemical Polymerization of the Diacetylenic Moiety under UV Irradiation



reported, the micellar structure in selective solvents is often stabilized by cross linking the micellar cores or shells.¹³ In the present assemblies, the improved stability through the cross-linking reaction of the diacetylenic moieties at the aggregate core, however, is not obvious; in fact, the aggregate solutions with and without polymerization were stable for months, as indicated by the steady, strong light-scattering intensities. Nevertheless, such responsive polymeric assemblies are of interest for many smart applications.

The formation of such hierarchical assemblies may involve collective noncovalent interactions among the building molecules. It is known that P4VP and aliphatic acids form stable, soluble complexes in their common solvent through hydrogen bonding between the pyridine rings and the carboxylic groups, as evidenced by the reduced NMR chemical shift of the carboxylic carbon from 178.0 to 175.5 ppm.¹⁴ Hence, it is quite reasonable to argue that the pyridine groups can also form hydrogen bonds with the carboxylic groups in DCDA. As shown in the Supporting Information section, the bands assigned to pyridine rings of pure P4VP at 1597, 1415, and 993 cm^{-1} shift to 1638, 1429, and 1024 cm^{-1} , respectively, in the DCDA/P4VP complexes. Indeed, no signals for the uncomplexed P4VP were observed for a stoichiometric DCDA/P4VP mixture (MR = 1/1). However, the interactions between the pyridine rings and the carboxylic acid groups were not found to be strong enough to form such supramolecular assemblies. For example, mixing P4VP with aliphatic acid (e.g., butyric acid and 1,12-dodecanedioic acid)

in CHCl_3/THF always results in transparent homogeneous solutions, and no aggregates were detected even at 50 mg/mL by dynamic light scattering (DLS). Other studies were also conducted by mixing P4VP with 2,2,7,7-tetramethyl-3,5-octadiyne (TO), a molecule that does not contain carboxylic groups but may be capable of $\pi-\pi$ stacking, under similar conditions. Similarly, no aggregates were detected by dynamic light scattering (DLS). However, mixing P4VP with DCDA under identical conditions resulted in mixtures with blue opalescence, indicating the formation of supramolecular assemblies.

Deriving a clear mechanism for the formation of such hierarchical aggregates is still a challenge. On the basis of our experimental observations, we believe that a collective effect of noncovalent interactions, such as the hydrogen bonding between P4VP and DCDA and the $\pi-\pi$ stacking of the diacetylenic moieties, is responsible for the formation of such supramolecular assemblies. As illustrated in Scheme 1, hydrogen bonding and $\pi-\pi$ stacking among building blocks produce a comb-shaped molecular assembly. Noncovalent interactions further assemble these comb-shaped molecules into hollow spheres, solid spheres, and rod-shaped micrometer-sized aggregates that are stabilized by the unbound P4VP segments. During the cooperative assembly process, the diacetylenic units within the DCDA were spatially arranged in a polymerizable fashion and topochemically polymerized upon ultraviolet (UV) irradiation, creating the blue polydiacetylenic aggregates containing the ene-yne alternating chains.¹¹ The mechanism of how the MR affects the mesostructure and morphology is still unclear, and additional studies are underway.

Summary

We have demonstrated a new approach to the formation of supramolecular assemblies with controlled morphologies from a homopolymer and small diacetylenic molecules. Cooperative assembly also spatially arranges the building molecules into ordered hexagonal and lamellar mesostructures, as evidenced by the XRD and TEM studies. Cross-linking polymerization of the diacetylenic moieties by UV irradiation results in a blue polymeric supramolecular assembly that can change color from blue to red upon external stimuli. These easily prepared, responsive assemblies are of great interest for smart carriers and other applications.

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Supporting Information Available: IR spectra of P4VP, DCDA, and DCDA/P4VP complexes at MR = 1/1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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