Spherical assemblies formed from $\pi$-conjugated alternating copolymers having fluorene and thiophene components

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Abstract. Self-assembly of conducting polymers were comprehensively studied by means of slow precipitation from polymer solutions upon addition of a vapor of nonsolvents. Polymers such as polyfluorene and polyythiophene hardly formed defined and discrete objects but only gave ill-defined aggregates. In contrast, some alternating copolymers having both fluorene and thiophene components in their repeating unit self-assembled into well-shaped spheres with submicrometer to several micrometer in the diameters. The differences in the assembling geometries derive from the crystallinity of the polymers, where the copolymers possess large steric hindrance on their backbone that reduces planarity of the polymers and inhibits anisotropic crystal growth. Changing the assembling parameters can systematically control diameter and deviation of the spheres.

1. Introduction

Construction of three-dimensional (3D) colloidal crystals have been focused much attention for obtaining novel optical properties such as optical band gap [1], nonlinear optics [2], and laser oscillation [3]. So far, various colloidal crystals consisting of beads of non-conjugated polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) were reported [1–3]. Meanwhile, few examples have been reported on photonic crystals consisting of $\pi$-conjugated polymers [4–7]. Examples of $\pi$-conjugated polymer photonic crystals include an inversed opal structure of poly(3-alkylthiophene) [4] and poly(paraphenylenevinylene) (PPV) [5,6], which are infiltrated into voids of silica or opal colloidal crystals. Another example is also from PPV spheres, prepared by an annealing of colloidal crystal of non-conjugated PPV precursors formed by so-called self-organized precipitation (SORP) method [7]. Photonic crystals consisting of $\pi$-conjugated polymers are expected to show novel optoelectronic properties such as enhanced electroluminescence, no-threshold laser oscillation, and highly-efficient photovoltaic conversion as the results of charge injection, long-lived excitons, and light confinement [8,9]. Thus, developing a formation of colloidal crystals from $\pi$-conjugated polymers will take great advantages for developing new polymer-based photonic crystals.

In general, polymer colloids are prepared by either direct generation during polymerization from the corresponding monomers (direct polymerization) or secondary generation such as rapid reprecipitation or emulsification of polymers (postpolymerization). Majority of the reported $\pi$-conjugated polymer colloids were achieved by the direct polymerization techniques such as dispersion polymerization and miniemulsion polymerization [10,11]. On the other hand, not many examples are reported on spherical assemblies of $\pi$-conjugated polymers by postpolymerization [10], including self-
assembly of amphiphilic \( \pi \)-conjugated homopolymers [12] or block copolymers [13–15]. One possible reason why \( \pi \)-conjugated polymers are difficult to give spherical assemblies by postpolymerization is attributed to their high rigidity and crystallinity [16,17]. \( \pi \)-Conjugation makes the polymer backbone planar and rigid, which lowers the flexibility of the polymers in contrast with non-conjugated polymers such as PS and PMMA. As the result of high planarity, \( \pi \)-conjugated polymers tend to stack on one another and crystallize anisotropically, often giving one-dimensional (1D) fibril or two-dimensional (2D) layered structures [16–19], not structurally isotropic spheres. Accordingly, one strategy for obtaining spherical assembly from \( \pi \)-conjugated polymers is to reduce the crystallinity, while without diminishing their electronic properties taking into consideration their optoelectronic applications.

In this proceeding, we show preparation of spherical assemblies from \( \pi \)-conjugated polymers by a slow precipitation from its solution upon addition of a vapor of nonsolvents. Precipitation mechanism of the vapor diffusion method is almost similar to the SORP method, in which the solvent is slowly evaporated from the polymer solution containing both ‘good’ and ‘poor’ solvents. Vapor diffusion method allows various combinations of the solvents including those having similar boiling points. We noticed that, by the vapor diffusion method, \( \pi \)-conjugated polymers having a single monomer component are very difficult to form well-defined spherical structures. In contrast, several alternating copolymers having two different \( \pi \)-conjugated molecular components tend to form quite well-shaped spheres quantitatively with its diameters ranging from a few hundreds of nanometers to several micrometers depending on the self-assembling condition.

2. Methods

Single-component polymers, F8, MDMOPPV, rr-P3HT, rra-P3HT, and alternating copolymers, F8BT, PCPDTBT, and F8T2 (Table 1) were purchased from Aldrich Chemical Co. Ltd. Alternating copolymers, F8TMT2 and F8EDOT (Table 1), were synthesized according to reported procedures [20,21]. For the preparation of self-assembled precipitates, typically, a 5-mL glass vial containing a solution of polymers (1 mg mL\(^{-1}\), 2 mL) was placed in a 50-mL glass vial containing 5 mL of a poor solvent to allow for vapor diffusion. CHCl\(_3\), CH\(_2\)Cl\(_2\), chlorobenzene (PhCl), tetrahydrofuran (THF), and toluene were used for polymer solution, while methanol (MeOH), acetone, and hexane were used as nonsolvents. While the mixture was kept at 25 °C for 72 h, the solution turned suspension. Morphology of the precipitates was observed by scanning electron microscopy (SEM).

3. Results and Discussion

3.1. Self-assembly of \( \pi \)-conjugated polymers

Typical fluorescent polymers, F8 and MDMOPPV, yielded pseudo-spherical objects from solvent combinations of toluene–acetone and CH\(_2\)Cl\(_2\)–MeOH, respectively, but the products were distorted in shape and heavily fused with one another. All the other combination of the solvents attempted only gave irregular aggregates or no precipitation. \( \text{rr-P3HT} \) gave only irregular aggregates under all solvent conditions examined. On the other hand, \( \text{rra-P3HT} \) formed spherical structures. However, the yielded spheres were not discrete but heavily fused with one another.

Next, we attempted self-assembly of alternating copolymers. F8T2 having both fluorene and thiophene moieties in the repeating unit only gave ill-defined aggregates for all solvent conditions attempted. However, of interest, F8TMT2 [20] having four methyl groups on the bithiophene unit of F8T2 forms discrete and quite well-shaped spheres (Figure 1). The average diameter \( (d_{av}) \) and its standard deviation \( (\sigma) \) are 2.7 and 0.39 \( \mu \text{m} \), respectively. Different solvent combinations such as CHCl\(_3\) and THF for good solvents and MeOH and acetone for nonsolvents also afforded spherical assemblies, but the \( \sigma \) values were larger by 1.5–3 times in comparison with that obtained for a solvent combination of CH\(_2\)Cl\(_2\)/MeOH. The increase of the deviation is likely derived from the difference of the diffusion rate of the solvents. Other solvent combinations only gave ill-defined aggregate or no precipitates.
Table 1. Summary of single-component polymers and alternating copolymers, assembling condition, geometry, and size.

| Polymer | Chemical Structure | $M_n$<sup>a</sup>, $M_w$/$M_n$<sup>b</sup> DP<sup>c</sup> | Solvent/Vapor<sup>c</sup> | Assembling Geometry | $d_{av}$ (σ) /µm |
|---------|--------------------|---------------------|----------------|-------------------|------------------|
| F8      | ![F8 Structure](image) | 15800, 3.70, 41 | Toluene/acetone | Distorted and Fused Spheres | 0.9–1.9 |
| MDMOPPV | ![MDMOPPV Structure](image) | 23000, –, 80 | CH$_2$Cl$_2$/MeOH | Distorted and Fused Spheres | 1.1–2.8 |
| rr-P3HT (regioregular) | ![rr-P3HT Structure](image) | 17500, –, 105 | CHCl$_3$/Acetone | Irregular Aggregates | – |
| rrra-P3HT (regiorandom) | ![rrra-P3HT Structure](image) | 29200, 3.16, 175 | CHCl$_3$/MeOH | Fused Spheres | 1.8 (0.61) |
| F8T2    | ![F8T2 Structure](image) | 26600, 2.66, 48 | CHCl$_3$/MeOH | Irregular Aggregates | – |
| F8TMT2  | ![F8TMT2 Structure](image) | 31800, 2.46, 52 | CH$_2$Cl$_2$/MeOH | Well-Shaped Spheres | 2.7 (0.39) |
|         |                    |                    | CHCl$_3$/MeOH | Well-Shaped Spheres | 2.4 (1.2) |
| F8EDOT  | ![F8EDOT Structure](image) | 27000, 3.81, 51 | CHCl$_3$/MeOH | Well-Shaped Spheres | 0.61 (0.18) |
|         |                    | 13800, 2.03, 26   |               |                   | 2.2 (0.78) |
|         |                    | 6300, 1.43, 12    |               |                   | 4.5 (2.1) |
| F8BT    | ![F8BT Structure](image) | 10000–20000, <3, 18–36 | CHCl$_3$/Acetone | Distorted Spheres and Irregular Aggregates | 4.2–7.8 |
| PCPDTBT | ![PCPDTBT Structure](image) | 7000–20000, –, 13–37 | CHCl$_3$/MeOH | Well-Shaped Spheres and Irregular Aggregates | 4.5 (0.55) |

<sup>a</sup> Estimated by gel permeation chromatography (GPC) calibrated on polystyrene standards or reported by company.

<sup>b</sup> Average degree of polymerization (DP), calculated from $M_n$ and molecular weight of the repeating unit.

<sup>c</sup> Initial concentration and assembling temperature were 1 mg mL$^{-1}$ and 25 °C, respectively.

Figure 1. SEM image of air-dried CHCl$_3$/MeOH suspension of F8TMT2.

Similar to F8TMT2, an alternating copolymer, F8EDOT [21] having ethylenedioxythiophene (EDOT) unit instead of tetramethylbithiophene (TMT2) unit also afforded well-defined spheres with a solvent combination of CHCl$_3$/MeOH. The $d_{av}$ and σ values were 610 and 180 nm, respectively, both
of which were remarkably smaller than those formed from F8TMT2. Different solvent combination such as CH2Cl2 as a good solvent and MeOH, hexane, and acetone as poor solvents also gave spherical assemblies, but they were somewhat distorted or fused with one another. Assemblies in the other solvent combination only gave ill-defined aggregates.

We further investigated other alternating copolymers, F8BT and PCPDTBT, which are known as donor (D)–acceptor (A) polymers and often used as electron-donating layers of recent polymer photovoltaics. These polymers gave mixtures of spheres and irregular aggregates. Spheres of F8BT were somewhat distorted with the diameters of 4.2–7.8 µm, while those of PCPDTBT were well-shaped with $d_{av}$ of 4.5 µm.

3.2. Size control of spherical assemblies

For colloidal crystals exhibiting photonic properties at the visible-light region, periodic structure of several hundreds of nanometer is required. The diameter of the spheres formed from F8EDOT corresponds to that length scale. Therefore, we used F8EDOT and investigated what factor determines the size and deviation of the spheres. F8EDOT having $M_n$ of 27,000 gave spheres with $d_{av}$ of 0.61 µm. When $M_n$ decreased to a half (13,800), $d_{av}$ increased to 2.2 µm, and further half of $M_n$ (= 6,300) resulted in an increase of $d_{av}$ to 4.5 µm. Initial concentration of the solution also affects the $d_{av}$ values, where $d_{av}$ of the resultant spheres decreased from 2.1 to 1.4 and 1.2 µm as the concentration of F8EDOT ($M_n = 27,000$) was increased from 0.5 to 1.0 and 2.0 mg mL$^{-1}$, respectively. Temperature also affects the sphere size and deviation to some extent, where aging at higher temperature resulted in the larger $d_{av}$ values ($d_{av}$ of 0.56, 0.67, and 0.69 µm for the spheres assembled at 0, 25, and 30 °C, respectively).

The changes of $d_{av}$ most likely relate to the rate of precipitation. Due to the high solubility, polymers having smaller $M_n$ precipitates with the longer aging time than those having larger $M_n$. Accordingly, for the small-$M_n$ polymers, nucleation and growth take place more slowly, leading to the formation of spheres having larger diameters. Low initial concentration also results in slow nucleation and growth of spheres, giving the larger spheres in comparison with that formed from high concentration. Temperature dependency is a little complicated, because solubility is higher at higher temperature, but, at the same time, diffusion of the nonsolvent occurs more rapidly. These factors affect oppositely for the precipitation rate. In the present case, assembly at the higher temperature results in the precipitation of spheres having larger diameters, hence the former (solubility change) is the dominant factor for $d_{av}$ of the spheres. According to these results, small-diameter spheres can be obtained by self-assembly of (i) large molecular weight polymers (ii) in high initial concentration (iii) at low temperature. Under such condition, nucleation of polymers occurs concurrently, resulting in large amount of small-size spheres.

Next, we discuss the deviation of the diameters. Spheres of F8EDOT with $d_{av}$ of 0.61 µm showed 30% deviation ($\sigma = 0.18$ µm), while those with $d_{av}$ of 4.5 µm has the larger deviation of 47% ($\sigma = 2.1$ µm). We assume that time lag of the nucleation causes the difference in the growth time of the spheres, thereby resulting in the large deviation of the diameters. In fact, F8TMT2 in CH2Cl2, upon vapor diffusion of MeOH, results in the spherical precipitates with the smaller $\sigma$ value than that in THF and CHCl3, where evaporation of the good solvent takes place more rapidly for CH2Cl2 than THF and CHCl3 (boiling points of CH2Cl2, THF, and CHCl3 are 40, 66, and 61 °C, respectively). In order to reduce the time lag of the nucleation, we further demonstrated self-assemblies using a wide-mouth petri dish instead of a narrow-mouth vial. Thus, the solution/vapor interface area was increased from 1.5 to 5.7 cm$^2$, while the depth of the solution was reduced from 0.8 to 0.2 cm. In this case, a complete precipitation occurred within only 12 h by a vapor diffusion of MeOH into CHCl3 solution of F8EDOT. The $d_{av}$ and $\sigma$ values of the obtained spheres were reduced by 28 and 50%, respectively, from those obtained using usual small-mouth vial ($d_{av}, 0.61 \rightarrow 0.44$ µm; $\sigma, 0.18 \rightarrow 0.09$ µm).

3.3. Mechanism for the formation of spherical assemblies

Why do spherical assemblies form upon slow diffusion of nonsolvents and why do only limited alternating copolymers assemble into such well-shaped spheres? From our results, spherical
assemblies tend to form when polar nonsolvents such as MeOH and acetone are diffused into the polymer solution. These nonsolvents have low affinity with the hydrophobic polymers having linear or branched aliphatic chains. As the result, the polymers possibly aggregate while minimizing the contact area with the polar nonsolvent, thereby gradually growing into a spherical geometry as thermodynamic products. In fact, simple evaporation of the solvent from the CHCl₃ solution of F8EDOT hardly yielded spheres but only gave an amorphous film. On the other hand, when MeOH was added in advance to the CHCl₃ solution of F8EDOT (CHCl₃/Methanol = 10/1 v/v), and the resultant suspension was heated to dissolve the polymer and then aged at 25 °C, precipitation readily resulted within several minutes. However, the resultant precipitates were ill-shaped and fused spheres. Therefore, slow diffusion of polar nonsolvent is one of important factors to yield well-shaped spheres. In colloidal sciences, amphiphilicity with large head group and small tail group is one of driving forces for spherical assemblies [12–14, 22–24]. However, in the present case, copolymers we utilized do not possess such amphiphilicity. Instead, polarity of good- and nonsolvents plays a crucial role for the colloidal formation.

Crystallinity of polymers is another important factors. Polymers possessing high rigidity or interchain crystallinity tend to crystallize anisotropically, which disturb the assembly into isotropic spherical geometry. In fact, rr-P3HT having high interchain crystallinity hardly formed discrete assemblies but only gave irregular aggregates, whereas rra-P3HT having low interchain crystallinity due to the random regularity of the hexyl chains formed pseudo-spherical structures. Furthermore, in case of F8TMT2 and F8T2, the former formed well-shaped spheres while the latter gave only ill-defined aggregates. Since four methyl groups on the bithiophene moiety in F8TMT2 disturb a planarity of the polymer, polymer backbone most likely forms twisted configurations, leading to disordered interchain packing. On the other hand, F8T2 possesses much planar structure, which enhances the interchain crystallinity. Copolymers F8BT and PCPDTBT also form spheres, but they are not quantitative and not well-shaped, possibly due to the rather high interchain crystallinity [25, 26].

We conducted X-ray diffraction (XRD) experiments to confirm differences of the crystallinity. However, except for rr-P3HT, diffraction peaks were hardly attained for all samples by conventional XRD studies, since long-range structural ordering of π-conjugated polymers are generally achieved by post-annealing of polymer films. Instead, photoemission spectra showed clear differences, giving important indication on their π-conjugation. CHCl₃ solutions of F8T2 and F8TMT2 show maximum photoluminescence peaks (λPLmax) of 499 and 468 nm, respectively, indicating that F8T2 has the larger π-conjugation length than F8TMT2 due to the high planarity of the polymer even in solution. The fluorescence spectra of the drop-cast film from CHCl₃ solution of F8T2 exhibited significant red shift (ΔλPLmax = 42 nm), and irregular aggregates of F8T2 afforded by slow precipitation showed further red-shifted fluorescence (ΔλPLmax = 46 nm). These results indicate that either expansion of the intrachain π-conjugation or interchain π-electronic interaction, or both of these, takes place in the solid state. In contrast, λPLmax of the cast film of the spheres of F8TMT2 (475 nm, ΔλPLmax = 7 nm), as well as that formed from CHCl₃ solution of F8TMT2 (474 nm, ΔλPLmax = 6 nm), were not so much shifted from λPLmax of the solution of F8TMT2. These results clearly indicate that neither expansion of intrachain π-conjugation nor interchain π-electronic interaction take place in the solid films of F8TMT2, irrespective of whether the aggregation takes place kinetically (solution-cast) or thermodynamically (spheres). Concerning F8EDOT, a certain red shift of λPLmax was observed by the formation of spheres (ΔλPLmax = 37 nm), which was rather large in comparison with that of F8TMT2 (ΔλPLmax = 6 nm) but not as large as that of F8T2 (ΔλPLmax = 46 nm). We assume that the degree of steric hindrance of the ethylenedioxy moieties in F8EDOT is smaller than that of the methyl groups in F8TMT2, which results in the smaller twisting of the π-conjugation in F8EDOT than F8TMT2. These results also support the fact that F8TMT2 easily forms well-defined spheres under various solvent combinations whereas F8EDOT forms spheres only in a limited solvent combination.
4. Conclusion
We studied self-assembly of π-conjugated polymers upon slow precipitation from their solution. While most representative π-conjugated polymers hardly yielded spherical assemblies, some alternating copolymers assembled into well-shaped spherical structures quantitatively. The main factor for spherical assembly is attributed to the low crystallinity of the polymers, where copolymers with steric hindrance in their backbone and thereby having low crystallinity tend to form spheres. Optimizing the self-assembling conditions can systematically control size and deviation of the spheres. Photocarrier lifetimes in the spheres were markedly enhanced in comparison with that of the samples without forming spheres. Yet more attempts are needed to create colloidal crystals such as precise control of the size and deviation, this research provides important knowledge for photonic applications using π-conjugated functional polymers.

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