



Preparation of conjugated poly(*p*-phenylene) hierarchical microspheres by nonsolvent vapor self-assembly and their fluorescent detection of metal ions



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ABSTRACT

The novel hierarchical microspheres from conjugated poly(*p*-phenylene)s can be self-assembled by the nonsolvent vapor method. The formation of hierarchical microspheres depends on the choice of polar nonsolvent vapor atmospheres, solvents, and the length of side chains. The intermolecular interactions, including the side-chain interactions and the π - π interactions between conjugated backbones, occur spontaneously to form various conformations and polymeric aggregates, which have an effect on the fluorescence wavelength of the polymer hierarchical microspheres. Our results demonstrate a facile way to prepare polymeric hierarchical microspheres and adjust their optical properties. Moreover, the hierarchical microspheres with rough surface show a highly selective fluorescence “turn-off” sensor for Fe^{3+} with almost no interference of other metal ions.

1. Introduction

In recent years, the design of well-defined polymeric structures has achieved considerable success because of the new or improved chemical and physical properties [1,2]. Polymeric micro-nano-scale patterns such as wire-like, sheet-like, spherical, cylindrical, and porous structures have been prepared and applied in various fields [3]. Among them, the three-dimensional polymeric microspheres as multifunctional materials promise great potential to offer exciting opportunities in many areas such as imaging agents, chemical sensors, and photonic and optoelectronic device materials [4–5]. In addition to the direct polymerization from the corresponding monomers, the dispersion methods from the preformed polymers are another simple and powerful bottom-up strategy to prepare the polymeric nano-microspheres [6–8].

Conjugated polymers have received much attention because they can provide more opportunities for developing optoelectronic devices with physical flexibility, ease of processing, and low cost [9–11]. Furthermore, the exploration and design of new functionalized materials and novel devices with good performance become the further research of conjugated polymers in the future. The unique thermal, optical, and electrical properties of conjugated polymers are attributed to their rigid backbone highly delocalized π -orbitals. The performance of polymer-based devices is closely related to the conjugated polymer morphology. For example, high rigidity and planarity can induce conjugated polymers to self-assemble low-dimensional structures such as nanofibrils and nanobelts. This can improve the charge carrier transport in organic

field-effect transistors [12,13]. However, the rigid steric hindrance of conjugated backbones is considered an obstacle to facilitate well-defined spherical assemblies. This problem can be partially resolved by amorphous conjugated polymers [14] or changing the chemical structures of polymers, such as the alternating copolymers [15]. Thereby, the preparation of spherical microstructures using crystalline conjugated polymers remains a valuable research topic.

Although homogeneous well-defined conjugated polymer microspheres cannot be prepared by the nonsolvent diffusion method [15,16], various morphology patterns gave us some enlightenment. The fiber-like or sheet-like nano- and microstructures were assembled by planar conjugated polymers due to the ordered polymer arrangement. If the assembly time was shortened, the crystallization process could be disrupted. It is possible to prepare spherical conjugated polymer structures by rapid precipitation.

As a typical aromatic conjugated polymer, substituted poly(*p*-phenylene)s (PPPs) have potential applications in optoelectronic devices and chemical sensors [17,18]. Because of PPPs rigidity and crystallinity, they were used as the building blocks to fabricate hierarchical spherical microstructures in this work. By using the nonsolvent vapor (NSV) method [19], the conjugated PPP hierarchical microspheres were first self-assembled in NSV atmospheres. After the evaporation of the solvents, well-defined hierarchical microspheres were obtained from the polymer solutions on glass substrates. The effects of NSVs, solvents, and the length of side chains on the formation of polymer hierarchical microspheres were discussed to have a further understanding about the

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NSV process. The optical properties of hierarchical microspheres and the fluorescence quenching by metal-ion were also investigated.

2. Experimental section

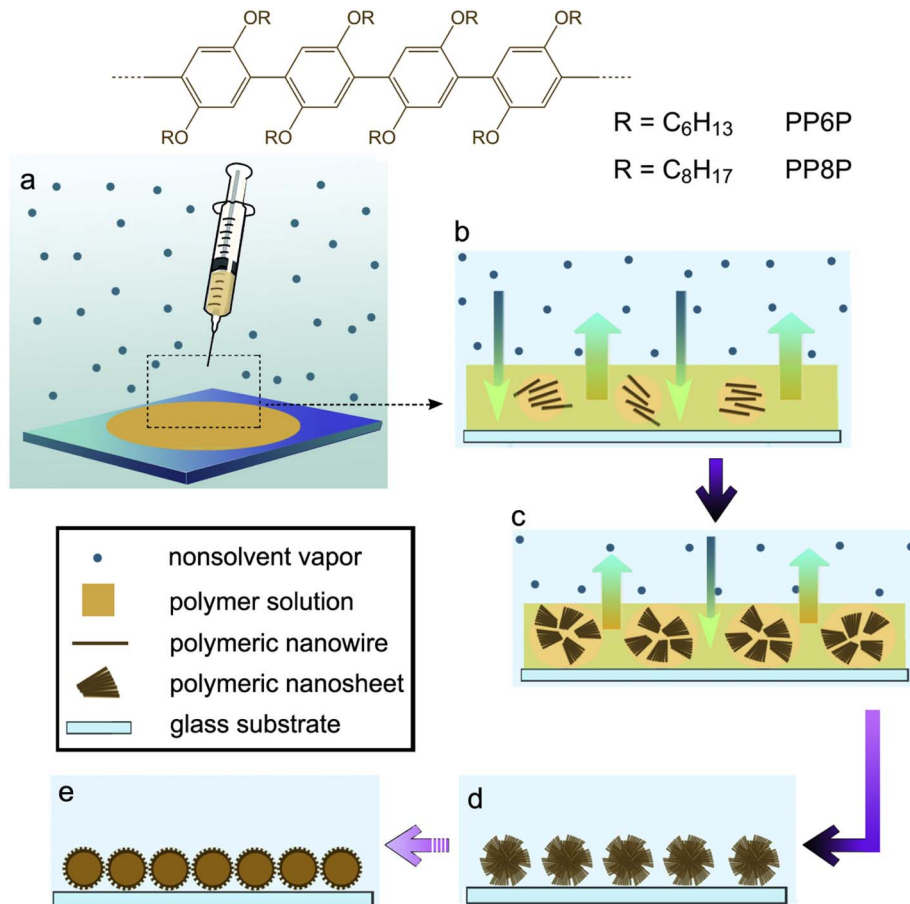
2.1. Materials

Analytical grade toluene (Tol), chlorobenzene (CB), dichloromethane (CH_2Cl_2), chloroform (CHCl_3), methanol (MeOH), ethanol (EtOH), and hexane (Hex) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Demineralised water was used throughout the work.

Poly(2,5-dialkoxyphenylene)s were synthesized by solid-state oxidative coupling polymerization [20] as described in Support information. In the experiment, poly(2,5-dioctyloxy-*p*-phenylene)s (PP8P, $M_n = 7.0 \times 10^3$, $M_w/M_n = 2.71$), poly(2,5-dihexoxy-*p*-phenylene)s (PP6P, $M_n = 7.5 \times 10^3$, $M_w/M_n = 2.83$), and poly(2,5-dibutoxy-*p*-phenylene)s (PP4P, $M_n = 10.0 \times 10^3$, $M_w/M_n = 3.15$) were used.

2.2. Microsphere formation

In our experiments, 3 mL of the nonsolvent (MeOH, EtOH, or Hex) was chosen to produce a saturated vapor atmosphere in a cap-sealed glass vessel. After successive cleaning with detergents, demineralized water, ethanol, and acetone, the glass substrates ($1 \times 1 \text{ cm}^2$) were positioned above the nonsolvent. Subsequently, 5 μL of poly(2,5-dialkoxyphenylene) solution with 5 mg mL^{-1} in the solvent (CH_2Cl_2 , CHCl_3 , Tol, or CB) was cast onto the surface of a glass substrate by a microsyringe under different vapor atmospheres at 25 °C. After complete evaporation of the solvents, a thin layer remained on the substrate. The self-assembly process is shown in Scheme 1.



Scheme 1. The self-assembly process in nonsolvent vapor atmosphere.

2.3. Characterization

The structures of polymers were characterized by FT-IR spectra of KBr powder-pressed pellets recorded on a Bruker Vector 22 spectrometer and ^1H NMR spectra recorded on a Varian 400-MHz spectrometer using CDCl_3 as the solvent. The relative molecular weight of the polymers was determined by a Waters GPC 1515, using THF as the eluent and polystyrene standards as the references. X-ray diffraction analysis was carried out using the X'Pert PRO MPD diffractometer, configured with a Cu radiation X-ray source ($\lambda = 0.1542 \text{ nm}$). The morphologies were observed by scanning electron microscopy (SEM) using a Hitachi S4800 scanning electron microscope. The fluorescence spectra were measured on a PE-LS55 fluorescence spectrophotometer.

2.4. Metal-ion quenching

PP6P films with hierarchical microsphere patterns self-assembled from different conditions were immersed in 10-mL aqueous solutions of metal ions of different concentrations for 30 s. The metal-ion quenching effect was then measured by the fluorescence spectra. For comparison, the metal-ion quenching effect of PP6P solutions and the bulk solid were also measured, and the results are provided in Support information.

3. Results and discussion

3.1. Self-assembly of polymeric hierarchical microspheres

The dispersal PP6P hierarchical microspheres were successfully fabricated from various solvents in a MeOH vapor atmosphere, as shown in Fig. 1a–d. Obviously, the details and sizes of the hierarchical

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