



Precipitation and sol formation from poly(*p*-phenylene)s solutions by spectroscopic study



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ABSTRACT

By UV–vis absorption, photoluminescence, and FT-IR spectroscopies, the relationship between conformations and photophysical properties of hairy-rod poly(2,5-dioctyloxy-*p*-phenylene)s in dilute solution was investigated in the good solvent, the poor solvent and the mixed good and poor solvents. The solvent quality such as polarity, aromaticity and solubility parameter can govern the conjugation length such as the extended, twist and shrinking conformations. By the addition of the polar poor solvent, the polymeric aggregates can be induced to form the colloidal particles and precipitate. In addition, the nonpolar poor solvent can interact with the flexible alkane side chains to form the three-dimensional networks. Further supports on the conjugated polymer aggregations can also be given by XRD and SEM techniques. Therefore, by changing the species and the proportion of the mixed solvents, the polymer aggregation structure can be controllable to prepare the conjugated polymeric supermacromolecular architectures.

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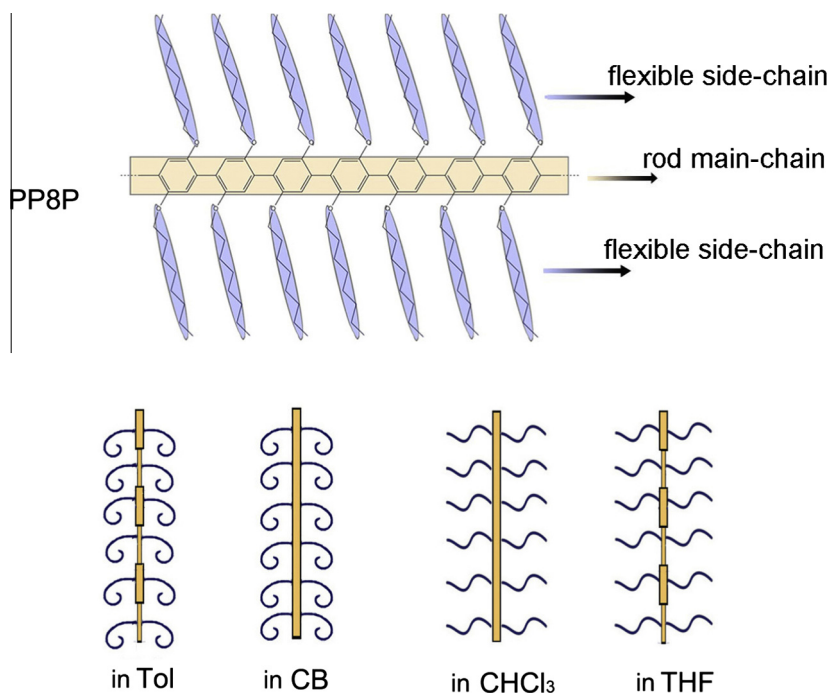
1. Introduction

Conjugated polymers have received much attention in the field of polymer science and application [1,2] due to their rigid backbone highly delocalized π -orbitals which can serve as media for charge carrier transport. However, the rigid-rod type conjugated polymers actually suffer from poor solubility. The flexible alkyl side chains attached to the stiff conjugated backbones endow them with high solubility in common organic solvents. This kind of polymer is also called hairy-rod polymer [3,4].

For hairy-rod polymers, among the flexible side chains, the rigid backbones, and the solvent molecules, there are different attractive interactions, which are the forces to tend to self-organize nanoscale structures in solution and bulk [5–7]. Moreover, the optoelectronic properties of conjugated polymers are substantially dependent on the morphologies of the supermacromolecular architectures. Devices with micro/nano scale have been an exciting and challenging research topic for researchers [8].

The conjugated polymeric micro/nanostructures are frequently affected by the processing conditions and methods. Recently, researchers have investigated the solvent parameters that dictate photophysical behaviors of conjugated polymers [9,10], which can alter substantially due to conformational changes of isolated chains [11] and interchain aggregation [12,13]. A good solvent can allow polymer chains to adopt an extended conformation, resulting in the increase of the effective conjugation length. In a poor solvent, the system minimizes interfacial contact owing to unfavorable polymer–solvent

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Scheme 1. Chemical structure of PP8P and a small conjugated segment of PP8P in good solvents.

interactions, reflected by a decrease of solubility, forcing chains to adopt a collapsed or aggregated conformation [10,14]. The precipitation can be obtained by adding a poor solvent into a good solvent solution that can be used as the purification of conjugated polymers [15,16]. In addition, gel formation has also been reported for conjugated polymers by addition of non-solvent alkanes into good solvents [17,18]. The detailed thermodynamic mechanism of the solvent-induced conformation and aggregation changes of hairy-rod polymers remains ambiguous. It is interesting to investigate the structural/morphological correlations between their solutions and condensed states, considering the potentially widespread applications of the solution-processable polymer semiconductors nowadays and in the near future [19,20].

The substituted poly(*p*-phenylene) (PPP) is a typical aromatic representative of hairy-rod polymers. As one of the most studied family of conductive polymers, PPP has the potential applications on the fabrication of light-emitting diodes, thin film transistors, and chemical sensors [21,22]. Yet a small number of reports have been described the solution behaviors of hairy-rod PPPs in dilute solutions [23–25].

In the following, we wish to describe the phase separation of poly(2,5-dioctyloxy-*p*-phenylene)s (PP8P) as a model representative for alkoxy-substituted conjugated polymers in the mixed good/poor solvents solution. The chemical structure of PP8P (Scheme 1) is constituted of an aromatic backbone with flexible alkoxy side chains, enabling us to select a wide range of solvents for varying magnitude of the polymer–solvent interactions.

We studied the optical properties of PP8P in the good solvent and the poor solvent, respectively. And the effect on the PP8P aggregation structures in the mixtures of good and poor solvents was also investigated. UV–vis absorption spectroscopy, photoluminescence (PL) spectroscopy, FT-IR spectroscopy, X-ray diffractions (XRD) and scanning electron microscopy (SEM) techniques were employed to characterize the polymer conformation changes, the aggregation process, and the morphologies.

2. Experimental section

2.1. Materials

Analytical grade anhydrous ferric chloride (FeCl_3), *n*-octylbromide, hydroquinone, dimethylsulfoxide (DMSO), toluene (Tol), chlorobenzene (CB), chloroform (CHCl_3), tetrahydrofuran (THF), ethanol (EtOH), methanol (MeOH) and hexane (Hex) were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 1,4-dioctyloxyphenylene was prepared by reacting hydroquinone and *n*-octylbromide in DMSO. Demineralised water was used throughout the work.

2.2. Synthesis of poly(2,5-dioctyloxy-*p*-phenylene)s (PP8P)

PP8P was synthesized by the solid-state oxidative coupling polymerization using FeCl_3 as the oxidative catalyst [26]. A mixture of 1,4-dioctyloxyphenylene (0.67 g, 2 mmol) and anhydrous FeCl_3 (1.00 g, 6 mmol) was placed into a mortar and

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