

Supramolecular Assemblies of a Semirigid Polyanion in Aqueous Solutions

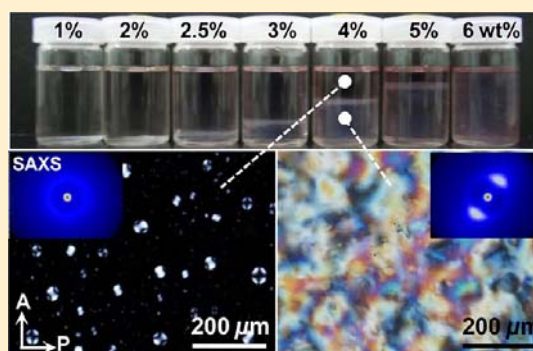
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ABSTRACT: In this article, we report the supramolecular assemblies of a semirigid polyelectrolyte, poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT) in water. Cryo-TEM observation and SAXS measurement reveal that PBDT forms bundle-like structure even in very dilute concentration, C_p , of 0.02 wt %. These bundle-like assemblies serve as new primary building blocks and self-assemble further as C_p increases, to form large associations with or without long-range orientation. When 2 wt % < C_p < 6 wt %, liquid–liquid phase separation occurs. Some of the supramolecular associations form bipolar liquid crystalline (LC) droplets via a typical nucleation and growth process. The droplets grow up by the coalescence of small ones and sediment under the gravity and coalesce to form a bottom nematic phase. When $C_p \geq 6$ wt %, the solutions are in a uniform nematic phase. The existence of these preliminary supramolecular assemblies of PBDT in aqueous solutions should be crucial for the formation of nematic LC phase at a significantly low C_p , as well as the formation of macroscopic ordered structures in hydrogels via electrostatic interaction between PBDT and oppositely charge multivalent metallic ion or polycation.



INTRODUCTION

Water-soluble rod-like macromolecules are ubiquitous in living organisms, such as deoxyribonucleic acid (DNA), microtubule (MT), and actin filaments (F-actin).^{1–5} These biomacromolecules usually carry negative charges along with the rigid or semirigid structures, endowing them with great abilities to form advanced architectures, which are crucial for generating elaborate functions of living organisms.^{5–11} For example, myosin shows a liquid crystalline (LC) structure in sarcomere, contributing to the formation and smooth motion of muscle fibers.² Safinya et al. have reported that DNA and cationic liposomes form complex and self-assemble into supramolecular LC phases (e.g., lamellar phase and inverted hexagonal columnar phase), which are supposed to be significant in gene delivery.^{10,11} However, the essential structure formation mechanisms are usually hard to investigate *in vivo* because of the complex biomolecular structures and unstable biological environments. In the case of *in vitro* studies, the natural biomacromolecules with the secondary structure are difficult to tune without denaturation during the extraction and chemical reaction. In alternative, it is feasible and significant to study the self-assembling behaviors of synthetic semirigid polyelectrolytes that mimic the natural biomacromolecules.^{12–19}

Wegner et al. have found that a rigid polyelectrolyte, dodecyl-substituted poly(*p*-phenylene)sulfonate (PPPS), forms cylindrical micelles in dilute aqueous solutions, even at a

concentration as low as 0.001 g/L.^{12–15} These micelles undergo further interactions at high polymer concentrations and form high ordered structures via axial or side-by-side aggregation. Mendes et al. have synthesized a series of sulfonated polyimides such as poly(*p*-sulfophenylene-terephthalamide) (sulfo-PPTA). The aqueous solutions of these polymers show uniform nematic LC phases at a significant low polymer concentration, around 2 wt %.^{16–19} They ascribed this ordered structure formation at such low concentration to the presence of supramolecular assemblies that behave as the building blocks of the nematic phase. In recent years, we focused on the self-assembly behaviors of a synthetic semirigid polyanion, poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT), in the aqueous solutions and hydrogels.^{20–32} The chemical structure of PBDT is shown in Scheme 1. We found that (i) PBDT aqueous solutions also show a significantly low critical concentration of nematic phase, C_{LC}^* , of 2.8, 2.2, and 1.5 wt % for weight-average molecular weight, M_w , of 8×10^4 , 1.8×10^6 , and 2.6×10^6 , respectively, much lower than those of common lyotropic LC macromolecules;³³ (ii) PBDT forms a variety of the self-assembling structures in aqueous solutions, ranging from isotropic cluster associations to fiber-like anisotropic

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