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Anisotropic Hydrogel from Complexation-Driven Reorientation of Semirigid Polyanion at Ca^{2+} Diffusion Flux Front

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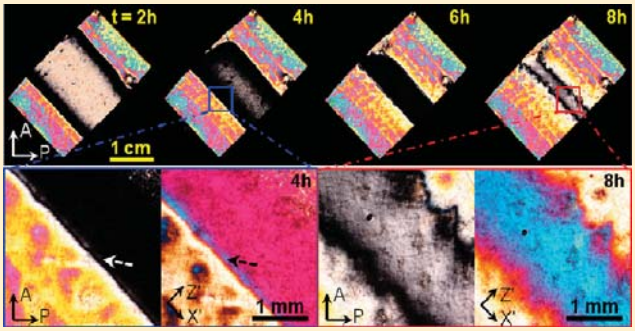
Supporting Information

ABSTRACT: We report a macroscopically anisotropic hydrogel developed by the facile dialysis of a synthetic semirigid polyanion in aqueous solution of multivalent cations. By the uniaxial diffusion of Ca^{2+} into two ends of a thin rectangular reaction cell containing semirigid polyanion poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide) (PBDT) aqueous solution, centimeter-scale anisotropic hydrogels with the PBDT molecules and their self-assembled fibrous bundles align in *perpendicular* to the Ca^{2+} diffusion direction are obtained. The anisotropic gel shows a higher elastic modulus and tensile fracture stress/strain in the direction parallel to the PBDT orientation than that of perpendicular direction. By observing *in situ* the gelation process, an extraordinary molecular reorientation of PBDT at the Ca^{2+} diffusion flux front is observed for the first time. The mechanism for the molecular reorientation is discussed in terms of complexation and gelation.



INTRODUCTION

Soft biotissues such as cartilage, muscle, and eyeball are in a wet gel-like state, including 30−80% water. These gels generally possess well-ordered structures that play a crucial role in executing the functions of living organisms.[1,2] For example, collagen fibers are closely packed with parallel arrays in tendons; these oriented collagen fibers endow the tendon with excellent mechanical properties.[1] Myosin shows a liquid-crystalline (LC) structure in sarcomere, contributing to the formation and smooth motion of muscle fibers.[1b,2b] In these biotissues, biomacromolecules such as DNA, filamentous actins (F-actin), and microtubules with rigid or semirigid structure and negative charges are significant to the formation of versatile self-assembled structures via noncovalent interaction.[3] It is well-known that a considerable amount of cationic proteins, liposomes, or multivalent cations are involved in the self-organization of these negatively charged semirigid biomacromolecules such as cytoskeleton organization and gene packaging.[4] These facts indicate the significance of electrostatic interaction during the self-assembly of biomacromolecules.

Inspired from the natural materials, lots of self-assembled structures of both biomacromolecules and synthetic polymers are developed in solutions and hydrogels by controlling the intermolecular ionic bonds, hydrophobic interactions and hydrogen bonds.[5] However, the oriented structures developed in the former works are usually limited in a submicrometer level, hydrogels with macroscopically anisotropic structure are rarely realized. Recently, we successfully developed hydrogels with millimeter-scale anisotropic domains by polymerizing a cationic monomer in the presence of a small amount of semirigid polyanion as dopant.[6] The semirigid polyion complex forms during the polymerization and self-assembles into ordered structures that are frozen by the subsequent chemically cross-linking process. Further increase in the size of anisotropic domains is difficult to achieve because of the occurrence of polyion condensation and resultant gel deformation.

A significant route to develop hydrogels with macroscopically anisotropic structure is through the reaction-diffusion process; the reaction and diffusion compete with each other and result in intricate spatial or temporal structures.[7] Dobashi and co-workers had developed a method to synthesize physical LC hydrogels in a semipermeable tube by dialyzing aqueous solutions of DNA or Curdlan in a multivalent cation solution, where biomacromolecules with semirigid structure and negative charges can form complexation with the multivalent cation.[8] The cationic ion diffusion into the dialysis tube induces the molecular orientation and physical gelation to form cylindrically symmetric structure up to the size of several centimeters. They claimed that the biomolecules orient along the cationic ions diffusion direction to form a radial structure.

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