ChemPubSoc Europe

DOI: 10.1002/chem.201304714

CHEMISTRY
A European Journal
Full Paper

Self-Assembly

Out-of-Water Constitutional Self-Organization of Chitosan–Cinnamaldehyde Dynagels

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Abstract: An investigation of the constitutional adaptive gelation process of chitosan/cinnamaldehyde (**C**/**Cy**) dynagels is reported. These gels generate timely variant macroscopic organization across extended scales. In the first stage, imine-bond formation takes place "in-water" and generates low-ordered hydrogels. The progressive formation of imine bonds further induces "out-of-water" increased reactivity within interdigitated hydrophobic self-assembled layers of **Cy**, with a protecting environmental effect against hydrolysis and that leads to the stabilization of the imine bonds. The hydrophobic swelling due to **Cy** layers at the interfaces reaches a critical step when lamellar self-organized hybrids are generated (24 hours). This induces an important restructuration of the hydrogels on the micrometric scale, thus resulting in the formation of highly ordered microporous xerogel morphologies of high potential interest for chemical separations, drug delivery, and sensors.

Introduction

Constitutional dynamic chemistry (CDC) brings into play the self-evolution of dynamic molecular and supramolecular systems toward the selection of discrete architectures from mixtures of exchanging components.[1] The self-assembling of the components into adaptive architectures across size scale, controlled by mastering constitutional affinities, embodies the flow of structural information from the molecular level toward nanoscale/microscale dimensions.[2]

Within this context, we recently proved that the progressive incorporation of hydrophobic synthons through imine-bond formation onto hydrophilic chitosan backbones produces the depletion of strongly hydrogen-bonded chitosan chains, thus resulting, in some cases, in the formation of stable chitosan hydrogels, films, or powders, which are a function of the nature of the grafted moiety in the Chitosan backbones.[3] The reorganization of hydrophobic/hydrophilic systems is probably connected to 1) a protecting environmental effect against hydrolysis and the stabilization of the reversible imino bonds at the molecular level[3a] and 2) the self-control of the balance of interactions, which is a determinant for the emergence of novel solid-phase formation and materials at the supramolecular level.[3b]

Previous studies in our laboratories[3a] have shown that among different formulations (i.e., films or powders)[3b] that can be obtained from various aldehydes, stable hydrogels can be prepared by treating cinnamaldehyde (**Cy**) with chitosan (**C**; Scheme 1).[3] Although the control of the hydrogel formation seems to be reasonable, the dynamic reversible equilibrium of the **Cy** imine-bond formation at the molecular level cumulated and the self-organization of **C**/**Cy** hydrophilic/hydrophobic supramolecular interfaces remain key challenges.

More generally, the formation of "dynamic gels" (i.e., dynagels) dynamic on both the molecular and supramolecular levels is reminiscent of a number of other nonexclusive constitutional systems, including helical and lamellar nanometric hybrid phases,[4a–c] cholesteric lyotropic systems,[4d] constitutional dynamic gels,[4e,f] self-replicating dynablocks[4g] or dynasurfaces,[4h] and so forth.

Herein, we report the investigation of the dynamic constitutional gelation process of **C**/**Cy** hydrogels and of the characteristics of the corresponding xerogels in an attempt to extend and engineer constitutional interactions to generate timely variant-adaptive macroscopic organization of **C**/**Cy** dynagels across extended scales.[2]

C/**Cy** hydrogels have been obtained by mixing solutions of **C** and **Cy** in water and acetone, respectively, at various $\mathbf{C}_{NH2}$/$\mathbf{Cy}_{CHO}$ molar ratios at 50 °C (see Scheme 1 and Table 1).

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201304714.