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Morphology-tuning by changing the composition of a binary hydrogel comprising thymidine and melamine

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ABSTRACT

We report on the self-assembly of a new two-component hydrogel of thymidine (T) and melamine (M) which formed supramolecular complex (≥0.1%, w/v) based on intermolecular hydrogen-bonding. The 3D morphologies were tuned by changing the molar ratio of T and M in aqueous medium from 3/1 to 1/3. The xerogels respectively showed rod, sheet and flower structures as observed under SEM. Fourier transform infrared (FT-IR) spectroscopy and wide angle X-ray scattering (WAXD) patterns confirmed that thymidine and melamine form supramolecular complexes through intermolecular hydrogen-bonding. The different structures of the complexes are proposed for the different compositions of the components.

1. Introduction

Small molecular hydrogels have attracted intense research interest because of their potential use as biocompatible scaffolds for tissue engineering, and pollutant capture and in drug delivery [1–11]. In most of the examples the hydrogelators are comprised of one component small molecules but recently interest in two-component hydrogels has increased [1,2]. Designing the order and orientation of molecular self-assembly through supramolecular interaction is a fascinating area of research to fabricate nano- and macro-structured materials like fibers, tapes, rods, helices, ribbons and hollow tubes [12–21]. Some of such superstructures were recognized as gels in organic/aqueous media with different properties. The use of binary gel systems [22–28] is more advantageous over one-component gels to tailor the structures and properties of the gels by functional modification of the components [29], changing one of the components [19], using different isomers [17], and changing the molar ratio of the components [26]. The ease of manipulation of the superstructures enables convenient control of the properties of the gels. Among the small molecular hydrogels, the high surface area of the nanostructures developed in the self-assembly process is the most attractive [29]. As short nucleotides are easy to design and achieve, they serve as an excellent model system for studying DNA helix formation in particular and biological self-assembly processes in general. New insights regarding the determinants that mediate the self-assembly of the various polypeptides and nucleotides into various nanostructure have a key impact both from the medical point of view as well as the technological one [30].

Carbonyl and acylamide groups have been frequently used to create supramolecular systems because of their capability to form hydrogen bonds [20]. Under deionized water environment, forming hydrogen bonds between the carbonyl group and the acylamide group decreases the hydrophilicity, which usually drives molecular aggregation in water [21]. Complementary hydrogen-bonding interaction between the diaminopyridine-type donor–acceptor–donor (DAD) hydrogen-bonding surface and imide acceptor–donor–acceptor (ADA) hydrogen-bonding surface is one of the most useful intermolecular glues. In the search for other complementary molecules that can produce hydrogels with melamine, thymidine is a promising candidate.

In this paper, we report on a two-component hydrogel of thymidine (T) (an important member of anticancer medicine) and melamine (M) based on supramolecular interactions between T and M. Because of the nine hydrogen bonding sites present in melamine (Scheme 1), and the planar, rigid structure favorable for stable π stacking, it is widely used as a gelling component [30–33] to create various aggregating structures [30–35] by combining with a complementary molecule. The molecular structures and hydrogen bonding sites of T and M are shown in Scheme 1a.

Thymidine is soluble in cold deionized water while melamine is soluble only in hot deionized water above 80 °C. It makes sense that T and M form a thermally reversible gel in the aqueous phase by effective hydrogen bonding interactions. In this letter, we present the gelation behaviors of T and M with different compositions. FTIR was used to investigate the H-bonding between M and T, and their mode of self-assembly. We demonstrated a simple method to produce new

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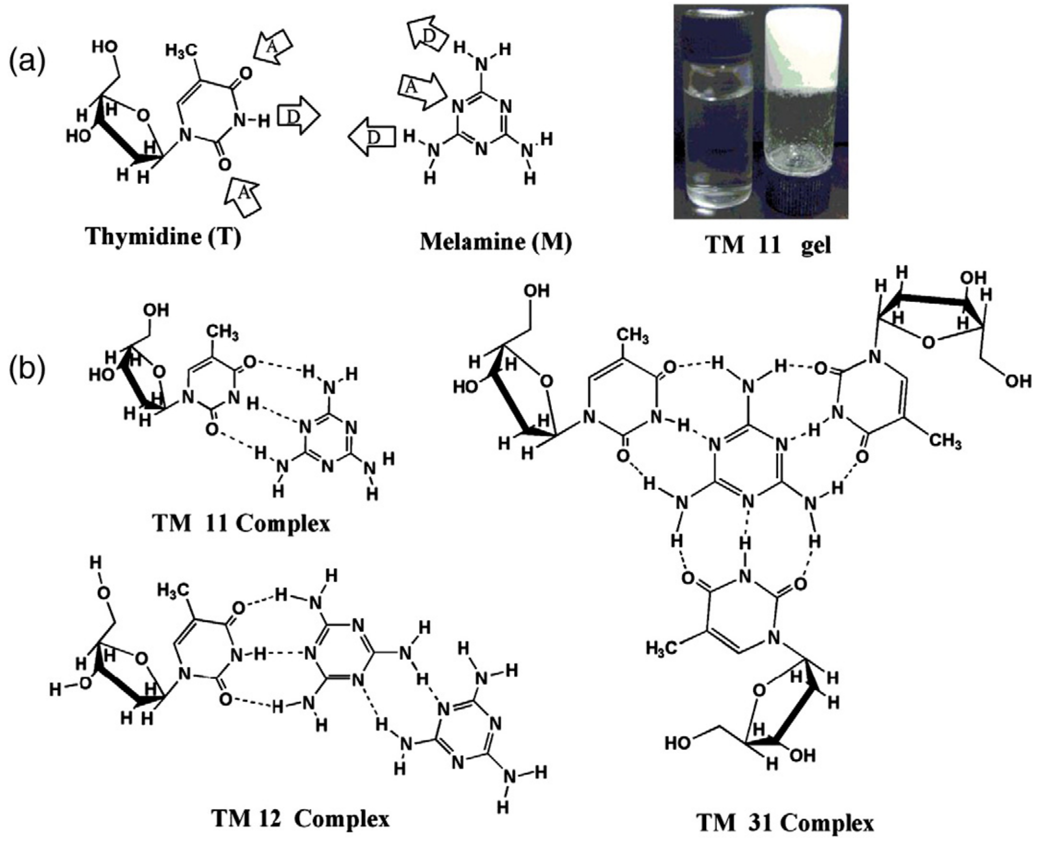

Scheme 1. Chemical structures and H-Bonding. (a) Chemical structures of T, and M, hydrogen-bonding donor and acceptor in their structures and visual image of a 0.1% (w/v) hydrogel of the TM11 complex. (b) Schematic illustration of the possible modes of H-bonding in TM complexes having different molar proportions of the components.

hydrogels and the manipulation of the gel morphologies and superstructures by changing the composition of T and M in an aqueous medium. The xerogels respectively showed rods, sheets and flower-like structures from the SEM images.

2. Experiment

2.1. Materials and methods

Thymidine (T) and melamine (M) were purchased from Shanghai Solarbio Bioscience & Technology Co. and were mixed in glass tubes at various molar ratios, such as 1:1 to make the TM11 gel. Deionized water was then added into these mixtures to make a total complex concentration of 0.1% (w/v), sealed, and heated to 120 °C to dissolve T and M. The solutions were then quenched to room temperature, yielding a white gel. Some of the hydrogels were then freeze-dried to produce dry TM complex. These gels were investigated by the methods described below. The other compositions of the complex (e.g., TM41, TM31, TM21, TM12, and TM13) were also prepared with the T:M molar ratio of 4:1, 3:1, 2:1, 1:2, and 1:3.

A. Scanning Electron Microscopy. To understand the network morphology of the gel, small samples of the freeze-dried TM complexes were dried in vacuum and coated with platinum for observation under a SEM JSM-6700F microscope operating at 5 kV.
B. Spectroscopy. FT-IR spectra of pure T, M, and TM xerogels were recorded using the KBr pellets of the samples in a Perkin–Elmer spectrophotometer. The spectra were collected at room temperature at a nominal resolution of 4.00 cm^{-1} and a number of sample scans equal to 1000. The FT-IR spectra were recorded in the 400–4000 cm^{-1} range using diffuse reflection.
C. The wide angle X-ray diffraction (WAXD) was carried out with a Bruker Avance D8 X-ray diffractometer. Scans were run at 40 kV and 30 mA over a scanning range of 2° to 23°2θ, a rate of 1°2θ/min, and a step size of 0.01°2θ. Slits were 0.5 mm (divergence) and 0.2 mm (receiving).

3. Results and discussion

Scheme 1 presents a representative visual image of the white gel formed in an inverted test tube. The SEM images of the xerogels of TM31, TM11, TM12, TM13, and the dried complexes of TM21 and TM41 from deionized water were presented in Fig. 1.

Fig. 1a shows that the TM31 xerogel is composed of randomly stacked short rods of 2 to 4 μm in length. The TM11 xerogel formed regularly packed rods (Fig. 1b left) with the width ranging from 0.2 to 0.8 μm and the length at about 1–2 μm (Fig. 1b right). In contrast, the TM12 xerogel was comprised of thin sheets stacking into clusters and these sheets were typically about 6 to 10 μm in width and about 10 μm in length (Fig. 1c right). Hundreds of the slices packed into hierarchical spheres that are 10 to 20 μm in diameter (Fig. 1c left). The TM13 xerogel shows flower-like structures (Fig. 1d left) comprised of curling sheets of about 6 to 10 μm in diameter (Fig. 1d right). The TM21 complex shows granules of 0.2 to 1 μm in diameter (Fig. 1e) and the TM41 complex shows flakes of about 1 to 5 μm in diameter (Fig. 1f).

In order to investigate the possible assembling mechanisms of these structures, we used FT-IR spectroscopy to characterize these gels. The comparison of the IR spectra of the corresponding T and M powders and their complexes from deionized water indicates the formation of intermolecular hydrogen bonds (Fig. 2). In sole T powder, the CONH (lactam) stretching modes of acylamino moieties are located at 3154 cm^{-1}, the —OH vibration modes are located at