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Investigation of the efficiency of gelation of melamine with the positional isomers of aminobenzoic acid

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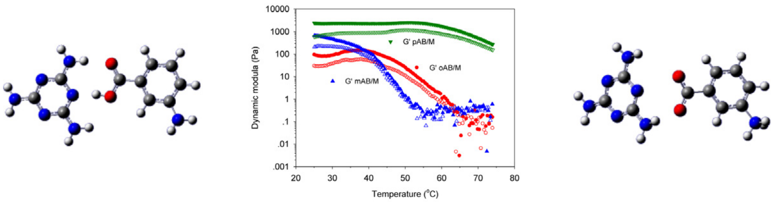
HIGHLIGHTS

- Gelation efficiency of melamine and positional isomers of aminobenzoic acids was investigated.
- Gelation efficiency is in the order of *p*-aminobenzoic acid/melamine>*m*-aminobenzoic acid/melamine>*o*-aminobenzoic acid/melamine.
- *p*- And *o*-aminobenzoic acids are in their unionized forms in both gel and sol states.
- Transformation from the unionized form to the zwitterionic form of *m*-aminobenzoic acid causes destabilization of the gel phase.

GRAPHICAL ABSTRACT

Gelation efficiency of melamine (M) and three positional isomers of aminobenzoic acid (AB) were investigated. The gelation and degelation of *m*AB/M in the uncharged and zwitterionic forms, respectively, were revealed reflecting its strong gel but easier degelation compared to *o*AB/M.



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ABSTRACT

Novel thermoreversible gelling systems consisting of the low-molecular-weight gelators, melamine (M) and three positional isomers of aminobenzoic acid (AB) were investigated. According to the rheological measurements, the gel strength at lower temperatures was in the order of *p*AB/M>*m*AB/M>*o*AB/M. This sequence was consistent with a computational analysis based on the stronger hydrogen bonding and the lower energy of each cluster. When heated, the sequence of the degelation temperature was in the order of *p*AB/M>*o*AB/M>*m*AB/M. This degelation temperature agreed with the DSC analyses which also demonstrated the thermoreversibility of these gel systems. It was surprising that the *m*AB/M which is a stronger gel than the *o*AB/M could be more easily converted to a sol than *o*AB/M. FTIR revealed that during heating, the *m*AB from the *m*AB/M could change from the uncharged form to the zwitterionic form (*m*ABz). In addition, the computational results indicated that the hydrogen bonding between the *m*ABz and M was much weaker than between the *m*AB and M. This may result in the lower degelation temperature of the *m*AB/M system. PXRD analyses showed different patterns of the mixtures compared to the individual compounds and indicated different interactions between M and the different ABs.

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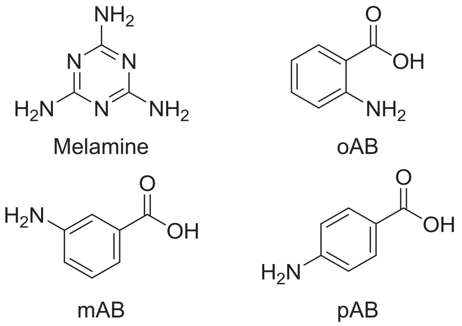

Fig. 1. Chemical structures of melamine and the positional isomers of aminobenzoic acid (AB).

1. Introduction

Hydrogels made from small molecules have generated much interest due to their potential use for oil recovery, templated nanoparticle synthesis, soft lithography, tissue engineering and controlled drug release [1–3]. Supramolecular hydrogels can be constructed by means of self-assemblies of small molecules, or low-molecular-weight gelators (LMWGs), based on van der Waals interactions, π–π interactions, hydrogen bonding or halogen bonding between the LMWGs [4–6]. In addition, by changing the structure, concentrations or molar ratios of a component, gel structures and properties can be quite easily modified [1,4,7,8].

In this study, two-component gel systems were investigated using melamine (M) and three positional isomers of aminobenzoic acid (AB): *ortho*-aminobenzoic acid (*o*AB), *meta*-aminobenzoic acid (*m*AB) and *para*-aminobenzoic acid (*p*AB) (Fig. 1). Each of the ABs have biologically activities: all are antimutagenic, *o*AB is vitamin L and *p*AB is part of the vitamin B complex [7,9,10]. Melamine has been widely used as a LMWG as it contains a large number of hydrogen-bonding sites (Fig. 1) that facilitate its use to form bicomponent gels [1,11,12]. In this work we used these 3 positional isomers of AB to individually interact with M. Different isomers of AB may demonstrate different interactions with M, that could result in different supramolecular complexations and gel properties. Due to the fact that *m*AB generally exists in a zwitterionic form (*m*ABz) [13], the interactions of M and *m*AB or M and *m*ABz were investigated. All gel properties were explored using differential scanning calorimetry (DSC) and rheological studies. The interactions between M and an individual AB were investigated using theoretical calculations and by Fourier transform infrared (FTIR) spectroscopy. In addition, the morphologies and thermal stability of the gels were investigated using a hot-stage microscope and the morphologies of the dried gels (xerogels) were determined using scanning electron microscopy (SEM). Furthermore, the crystallinity of the xerogels was determined using powder X-ray diffraction (PXRD).

2. Materials and methods

2.1. Materials

Melamine was obtained from Aldrich (USA), *o*AB from Fluka Chemie GmbH (Switzerland), *m*AB from Merck Schuchardt OHG (Germany) while *p*AB was from Sigma (USA). All other chemicals used were of analytical grade.

2.2. Preparation of oAB/M, mAB/M and pAB/M gels

Appropriate weights of the individual AB and M in 1:1 mole ratios were added to doubly distilled water to the required 3% w/v of the total components. The mixtures were heated to about 115 °C and left to cool to room temperature at which temperature all samples became real gels. For the FTIR, SEM and PXRD studies, all gels were lyophilized to obtain the xerogels. To investigate the zwitterionic and nonionic forms of *m*AB/M by FTIR, *m*AB/M gel was heated at about 60 °C, the obtained *m*AB/M sol was then dried using a rotary evaporator and the dried sample was left in a high vacuum chamber overnight.

2.3. DSC measurements

The DSC measurements were performed using a PerkinElmer DSC7 (PerkinElmer) equipped with a refrigeration cooling system. The heating and cooling rates were set as previously described [14]. Samples (3% w/v of *o*AB/M, *m*AB/M and *p*AB/M) were heated in sealed aluminium pans from 25 °C to 120 °C at a heating rate of 10 °C/min. The samples were held at that temperature for 5 min and cooled to 5 °C at a cooling rate of 5 °C/min. Subsequently, a second heating and cooling cycle were carried out at the same heating and cooling rates.

2.4. Rheological measurements

The rheological tests were performed using a strain-controlled rheometer (ARES 100FRTN1, Rheometric Scientific, NJ, USA). The rheometer was equipped with two sensitive force transducers for the measurements of torque that ranged from 0.004 to 100 g.cm. Parallel plate geometry (25 mm diameter and a 0.5 mm gap) were used. Samples in the liquid state were loaded onto the bottom plate of the rheometer at 65 °C. To prevent dehydration, the sample surface was covered with a thin layer of low viscosity silicone oil. All rheological measurements were performed at strains in the linear viscoelastic range (lower than 2% strain). The temperature sweep measurements were carried out at an angular frequency of 1 rad/s and at a heating rate of 0.5 °C/min that ranged from 25 to 74 °C. For the frequency sweep measurements, the samples were allowed to equilibrate at 25 °C on the bottom plate before being measured.

2.5. FTIR measurements

FTIR spectra were obtained using a PerkinElmer Spectrum One FTIR spectrometer (PerkinElmer, Waltham, MA, USA) equipped with a DTSG detector. The sample was ground with KBr in an agate mortar to a fine powder and then pressed into a disc under high pressure. All spectra were recorded from 4400 to 450 cm^{-1} by averaging 16 scans at a 2 cm^{-1} resolution.

2.6. Computational methods

All ab initio calculations were performed using the Gaussian 03W program [15]. The study began by the full geometry optimization of the M, *o*AB, *m*AB (both in the uncharged, and the zwitterionic forms,) and with *p*AB molecules at the MP2/6-311 ++G(2d,2p) calculations. The optimized structures of these molecules (Fig. S1) were further used to generate the trial structures of the AB/M clusters. Since the mole ratio of the AB and M in each AB/M cluster in the experimental method was 1:1, calculations of the 1:1 AB/M clusters were performed.

An AB molecule was initially placed at various hydrogen bond (H-bond) sites of M. The 10, 10, 10 and 5 plausible structures of the 1:1 *o*AB/M (Fig. S2), 1:1 *m*AB/M (Fig. S3), 1:1 *m*ABz/M (Fig. S4) and 1:1 *p*AB/M (Fig. S5) clusters, respectively, were created and optimized at the B3LYP/6-311 ++G(2d,2p) level. Subsequently, the lowest-lying energy structures of the 1:1 clusters of *o*AB/M, *m*AB/M, *m*ABz/M and *p*AB/M derived from the B3LYP calculations were fully reoptimized at the MP2/6-311 ++G(2d,2p) level.