Influence of Ultrasound Treatment on Assembling Structures and Properties of Supramolecular Hydrogels Formed from 1,3,5-Benzenetricarboxylic Acid and 4-Hydroxypyridine

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A new gelator synthesized from 1,3,5-benzenetricarboxylic acid (BTA) and 4-hydroxypyridine (PHP) was capable of gelling water under different ultrasound power. The resulting gels were investigated by gel-to-sol dissociation temperature (T_{gel}), SEM, DSC, and rheology measurement, which showed that the assembling structures and gel properties were correlated to the ultrasound power.

Supramolecular gels gelled by low-molecular-weight compounds (gelators) have attracted great attention recently owing to their versatile application in controlled drug release, oil recovery, tissue engineering, and so on.[1–4] During formation of the gel, the environmental stimulation such as cooling speed plays important roles in controlling the gel structures and properties.[5,6] Recently, Naota et al.[7,8] reported the sound-induced gelation of palladium-bound peptides. Li et al.[9] studied the effect of ultrasound on gel formation of l-glutamic acid-based dendritic compounds. We described the gelation under ultrasound treatment.[10] However, it is still not clear how the structures and properties of the gels change as the ultrasound power. In this paper, we prepared a new gelator from 1,3,5-benzenetricarboxylic acid (BTA) and 4-hydroxypyridine (PHP). The gels prepared under different ultrasound power were investigated by multiple techniques.

The gelator was synthesized from BTA and PHP at their molar ratio of 1:2 according to our previous synthetic procedure.[5,6] The IR spectrum displays the characteristic peak[11] of hydrogen bond formed between pyridyl and carboxylic groups at 1894 cm^{-1}. The ^{1}H NMR spectrum gives only three peaks[11] at 8.63 (for Ar–H), 7.73 (for pyridyl H-2) and 6.21 ppm (for pyridyl H-3) with their integral ratio of about 3:4:4, therefore two PHP molecules linking to one BTA via hydrogen bond during forming the gelator. The X-ray powder diffraction (XRD) spectrum of powder sample of the gelator is shown in Figure 1. There is the smallest angle peak at 6.08° (2θ), corresponding to a d-spacing of 1.46 nm, and such d-spacing shows good agreement with the calculated length (1.54 nm) of the gelator molecule depicted in Figure 1.

During forming the gel, the gelator concentration was controlled at 1.5 wt %. Firstly, 0.015-g gelator was added into 0.985 g distilled water in a test tube to form a suspension. After heated at 90 °C, the suspension gradually turned into a transparent solution. The tube was taken out and immersed into an ultrasonic vessel (40 kHz) at 20 °C under different ultrasonic power listed in Table 1. During the sonication process, fiber-like aggregates were noticed firstly in the solution. Afterwards, the fibers elongated and entangled with each other until an opaque hydrogel was formed at a time of 2–3 min. The gel kept stable even the tube was turned upside down, indicating the formation of a supramolecular hydrogel. Table 1 indicates that higher ultrasonic power results in gel with higher T_{gel}. Without ultrasonic treatment, the gelling system was partly gelled even the tube was cooled under room temperature for 6 h.

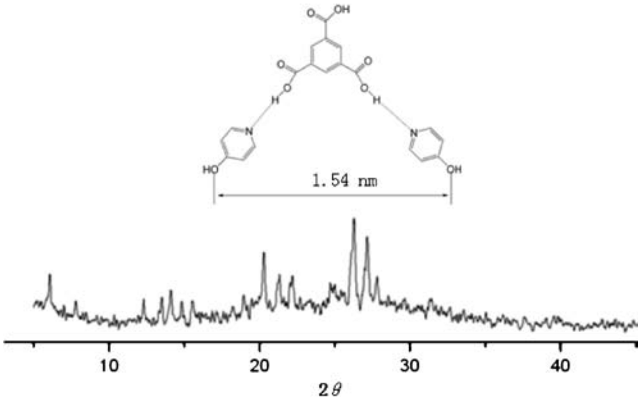

Figure 1. XRD of the gelator and the calculated length of gelator repeating unit by MOPAC program in Chem3D.

The dried gels (xerogels) were obtained after drying the gels completely under vacuum. To understand the assembling structures of the gels formed under different ultrasonic power, the xerogels were viewed directly by SEM using a JSM-6301 instrument. The SEM results in Figure 2 indicate that all the xerogels possess fibrous networks and the network density increases as increasing the ultrasonic power. The approximate average width of the aggregating fibers is summarized in Table 1, which becomes smaller as higher ultrasonic power applied. Therefore, the ultrasonic power provides an effective way to control the size of the assembling structures.

Table 1. Influence of ultrasonic power on the properties of the gels

Ultrasonic power/W	T_{gel} /°C	Fiber width/nm[a]	ΔH/J·g^{-1}	Q_f/%
200	51	500–800	243.6	72.9
300	54	300–500	278.2	83.2
400	56	100–350	281.4	84.3
500	63	100–250	286.3	85.7

[a] Image analyses were carried out using ImageJ 1.31 (The National Institutes of Health, USA, http://rsb.info.nih.gov/ij/).

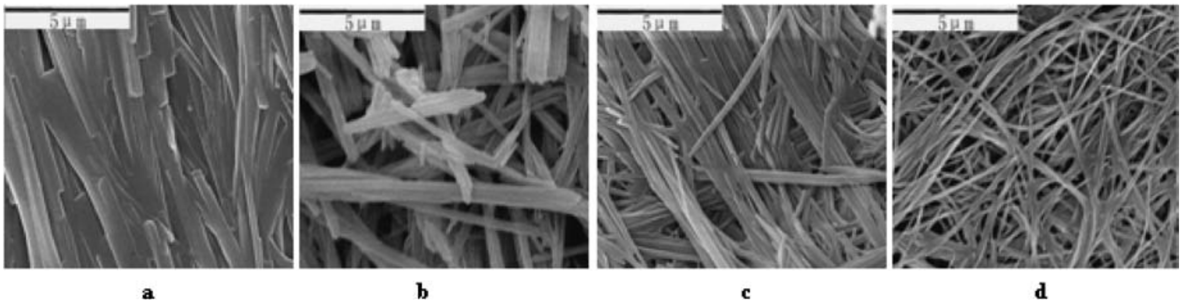

Figure 2. SEM photographs of assembling fibers formed under ultrasonic power of (a) 200, (b) 300, (c) 400, and (d) 500 W.

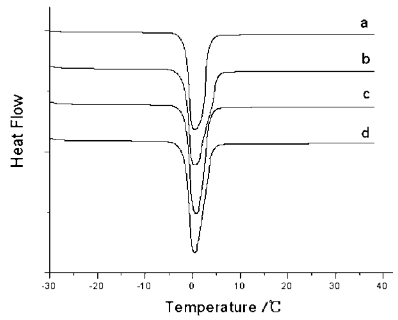

Figure 3. DSC curves of hydrogels formed under ultrasound power of (a) 200, (b) 300, (c) 400, and (d) 500 W.

The state of water within the gels was measured by using a Dupont-2400 differential scanning calorimeter.[10] Figure 3 shows the DSC curves of hydrogels formed under different ultrasound power. The integrated endotherm (ΔH) for the phase transition of water absorbed in the gels are listed in Table 1. The gravimetric content of the freezing bonded water (Q_f) is obtained by the ratio of ΔH and the integrated endotherm for pure water at 273 K. From Table 1, the Q_f increases gradually as increasing the ultrasonic power. Higher ultrasonic power resultes in smaller aggregating fibers, which provide stronger attraction to water molecules and give a higher content of Q_f.

We also measured the rheology of the gels by using a Physica MCR300 (Physica Instrument Corporation, Germany) rheometer. The data obtained from the stress-controlled rheometer are depicted in Figure 4, which reveals the typical linear viscoelastic behavior of a weak gel under different ultrasonic power.[12,13] Both storage modulus G′ and loss modulus G″ increase as ultrasound power increases. Therefore, higher ultrasonic power helps the formation of more elastic network. According to the gel morphologies in Figure 2, higher ultrasound power creates smaller superstructures which form stronger interaction with solvent molecules through their surface functional groups, therefore providing the gel with higher dynamic modulus. It should be emphasized that the gels were very fragile and the linear viscoelastic behavior could be measured only at low frequency values. At high-frequency value the storage modulus G′ falls while the loss modulus G″ increases dramatically, indicating the 3D cohesion to alter into a more liquid-like system. In summary, higher ultrasound power gives the gel with higher stability and smaller aggregates, which is helpful for understanding the function of ultrasound during gel formation.

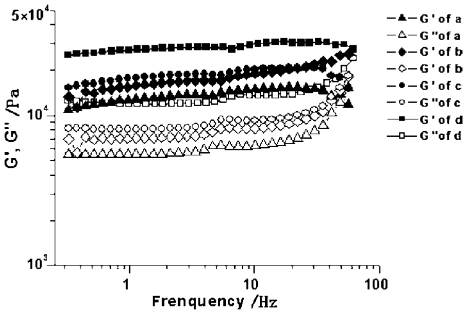

Figure 4. Dynamic moduli, G′ (solid) and G″ (hollow) vs. frequency on double logarithmic scale for the gels formed under ultrasonic power of (a) 200, (b) 300, (c) 400, and (d) 500 W.

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References and Notes

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11 Data of gelator: ^{1}H NMR (DMSO-d_6, 25 °C, 300 MHz): δ 8.63 (s, s, 3H, Ar–H), 7.73 (d, $J = 5.68$ Hz, 4H, pyridyl H-2), 6.21 (d, $J = 5.49$ Hz, 4H, pyridyl H-3). IR (KBr, γ): 1894, 1688 (–CO–), 3104 (carboxylic –OH) cm^{-1}. These data are available electronically as the Electronic Supporting Information on the CSJ-Journal Web site; http://www.csj.jp/journals/chem-lett/.
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