A Solvent-Driven Organogel Shrinkage

Chunsheng Shi and Jin Zhu*

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Received February 9, 2007
Revised Manuscript Received March 29, 2007

Gels are a class of condensed matter characterized by the existence of a three-dimensional microscopic network over macroscopic distances that immobilizes a fluid component.[1] They are classified into two different categories according to the nature of the network entanglement: chemical gel, fashioned with covalent bonding, and physical gel, formed through weak noncovalent interactions including hydrogen bonding, electrostatic interactions, coordination bonding, and so forth. Cross-linked polymer hydrogels, which belong to the former category, were found to undergo abrupt changes in volume,[2] from a highly swollen state to a shrunken state, in response to a variety of external stimuli.[3] This volume phase transition is arguably one of the most intriguing phenomena, the full explanation of which could potentially unveil the principle underlying the molecular interactions in both synthetic and biological systems.[4] Parallel with these developments are emerging efforts directed at the discovery and design of low-molecular-mass organic gelators, which are capable of forming intertwined networks by self-assembly into supramolecular architectures.[5] To extend the utility of this class of gels, a challenging issue is how to control their physical dimensions by exerting external stimuli. In this regard, only very few studies have been carried out on supramolecular hydrogels thus far.[6] Herein we report on the observation of an organogel shrinkage induced by an external stimulus.

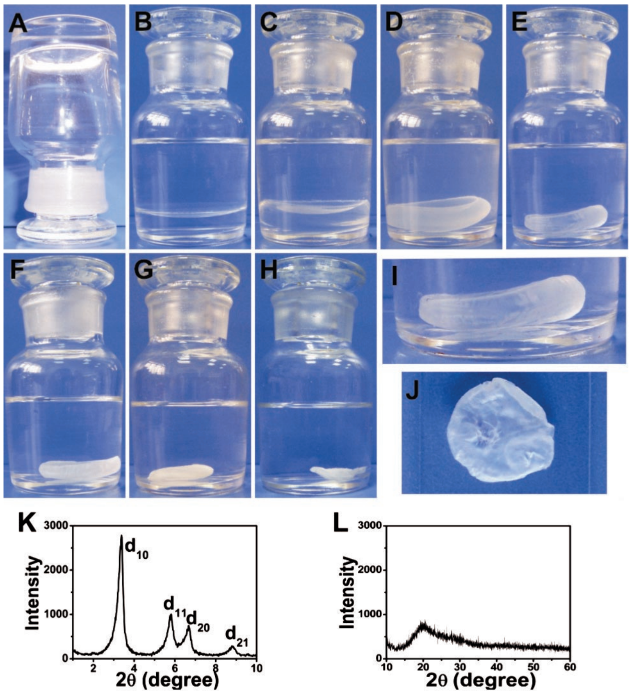

Figure 1. (A) As-prepared highly swollen gelled product. Evolution of the macroscopic outlook of the gel structure, with images acquired (B) 0 min, (C) 5 min, (D) 15 min, (E) 40 min, (F) 60 min, (G) 100 min, and (H) 160 min after the addition of acetone. (I) Enlarged view of part E. Notice that the decanting of the solution and addition of acetone every 20 min altered the location of the gel in the glass bottle. Images E−G were captured at the end of each round. (J) The final collapsed gel after the evacuation procedure. (K) SAXS and (L) WAXS profiles of the shrunken gel and associated indexation at room temperature using Cu Kα irradiation.

The synthesis of the native organogel,[7] which contains a substantial amount of liquid component and exhibits a highly swollen macroscopic outlook, is accomplished using a mixture of 1-octadecene (ODE), oleic acid (OLA), and cadmium acetate.[8] In a typical experiment, ODE (5 mL, 15.6 mmol), OLA (0.064 mL, 0.2 mmol), and cadmium acetate (0.0266 g, 0.1 mmol) were combined in a Schlenk flask and degassed for 1 h at room temperature. The mixture was then back-filled with argon and heated to 200 °C under constant stirring. One observation worthy of noting during the heating process was that, at around 160 °C, the initially insoluble cadmium acetate was completely dissolved and the whole mixture turned clear, indicative of the exchange of carboxylate ligands at the metal center and the formation of cadmium oleate. High-temperature ligand exchange has been adopted, by using rhodium acetate as the metal source, for the preparation of rhodium complexes ligated with long-chain carboxylates.[9] After reacting for 1 h at 200 °C, the solution was then allowed to cool to room temperature and left standing for 3 days to effect the gelation (Figure 1A). By challenging the native gel with a variety of solvents, we were able to identify acetone as an appropriate medium for inducing the gel collapse. The shrinking process could be followed visually by inspecting the macroscopic outlook of the gel. Interestingly, upon the addition of 20 mL of acetone, the native gel (Figure 1B), which originally took the shape of the container, started to peel off of its surface (Figure 1C), accompanied by the formation of so-called skin layer. By decanting the liquid outside the gel and adding fresh

---

(1) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133.
(2) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.
(3) (a) Annaka, M.; Tanaka, T. *Nature* **1992**, *355*, 430. (b) Yoshida, R.; Uchida, K.; Kaneko, Y.; Sakai, K.; Kikuchi, A.; Sakurai, Y.; Okano, T. *Nature* **1995**, *374*, 240. (c) Matsuo, E. S.; Tanaka, T. *Nature* **1992**, *358*, 482. (d) Tanaka, T.; Nishio, I.; Sun, S. T.; Ueno-Nishio, S. *Science* **1982**, *218*, 467.
(4) Kokufuta, E. *Langmuir* **2005**, *21*, 10004.
(5) George, M.; Weiss, R. G. *Acc. Chem. Res.* **2006**, *39*, 489.
(6) (a) Kiyonaka, S.; Sugiyasu, K.; Shinkai, S.; Hamachi, I. *J. Am. Chem. Soc.* **2002**, *124*, 10954. (b) Zhang, Y.; Gu, H.; Yang, Z.; Xu, B. *J. Am. Chem. Soc.* **2003**, *125*, 13680. (c) Zhou, S.-L.; Matsumoto, S.; Tian, H.-D.; Yamane, H.; Ojida, A.; Kiyonaka, S.; Hamachi, I. *Chem. Eur. J.* **2005**, *11*, 1130.
(7) (a) Lawrence, A. S. C. *Trans. Faraday Soc.* **1938**, *34*, 660. (b) Evans, E. A. *J. Inst. Pet.* **1950**, *36*, 367. (c) Cooper, W. *Chem. Ind.* **1995**, *74*, 1741.
(8) ODE (technical grade, 90%), OLA (technical grade, 90%), and Cd(OAc)$_2$·2H$_2$O (99.99+%) were purchased from Aldrich Chemical Co. Acetone (analytical reagent) was obtained from Shanghai Lingfeng Chemical Co. All chemicals were used as received.
(9) Giroud-Godquin, A. M.; Marchon, J. C.; Guillon, D.; Skoulios, A. *J. Phys. Chem.* **1986**, *90*, 5502.

10.1021/cm070406b CCC: $37.00

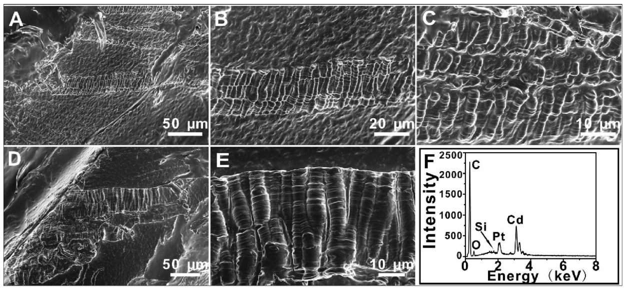

Figure 2. (A−E) SEM images of the shrunken gel. The gel was pre-coated with a layer of Pt several nanometers thick before imaging. (F) EDS spectrum of the shrunken gel. The gel was placed on a piece of silicon wafer and pre-coated with a 5 nm thick layer of Pt, which led to the observation of Si and Pt signals.

acetone every 20 min, one was able to continuously observe gel shrinkage (Figure 1D−G), apparently through the convective outflow of fluid component out of the gel due to the accumulation of internal pressure, in a manner analogous to cross-linked polymer systems demonstrated by Kaneko et al.[10] The gel collapsed into a highly shrunken structure after eight rounds of exchange of acetone (Figure 1H). Macroscopically, the thickness of the skin layer varies from location to location, as evidenced by the observation of both opaque and transparent areas on its surface (Figure 1I). The resulting viscous material was then evacuated to remove residual acetone (Figure 1J) and subjected to further characterization. Solvents other than acetone did not lead to the occurrence of a similar shrinking phenomenon. For example, addition of methanol resulted in the complete destruction of the gel framework and formation of dispersed oily droplets in the fluidic solution.

In contrast to the disordered structure of the native gel, the shrunken gel displays meso-scaled liquid crystalline order at room temperature, as revealed by small-angle X-ray scattering (SAXS; Figure 1K). Four Bragg reflections were identified in the small-angle region, with one intense and sharp reflection at $2\theta_1 = 3.40°$ ($d_1 = 26.0$ Å) and three relatively weak reflections centered respectively at $2\theta_2 = 5.84°$ ($d_2 = 15.1$ Å), $2\theta_3 = 6.70°$ ($d_3 = 13.2$ Å), and $2\theta_4 = 8.88°$ ($d_4 = 9.95$ Å). The reciprocal d spacings are in the ratio of $1{:}\sqrt{3}{:}\sqrt{4}{:}\sqrt{7}$, which could be indexed as a hexagonal columnar phase ($\mathrm{Col_h}$). A broad and diffuse scattering band, at $2\theta_5 = 19.7°$ ($d_5 = 4.5$ Å), was also observed by the wide-angle X-ray scattering (WAXS) (Figure 1L), reflecting the liquid-like conformationally disordered structure formed from long olefinic chains of the molecular species.

Characterization by scanning electron microscope (SEM) revealed a highly densely packed structure (Figure 2A), in contrast to the porous morphology typically associated with the xerogels,[11] suggestive of fundamentally different pathways for the collapsed gel formation. The most striking feature of the gel is parallelly aligned, single- and multilayered bamboo-like structures consisting of one-dimensionally spaced micrometer-scaled disc blocks of varied sizes (Figure 2B,C). We expect that a significant portion of the bulk material is made of bamboo-like structures, as evidenced by the observation of such morphology in the entire exposed area of a disrupted surface, as well as dotted spots distributed around, presumably resulting from vertical alignment of the structures (Figure 2D). A magnified image showed that bamboo-like structures were extensively inter-connected, generating substantial amount of branching points (Figure 2E). Energy-dispersive X-ray spectroscopy (EDS) established that the gel was comprised of Cd, O, and C (Figure 2F). The elemental composition was also confirmed independently by X-ray photoelectron spectroscopy. Cd 3d spectra revealed two peaks (405.6 and 412.5 eV), corresponding to the $3d_{5/2}$ and $3d_{3/2}$ components, respectively. The Auger $\mathrm{Cd_{MNN}}$ feature, with kinetic energy located at 380.0 eV, was observed by Auger electron spectroscopy. The values of photoelectron binding energy and Auger kinetic energy compare well with those of $Cd(OH)_2$,[12] allowing for an assignment of valence state of +2 for Cd in the gel. The asymmetric carboxylate stretching vibration ($\nu = 1534$ $\mathrm{cm^{-1}}$), indicative of the deprotonated form,[13] was identified by infrared spectroscopy, consistent with its coordination to cadmium.

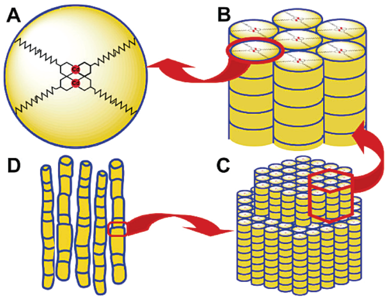

Figure 3. Schematic description of the proposed molecular packing model for the collapsed gel. ODE is omitted in the scheme. Molecular-level building block ($Cd_2(OOC{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}CH_3)_4$; A), meso-scaled structure (B), bamboo-like architecture (C), and parallel alignment of bamboo-like architecture (D) are illustrated. Note that the atoms directly coordinated to Cd (red sphere) in the paddle wheel unit are O and the rest of the atoms are C on the olefinic chains. Hydrogen atoms are omitted for clarity. The apical sites of Cd are likely to be occupied by carboxylates from neighboring paddle wheel units.[14] In this scheme, the depicted side chains of deprotonated OLAs are fully elongated and do not interdigitate. In reality, the side chains take cis conformations in the double bonds, and from the intercolumnar distance calculated from SAXS, they are either bent back or intertwined.

A molecular packing model, which is consistent with the above data and takes into account prior literature reports, could therefore be proposed for the collapsed gel structure (Figure 3).[14] At the molecular level, individual binuclear dicadmium tetraoleate,[15] in the shape of paddle wheel, is assembled. In the swollen gel state, intermolecular interactions between paddle wheel building blocks lead to the three-dimensional networked structure, which holds significant amount of ODE.[16] In the collapsed gel state, the paddle wheel units are stacked on top of one another to form the

---

(10) Kaneko, Y.; Yoshida, R.; Sakai, K.; Sakurai, Y.; Okano, T. *J. Membr. Sci.* **1995**, *101*, 13.

(11) Moniruzzaman, M.; Sundararajan, P. R. *Langmuir* **2005**, *21*, 3802.

(12) Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F. *Handbook of X-Ray Photoelectron Spectroscopy*; Muilenberg, G. E., Eds.; Perkin Elmer: Eden Prairie, MN, 1979.

(13) (a) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003**, *15*, 2854. (b) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

(14) Poizat, O.; Strommen, D. P.; Maldivi, P.; Giroud-Godquin, A. M.; Marchon, J. C. *Inorg. Chem.* **1990**, *29*, 4851.

(15) Wang, R.; Han, L.; Jiang, F.; Zhou, Y.; Yuan, D.; Hong, M. *Cryst. Growth Des.* **2005**, *5*, 129.

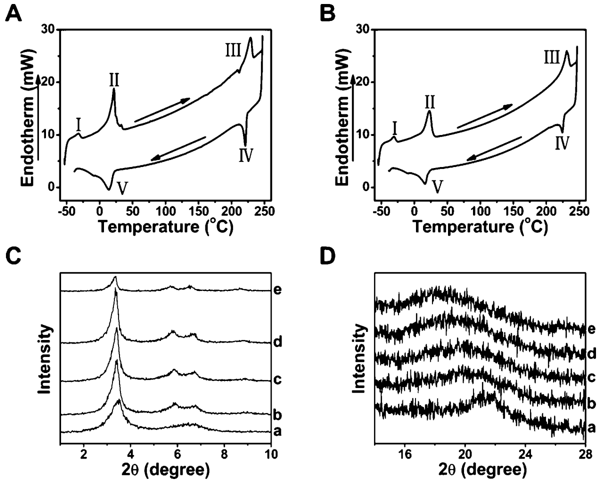

Figure 4. (A and B) DSC thermograms of the shrunken gel in argon during the first and second heating/cooling cycles. The heating and cooling rates were 20 °C min^{-1}. Three endothermic (I, II, and III) and two exothermic (IV and V) transitions were identified for the heating and cooling scans, respectively. The third exothermic transition could not be measured for instrument reasons. (C and D) SAXS and WAXS profiles of the shrunken gel at various temperatures using Cu Kα irradiation. Curves a−e correspond respectively to the data collected at −60 °C, −30 °C, −10 °C, 23 °C, and 100 °C in vacuum for the first heating run.

columnarly shaped structure, the extension of which in a close-packed fashion yields the expected hexagonal columnar mesophase, with a slight amount of trapped ODE. The proposed model is strongly supported by prior documentation of the gelling capability displayed by dicopper tetracarboxylates for hydrocarbons,[1,17] as well as the discotic mesophases fromed by dirhodium, dicopper, diruthenium, and dimolybdenum tetracarboxylates.[18] Built upon the meso-scaled structure, controlled alignment of micrometer-scaled disc segments affords one-dimensional bamboo-like architecture. Further alignment of the bamboo-like structure generates another level of structural organization. The four-tiered architecture complements, in both size regime and structural complexity, the macroscopic patterns formed by cross-linked polymer hydrogels.[3c]

Thermal properties of the shrunken gel were evaluated by differential scanning calorimetry (DSC) and variable temperature SAXS and WAXS. Three endothermic and two exothermic transitions were revealed by DSC (Figure 4A,B). Transition I is ascribed as a mesophase transformation, from a lamellar phase (at −60 °C, $2\theta_1 = 3.51°$, $d_1 = 25.1$ Å, $2\theta_2 = 6.47°$, $d_2 = 13.6$ Å, indexable reciprocal d spacing ratio $\sim$ 1:2)[19] to a hexagonal columnar phase, as evidenced by changes in the patterns of small-angle reflections (Figure 4C, curves a−c). Transition II is attributed to the melting transition of the so-called mesomorphic phase, formed by ODE and/or olefinic chains of OLA.[20] There is no change in the structure of the liquid crystalline mesophase, as revealed by virtually identical reflection patterns in the SAXS diffractograms (Figure 4C, curves c−e). The exact shape of the transition II in the DSC thermogram (Figure 4A) in the first heating run varies for samples left at room temperature for different periods of time, indicating that annealing induces the formation of mesomorphic crystalline domains with different sizes and defects. However, the effect of annealing on the overall phase structure, including liquid crystalline mesophase and mesomorphic phase, from the nanoscopic to the macroscopic regime, is not clear at this point. Transition III is associated with the transformation from liquid crystalline mesophase to isotropic liquid, accompanied by partial decomposition of the material. The assignment of transitions II and III is supported by polarized optical microscopy investigations. The reflections at both small- and wide-angle regions shift to lower angles with the increase of temperature (Figure 4C,D), reflecting an increase in the interchain distance caused by thermal expansion of the gel.

In summary, a solvent-driven organogel shrinking process in a supramolecular system has been uncovered. By introducing a distinct member to the repertoire of stimuli-responsive gel materials, we anticipate an increasing role by supramolecular self-assembly in the controlled gel state and ordered structure formation, given largely unexplored chemical space in this context. The phenomenon warrants further investigation, from both theoretical and experimental standpoints, by virtue of its relevance to how changes in molecular interactions could vastly alter morphologies of the condensed matter at different length scales.

Acknowledgment. J.Z. acknowledges support from the National Natural Science Foundation of China (20604011), the Six-Profession Talents Summit Program of Jiangsu Provinve (06-A-018), and the Program for New Century Excellent Talents in University (NCET-06-0451).

CM070406B

---

(16) (a) Weng, W.; Beck, B.; Jamieson, A. M.; Rowan, S. J. *J. Am. Chem. Soc.* **2006**, *128*, 11663. (b) Kuroiwa, K.; Shibata, T.; Takada, A.; Nemoto, N.; Kimizuka, N. *J. Am. Chem. Soc.* **2004**, *126*, 2016.

(17) (a) Terech, P.; Schaffhauser, V.; Maldivi, P.; Guenet, J. M. *Europhys. Lett.* **1992**, *17*, 515. (b) Terech, P.; Schaffhauser, V.; Maldivi, P.; Guenet, J. M. *Langmuir* **1992**, *8*, 2104.

(18) Giroud-Godquin, A.-M.; Maitlis, P. M. *Angew. Chem., Int. Ed.* **1991**, *30*, 375.

(19) Yang, X.; Lu, Q.; Dong, S.; Liu, D.; Zhu, S.; Wu, F.; Zhang, R. *J. Phys. Chem.* **1993**, *97*, 6726.

(20) For investigations of the mesomorphic phase in crystalline polymers, see: Androsch, R.; Wunderlich, B. *Macromolecules* **2001**, *34*, 5950 and references therein.