Supplementary Material (ESI) for Soft Matter

Molecular gels-based control release devices for pheromones†

Swapnil Rohidas Jadhav,[a] Bor-Sen Chiou,[b] Delilah Wood,[b] DeGrande Hoffman,[b] Gregory M. Glenn,*[b] and George John*[a]

[a] Department of Chemistry, The City College of New York, and The Graduate School and University Center of The City University of New York, 160 Convent Ave, NY, NY-10031.USA.
Tel: (+1) (212) 650-8353; Fax: (+1) (212) 650-6107.
E-mail: john@sci.ccny.cuny.edu

[b] Western Regional Research Center, United States Department of Agriculture, Agricultural Research Service. 800 Buchanan Street, Albany, California 94710. USA.
E-mail: greg.glenn@ars.usda.gov

Table of contents

Supplementary Material (ESI) for Soft Matter

Experimental Section

Materials. 2-Heptanone (CAS registry No. 110-43-0) was purchased from the Sigma-Aldrich Co. (St. Louis, MO). Peach fruit film (100 μm thickness) processed from a 3:1 blend of peach puree:pectin (Origami Foods, Stockton, CA) was used as a vapor barrier film for making control-release devices. Beeswax was purchased locally (Protex, Berkeley, CA).

Gelation and Gel Characterization

2-Heptanone Gels. Gels containing 2-heptanone were made by weighing the prescribed amount of mannitol octanoate (M8) in an empty glass vial (1.5 cm dia., 2.5 cm length) and pipetting the 2-heptanone to obtain 3%, 5%, or 7% wt/v of M8 in 2-heptanone. The vial was capped and then partially submerged in a water bath (80°C) using a clamp. The vial contents were swirled intermittently to facilitate dissolution. Once the M8 had completely dissolved in the 2-heptanone, the temperature of the water bath was slowly lowered. The M8 began crystallizing and eventually formed a solid, semitransparent gel upon further cooling. Formation of gel was confirmed when no gravitational flow of 2-heptanone was observed on inversion of a vial.

Gel-sol melting temperature (T_g). Gel melting temperature was determined by typical tube inversion method.[1,2] In a 2 mL scintillation vial gel was prepared as described above; the vial was immersed in the oil-bath 'upside down' and slowly heated. The temperature at which the viscous gel melted down was recorded as T_{gel}.

[1] F. M. Menger and K. L. Caran, *J. Am. Chem. Soc.*, 2000, **122**, 11679-11691.

[2] P. K. Vemula and G. John, *Chem. Commun.*, 2006, 2218-2220.

Differential Scanning Calorimetry (DSC). 2-Heptanone gels with 7% wt/v concentration of M8 in 2-heptanone was made as previously described. After cooling to room temperature, approximately 25 mg of gel was loaded and sealed in a stainless steel DSC capsule (model 1536,

Perkin Elmer, Waltham, MA). Sample was heated from 25 ^{o}C to 95 ^{o}C in a DSC (model 2910 TA Instruments, New Castle, DE) and then cooled to room temperature at a rate of 5 ^{o}C/min.

Optical Microscopy. Gel formation was monitored through a flat-bottomed 25 ml glass vial containing 2-heptanone (2 ml) and gelling agent (3 %w/v). The gelling agent was dissolved in 2-heptanone by heating to 80°C in a water bath. Crystallization and gel formation during cooling were documented using a digital camera (Retiga 2000R, Q-Imagining, Surrey, BC, Canada) mounted on a stereo light microscope (Leica Model MZ 16F, Leica GmBH, Wetzlar, Germany). Photographs were taken every 3 seconds starting at the moment the first crystal was observed.

Scanning Electron Microscopy (SEM). SEM was done by first preparing a 5 %wt/v M8 gel in 2-heptanone as previously described. The gel was removed from the glass vial and sliced into pieces (ca. 5 mm). The samples were immediately placed in the chamber of a critical point dryer (Tousimis Autosamdri 815, Tousimis, Rockville, MD) and equilibrated in liquid CO_2 for several hours to displace the 2-heptanone. After several exchanges over a period of several hours the samples were critical point dried before sputter coating with gold-palladium in a Denton Desk II Sputter Coating Unit (Denton Vacuum, Inc., Moorestown, NJ). The samples were viewed and photographed with a Hitachi S4700 field emission scanning electron microscope (Hitachi, Japan).

Mechanical Properties. The mechanical properties of the gels were determined using both a penetrometer test as well as rheometry.

Penetrometer Test: 3%, 5%, and 7% wt/v M8 gels in 2-heptanone was prepared in glass vials as previously described. Gel thickness was approximately 30 mm. Penetrometer tests were performed without removing the gels from the vials so that measurements could be recorded on undisturbed sample. Penetrometer tests were performed by pressing a flat-faced cylindrical probe (8 mm dia.) into the gel sample to a depth of 3 mm at a rate of 5 mm/min using a universal testing machine (model 4500, Instron Corp., Canton, MA). A load cell (100 N) was used to detect compressive force. Peak force, modulus, and toughness were determined from

force/deformation data. Five samples were tested for each of the glycolipid concentrations prepared.

Dynamic Rheological Tests: Gel samples were performed using a Peltier plate rheometer (TA Instruments, model AR2000, New Castle, DE). The gel was scooped from the vials with a spatula and placed on a Peltier plate. A stainless steel parallel plate (60 mm) was lowered onto the sample. The sample thickness was held constant at 1 mm. Dynamic rheological tests were used to characterize the elastic modulus (*G')* and viscous modulus (*G"*). The elastic modulus is a measure of the solid-like response of the material, whereas the viscous modulus is a measure of the liquid-like response of the material. All dynamic measurements were obtained at a frequency of 1 rad/s and a strain of 2%. In addition, all experiments were performed within the linear viscoelastic region.

Infra-red (IR) spectroscopy. IR spectroscopic analysis of the 2-heptanone and M8 gel in 2-heptanone (5 %wt/v) was performed using Nicolet 380 FT-IR spectrophotometer in ATR mode.

X-ray diffraction studies. A small portion of a wet and xerogels of M8 gel in 2-heptanone (5 %wt/v) sample was transferred in a sample holder and immediately the reflectance was measured. The XRD measurement was performed on PANalytical X'Pert PRO with MPD PW 3040/60 generator S/N DY 2974 and monochromatic Cu-Co radiation (45 kV, 40 A). XRD measurement on the plain M8 powder was also performed in same manner.

Pheromone Release Experiments

Biodegradation. The relative degradation rate of samples was determined using a respirometer (Micro-Oxymax System, Columbus Instruments, Columbus, OH). The respirometer CO_2 sensor was calibrated with a CO_2 standard gas (8,000 ppm). The carbon content of the samples (60.8%) was determined according to ASTM methods using a CHN elemental analyzer (Perkin Elmer 2400, Boston, MA). The analyzer was equipped with a thermoconductivity detector and was

operated using helium gas. The combustion temperature was 975 °C and the reduction temperature was 680°C.

Commercial compost was purchased locally and adjusted to 58 % moisture (dry weight basis). The glass sample bottles (250 ml) were filled with 20.0 g compost and 0.30 g test sample that was gently mixed with the compost. The sample bottles were initially flushed with CO_2-free air and sealed. Respirometry experiments were conducted at room temperature (22^{o}C) and CO_2 concentration was read every 12 hr. Three replications were tested for each treatment and data were expressed in terms of percentage mineralization.

Evaporation Rate. The relative rate of evaporation between liquid 2-heptanone and a 2-heptanone gel (M8 concentration 7 %wt/v) was determined by monitoring weight loss of both materials under the same conditions. The tests were performed using aluminum sample dishes (50 mm dia., 20 mm depth). The dishes were filled (5 g) with 2-heptanone liquid (control) or gel (treatment). For making a dish containing gel, the mixture of 2-heptanone and M8 (7 %wt/v) was heated to sol state and the solution (~ 5 g) was poured into an aluminum sample dish and immediately covered to minimize evaporation. The samples were allowed to equilibrate 1 hr at room temperature. All samples were uncovered and placed in a poly(methyl methacrylate) cabinet equipped with a ventilation fan. The airflow velocity was 9.8 m/s, and the airflow volume was 4.7 volume changes per second (9.9 m^3/min). All tests were performed at room temperature. The samples were weighed regularly to monitor weight loss.

Controlled-Release. Control-release devices made with M8 gel in 2-heptanone (7 %wt/v) were compared with a standard control-release device made with beeswax as a reservoir material. The beeswax devices were made by first preparing the reservoir material. This was accomplished by dissolving beeswax in 2-heptanone (1:1) in a sealed glass jar at elevated temperatures (80 ^{o}C). The molten mixture was poured into a disk mold (3 mm thick, 10 cm diameter) and allowed to cool and solidify. Specimens weighing 3.2 g were cut from the beeswax/2-heptanone disc and sealed within a vapor barrier film envelope using a heat sealer (Model 2526, Clamco, Cleveland, OH) operated at 405 °C. The M8 gel in 2-heptanone (% 7wt/v) was heated to sol state in a water

bath and sample weighing 3.2- 3.5 g was poured into a film envelope and sealed closed as previously described and in the literature.[3]

All control-release experiments were performed in duplicate. Loss of 2-heptanone from the devices was measured as weight loss. To activate release of 2-heptanone, an 8 mm hole was made in the film envelope of each sample. Experiments were run until 50% or more of the 2-heptanone had been lost.

[3] G. M. Glenn, A. P. Klamczynski, C. Ludvik, J. Shey, S. Imam, B. –S. Chiou, T. McHugh, G. DeGrandi-Hoffman, W. Orts, D. F. Wood and R. Offeman, *J. Agric. Food Chem.*, 2006, **54**, 3297.

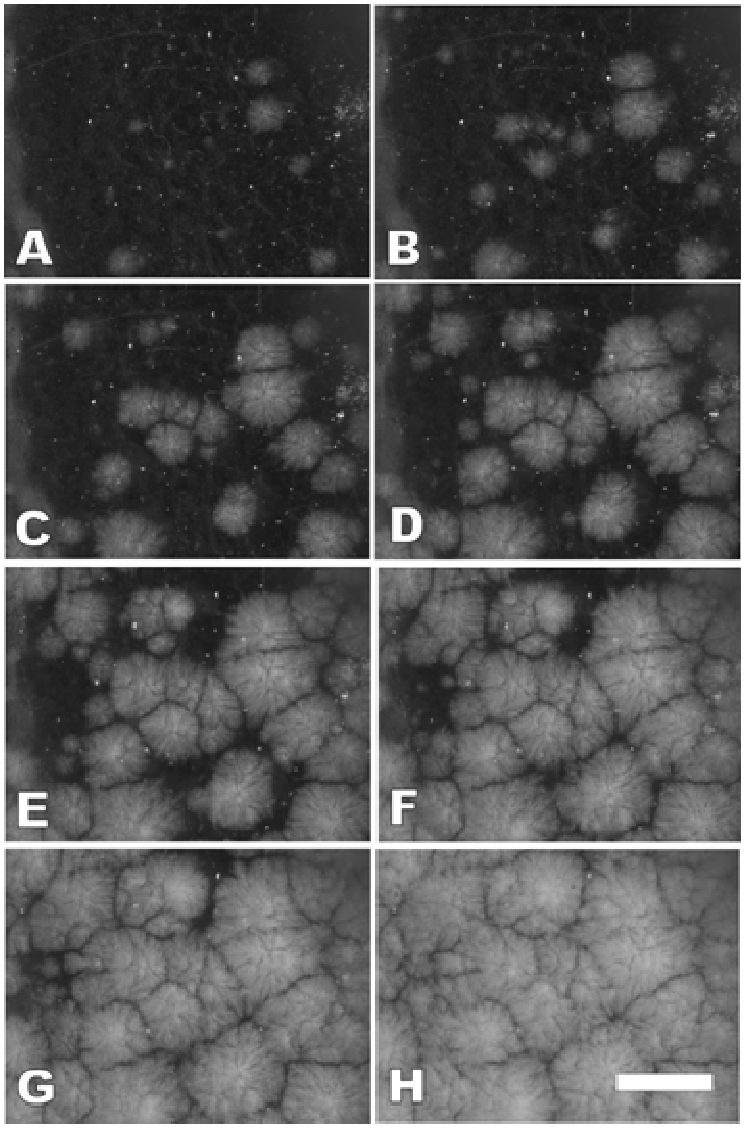

Figure S1. Optical Micrographs of sequential views during the gelling process of M8 in 2-heptanone (3 %wt/v). Scale bar = 1 mm.

Light microscopy was effective in documenting the gelling behavior of the M8 in 2-heptanone. Samples that were heated to 80°C and cooled typically demonstrated the appearance of small crystals (Fig. S1 A). The crystals quickly grew and new crystals formed randomly throughout the mixture upon further cooling. Sequential micrographs of the crystals revealed that the crystals typically grew until they reached adjacent crystals (Fig. S1 A-H). Individual crystals initially

remained distinct as the void spaces were filled. With time, however, it became more difficult to distinguish individual crystals as the gel solidified (Fig. S1 H). Crystal diameters were as large as 1 mm (Fig. S1 H).

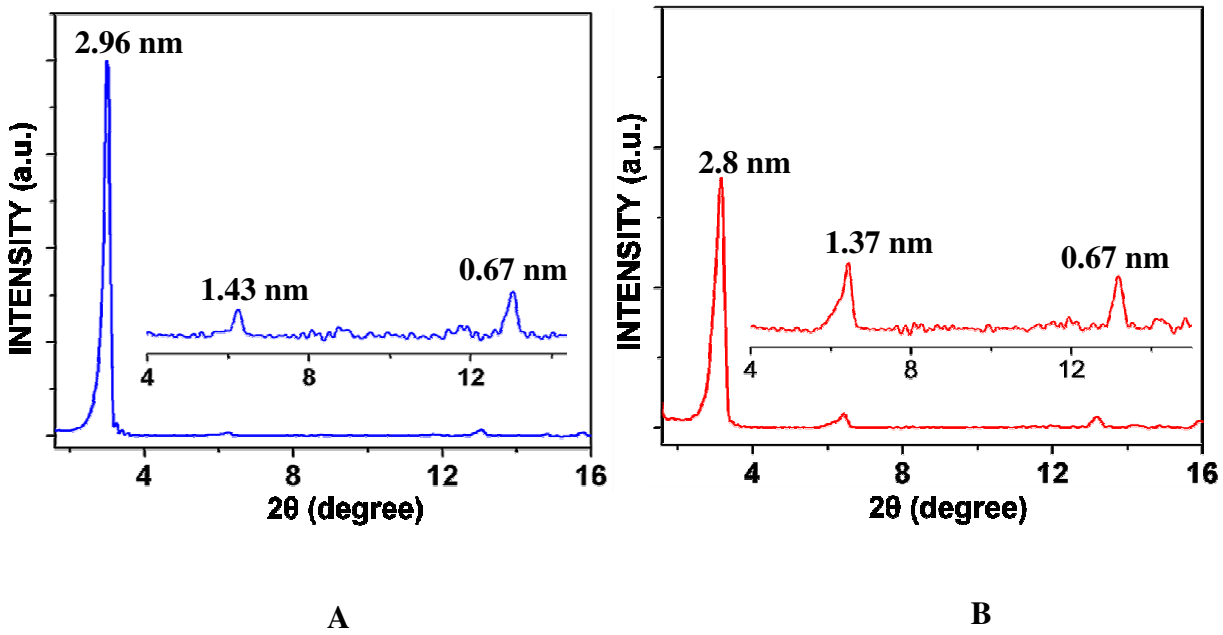

Figure S2. **A**. X-ray diffraction (XRD) pattern of **M8** powder with an inset of showing the magnified region from 2θ= 4-14°. **B.** XRD pattern of xerogel of **M8** 2-heptanone gel with an inset showing the magnified region from 2θ = 4-15°. In the both the samples, the spacings (*d*) obtained between successive peaks follow the ratio of 1:1/2:1/3, which is characteristic of lamellar stacking. Thus, in both (powder and xerogels) the samples, the M8 aggregates in similar pattern to produce lamellar structure with periodicity of 2.96 and 2.8 nm respectively.

Supplementary Material (ESI) for Soft Matter

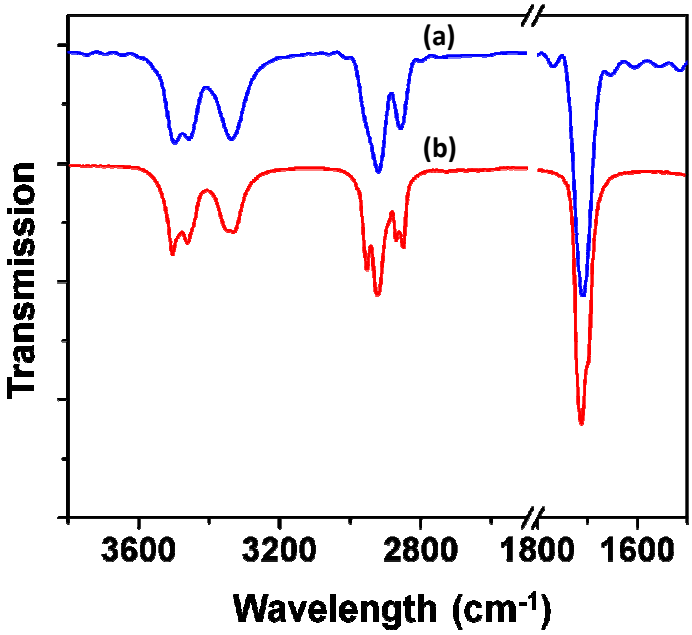

Figure S3. I. FTIR spectra of (a) **M8** solid (b) **M8** 2-heptanone gel. Analyzing the IR spectrums, it can be concluded that the wavenumbers of group frequencies of powder sample of M8 are on par with the gel samples. Thereby, indicating that the M8 in the gel state may exhibit similar aggregation mode as in the crystalline state, as confirmed from the analysis of XRD data too.

Supplementary Material (ESI) for Soft Matter

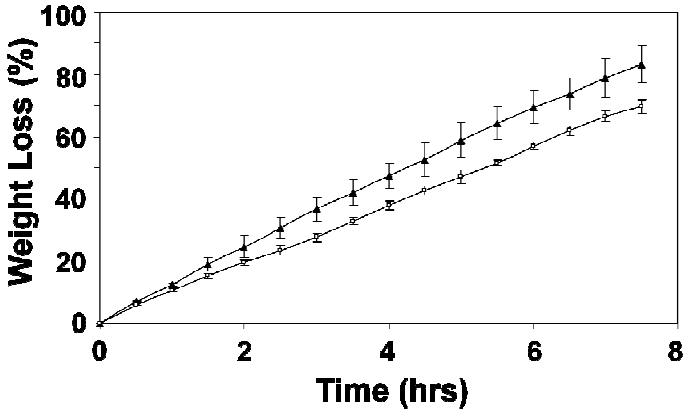

Figure S4. Weight loss from evaporation of 2-heptanone from a liquid (O) or 2-heptanone gel (▲).

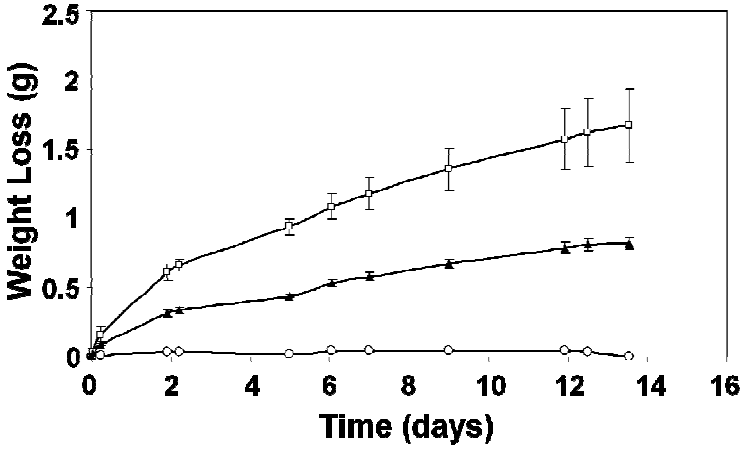

Figure S5. Weight loss over time of control-release devices. The control (O), which was sealed in vapor barrier film, had very little weight loss during the time period tested. The device containing 2-heptanone gel (□) had double the weight loss compared to the devices containing beeswax (▲).