Supporting Information for

Yielding Behavior of Tough Semicrystalline Hydrogels

Cigdem Bilici[1] , Semra Ide[2,3], and Oguz Okay[*1]

[1] Istanbul Technical University, Department of Chemistry, 34469 Maslak, Istanbul, Turkey
[2] Hacettepe University, Department of Physics Engineering, 06800 Beytepe, Ankara, Turkey
[3] Hacettepe University, Department of Nanotechnology and Nanomedicine, 06800 Beytepe, Ankara, Turkey

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Experimental part

Hydrogel preparation and gel fraction measurements. The monomers N, N-dimethylacrylamide (DMA), n-octadecyl acrylate (C18A), lauryl methacrylate (C12M) and the initiator Irgacure 2959 were received from Aldrich and used without further purification. The hydrogels were prepared by bulk copolymerization of DMA with the hydrophobic monomers C18A and C12M in the presence of Irgacure 2959 as the photoinitiator at a concentration of 0.1 wt.% (with respect to the monomers). The hydrophobe content of the comonomer feed was fixed at 30 mol% while the amount of C12M was varied between 0 and 20 mol%. The monomers DMA, C18A, and C12M were first mixed and thoroughly stirred at 45 °C to obtain a homogeneous solution. After addition of the initiator Irgacure 2959 and bubbling nitrogen, the monomer mixtures containing the initiator were transferred into several pipettes of 7.5 mm in diameter as well as into rectangular plastic molds (200x13x0.9 mm). The polymerization was conducted at 23±2 °C for 1 day under UV lamp at a wavelength of 360 nm. After polymerization, the copolymer samples were immersed in a large amount of water for several days by replacing water every day to extract any soluble species. The water temperature was 70 °C and 23±2 °C for the first and following days, respectively. The initial high-temperature immersion period above the melting temperature of the crystalline domains of the hydrogels is to provide that the network chains assume their relaxed conformation. After equilibrium swelling in water at 23±2 °C, the gel samples were taken out of water and freeze-dried. The water content of the hydrogels was calculated as H_2O % = 10^2 (1 – m_{dry}/m) where m and m_{dry} are the swollen and dried masses of the gel sample. The gel fraction W_g, that is, the conversion of monomers to the water-insoluble polymer was calculated from the masses of dry polymer network and from the comonomer feed.

Rheological experiments. Rheological measurements were performed on Gemini 150 Rheometer system, Bohlin Instruments, equipped with a Peltier device for temperature control. Hydrogel samples

equilibrium swollen in water were subjected to dynamic experiments between the parallel plates of the rheometer. The upper plate (diameter 20 mm) was set at a distance of 900−1100 μm, depending on the swelling degree of the hydrogels. During all measurements, a solvent trap was used to minimize the evaporation. Viscoelastic behavior of the hydrogels depending on temperature was measured during heating-cooling cycles between 25 and 65 °C at a fixed rate of 1°C·min^{-1}. An angular frequency of $\omega =$ 6.28 rad·s^{-1} and a deformation amplitude $\gamma_o = 0.001$ (0.1%) were selected to ensure that the oscillatory deformation is within the linear regime. The changes in the dynamic moduli of gels were monitored during the course of the cycle as a function of temperature. The samples were also subjected to frequency sweep tests at $\gamma_o = 0.001$.

DSC measurements. DSC measurements were conducted on a Perkin Elmer Diamond DSC under a nitrogen atmosphere. The gel samples equilibrium swollen in water were cut into small specimens of about 10 mg weight and sealed in aluminum pans. Then, they were scanned between 25 and 65 °C with a heating and cooling rate of 5 °C·min^{-1}. From the DSC curves, enthalpy changes during melting, ΔH_m, were calculated from the peak areas. The degree of crystallinity, f_{cry}, that is, the fraction of C18A units in crystalline domains, was estimated by $f_{cry} = x_{HM} \Delta H_m / \Delta H_m^o$, where x_{HM} is the mole fraction of the hydrophobic monomer in the comonomer feed and ΔH_m^o is the melting enthalpy of crystalline C18A units. ΔH_m^o was taken as 71.2 kJ.mol^{-1} from previous works on the melting behavior of long n-alkyl chains exhibiting a hexagonal crystal structure.[1-4]

Small (SAXS) and wide angle X-ray scattering (WAXS) measurements. SAXS and WAXS data were collected at 23 °C with an exposure time of 900 s using HECUS-SWAXS system (Graz, Austria).[5-7] Nickel filtered CuK$_\alpha$ radiation ($\lambda = 0.154$ nm) operating at 50 kV / 40 mA was used as X-ray source. Two linear position sensitive detectors (PSDs) were used for SAXS and WAXS data ranges.

Mechanical tests. Uniaxial elongation measurements were performed on swollen hydrogel samples at 23±2 °C on Zwick Roell test machine with 500 N load cell. All the tests were performed on rectangular hydrogel samples (1x5x20 mm) under following conditions: Strain rate = between $1.7x10^{-3}$ and $1.7x10^{-1}$ s^{-1}; sample length between jaws = 10 mm. Load and displacement data were collected during the experiments. The stress was presented by its nominal value σ_{nom}, which is the force per cross-sectional area of the undeformed gel specimen, while the strain is given by λ, the deformation ratio (deformed length/initial length). The strain ε is also defined as the change in the length relative to the initial length of the gel specimen, i.e., $\varepsilon = \lambda - 1$. The Young's modulus E was calculated from the slope of stress–strain curves between 0.5-1.5% deformations. The yield energy U_y and the energy to break (toughness) W were calculated from the areas below the stress-strain curves up to the yield point and to the fracture point, respectively. The successive elongation tests were conducted at a constant strain rate of $8.3x10^{-2}$ s^{-1} to a maximum elongation ratio, followed by retraction to zero force and a waiting time of 5 min, until the next cycle of elongation.

References

1. Mogri, Z.; Paul, D.R. Gas sorption and transport in side-chain crystalline and molten poly(octadecyl acrylate). *Polymer* **2001**, 42, 2531-2542.

2. Bisht, H.S.; Pande, P.P.; Chatterjee, A.K. Docosyl acrylate modified polyacrylic acid: synthesis and crystallinity. *Eur. Polym. J.* **2002**, 38, 2355-2358.

3. Broadhurst, M.G. An analysis of the solid phase behavior of the normal paraffins. *J. Res. Natl. Bur. Stand. A* **1962**, 66A, 241-249.

4. Jordan, E.F.; Feldeisen, D.W.; Wrigley, A.N. Side-chain crystallinity. I. Heats of fusion and melting transitions on selected homopolymers having long side chains. *J. Polym. Sci. A-1: Polym. Chem.* **1971**, 9, 1835-1851.

5. Masalci, O.; Kazanci, N.; Orujalipoor, I.; Ide, S. Nano-structural analysis of a lyotropic liquid crystal (TTAB + water + decanol ternary) system by salt (NH4Br) addition. *Mol. Cryst. Liq. Cryst. Sci. Technol.* **2015**, 609, 70–79.

6. Ozcan, Y.; Ide, S.; Butun, V.; Jeng, U-S.; Lai, Y-H.; Su, C-H. Micellization behavior of tertiary-amine-methacrylate-based block copolymers characterized by small-angle X-ray scattering and dynamic light scattering. *Mater. Chem. Phys.* **2013**, 138, 559-564.

7. Goktas, M.; Cinar, G.; Orujalipoor, I.; Ide, S.; Tekinay, A.B.; Guler, O. Self-assembled peptide amphiphile nanofibers and PEG composite hydrogels as tunable ECM mimetic microenvironment. *Biomacromolecules* **2015**, 16, 1247-1258.
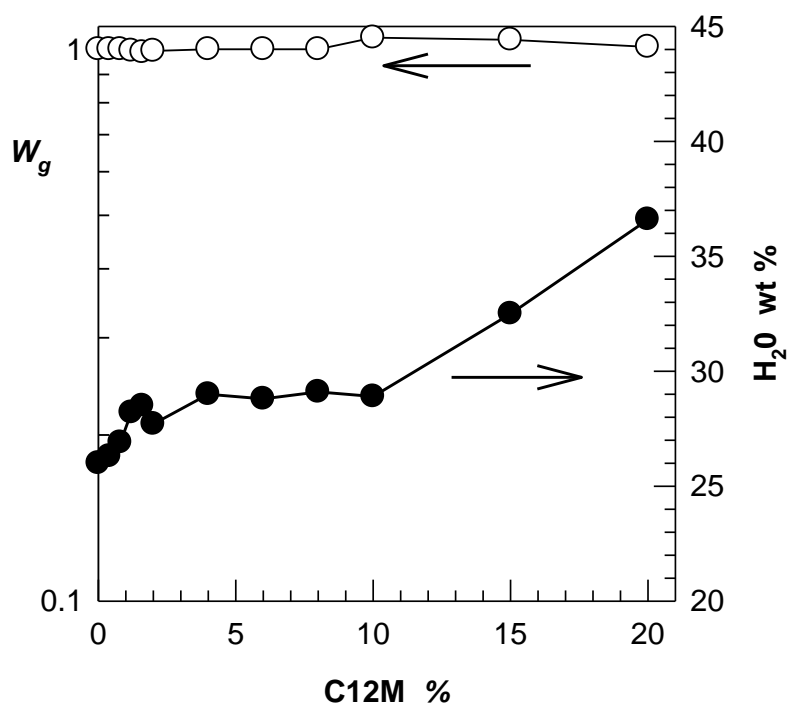
Figure S1. Gel fraction W_g and the water content (H_2O wt%) of the hydrogels plotted against C12M %.
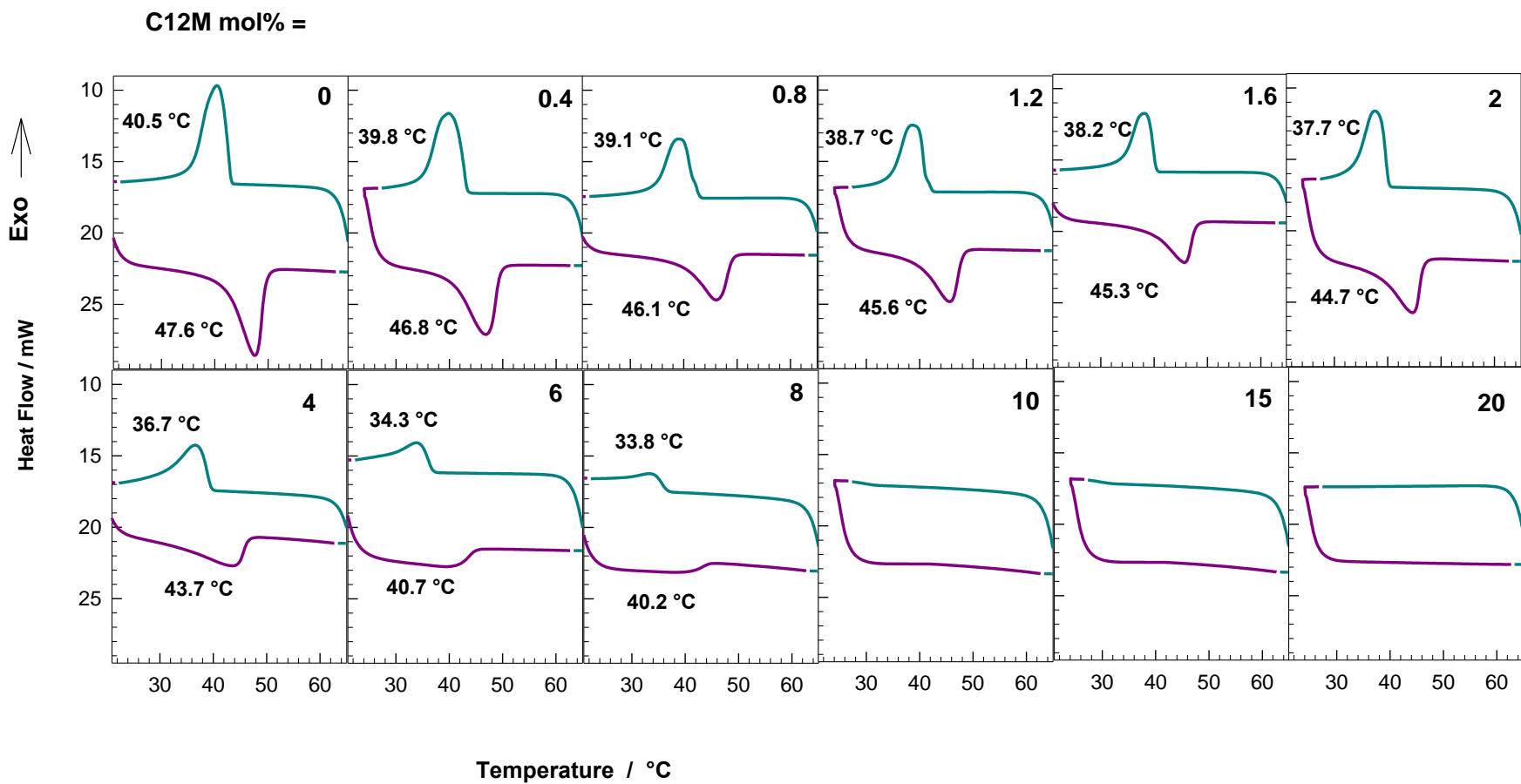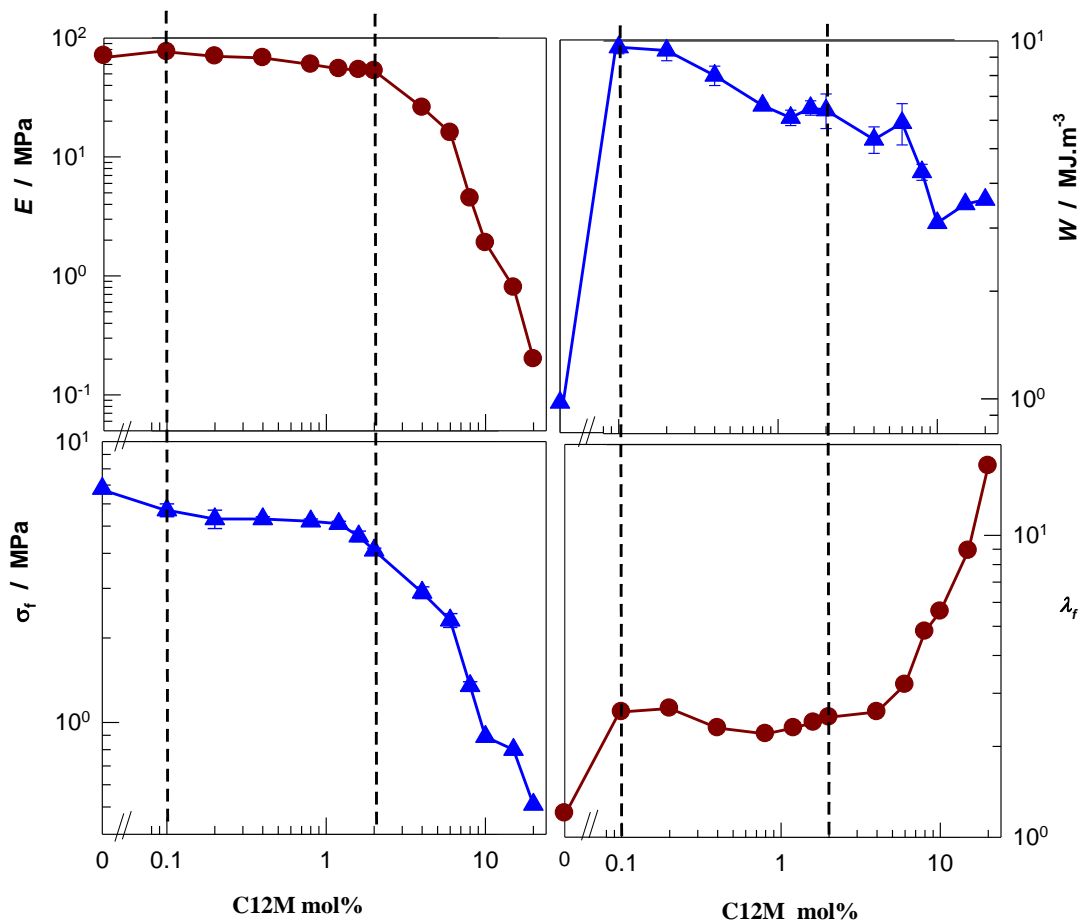
Figure S2. DSC scans of the hydrogels containing various amounts of C12M as indicated. The melting and crystallization temperatures are also indicated.
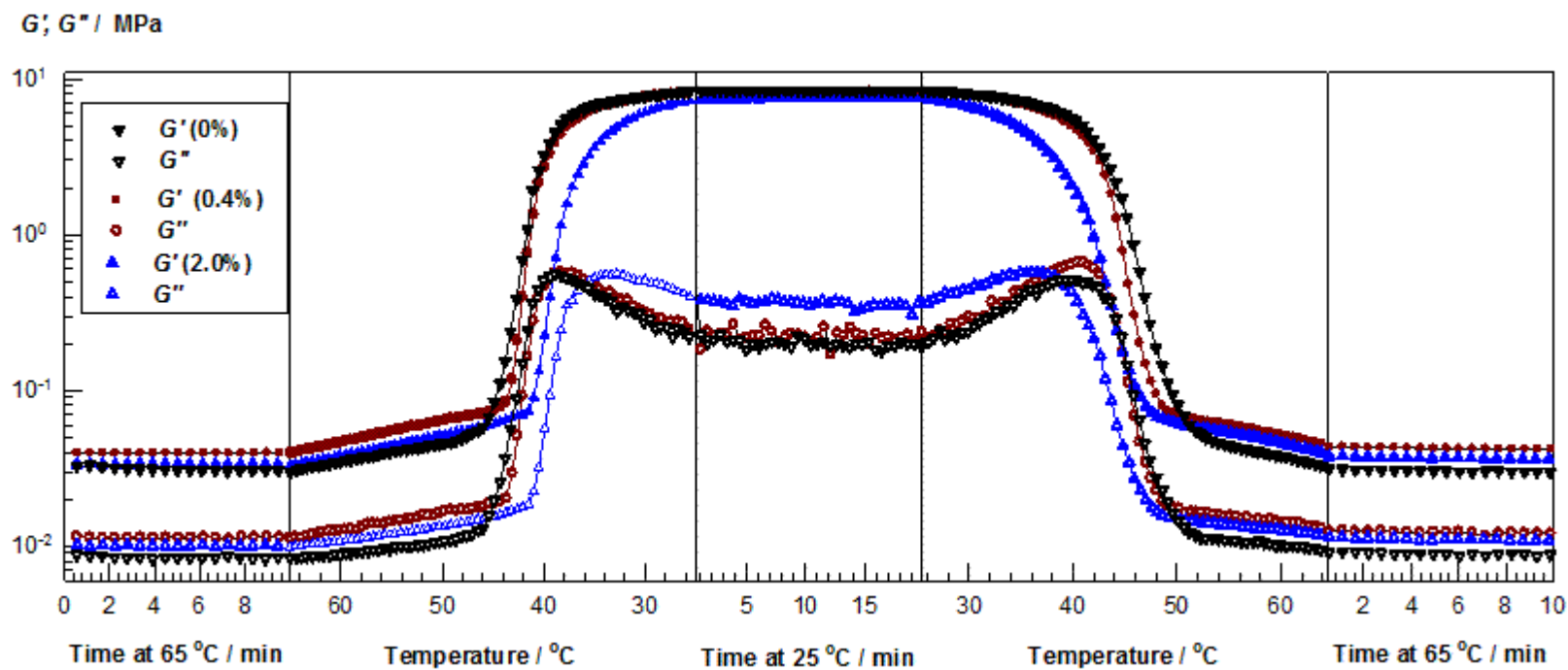
Figure S3. G' (filled symbols) and G'' (open symbols) of the hydrogels without (triangles down) and with 0.4 (circles) and 2% C12M (triangles up) during cooling and heating scans. $\omega = 6.3$ rad·s^{-1}. $\gamma_o = 0.001$.

Figure S4. Young's modulus E, fracture stress σ_f, toughness W, and elongation to break λ_f of the hydrogels plotted against C12M %. The dashed vertical lines represent the data obtained at 0.1 and 2% C12M. $\dot{\varepsilon} = 8.3\mathrm{x}10^{-2}\ \mathrm{s}^{-1}$.
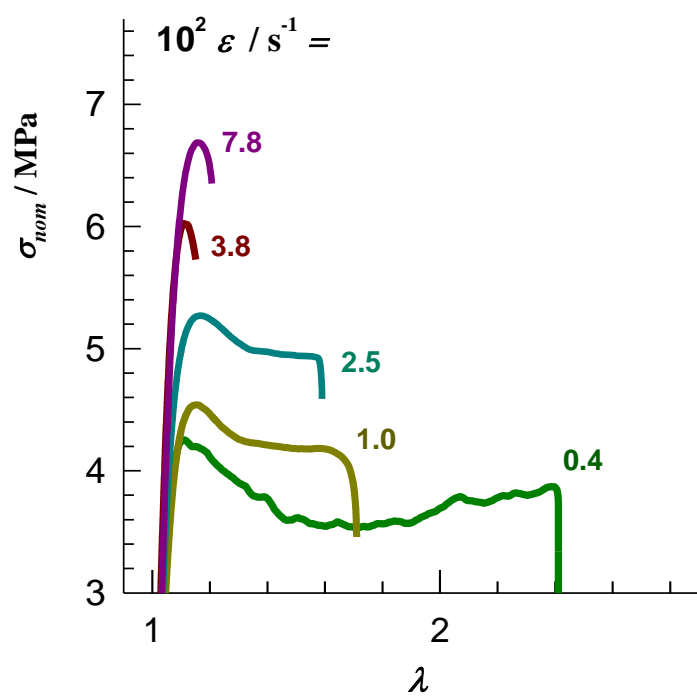
Figure S5. Tensile stress-strain curves of the hydrogels without C12M at various strain rate $\dot{\varepsilon}$.