Toughness improvement and anisotropy in semicrystalline physical hydrogels

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Experimental part

Preparation of isotropic hydrogels

The monomers N, N-dimethylacrylamide (DMAA), n-octadecyl acrylate (C18A), lauryl methacrylate (LM) and the initiator Irgacure 2959 were received from Aldrich and used without further purification. The hydrogels were prepared by bulk copolymerization of DMAA with the hydrophobic monomers C18A and LM 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 0 and 0.1 mol% for the hydrogels denoted as 0LM and 0.1LM, respectively. The monomers DMAA, 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 (1x5x20 mm). The polymerization was conducted at 23±2 °C for 24 h 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 24±1 °C for the first 3 days 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.

Swelling tests and gel fractions of isotropic and anisotropic hydrogels

After equilibrium swelling of the hydrogels in water at 23±2 °C, the gel samples were taken out of water and freeze-dried. The weight swelling ratio was calculated as $q_w = m/m_{dry}$, 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. The gel fraction W_g of the hydrogels reported here were unity indicating complete conversion of the monomers into the polymer.

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. The hydrogel samples were subjected to frequency sweep tests at a strain amplitude $\gamma_0 = 0.001$.

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, x_c, that is, the fraction of C18A units in crystalline domains, was estimated by $x_c = x_{HM} \Delta H_m / \Delta H_m^o$, 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 CuKα radiation (λ= 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 = 5 min^{-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 energy to break (toughness) W was calculated from the area below the stress-strain curves up to the fracture point. The successive elongation tests were conducted at a constant strain rate of 5 min^{-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.

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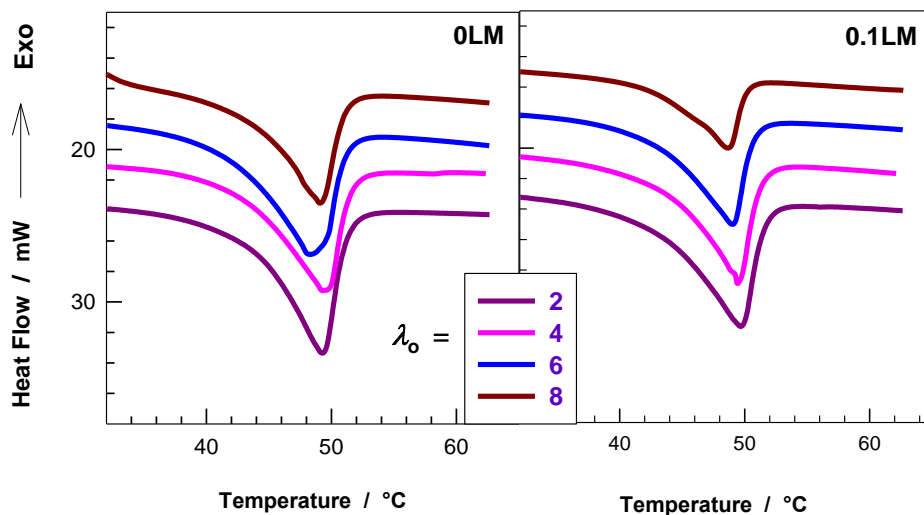
Figure S1. DSC scans of 0LM (left) and 0.1LM hydrogels (right) at prestretch ratios λ_o between 2 and 8.
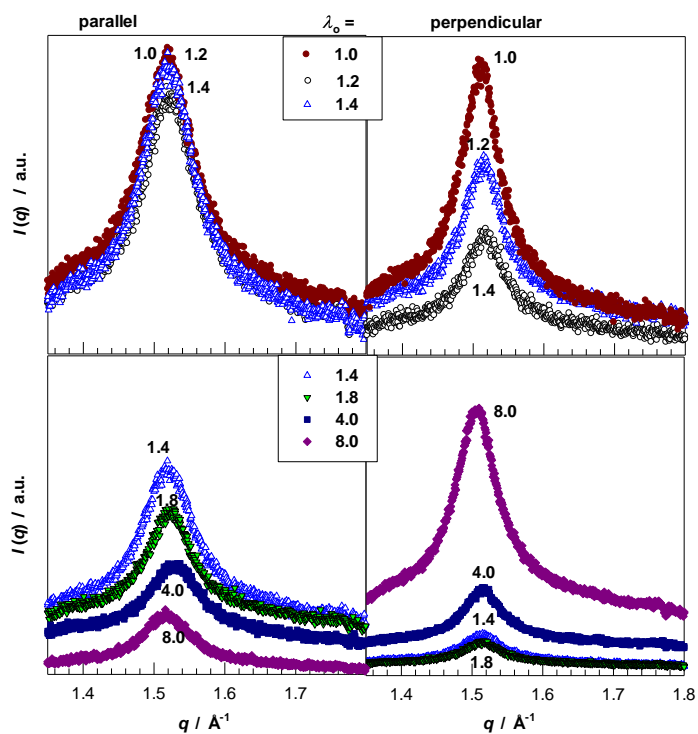

Figure S2. WAXS profiles of 0.1LM hydrogels at various prestretch ratios λ_o indicated. The data were recorded in directions parallel (left panel) and perpendicular to the prestretching direction (right panel).
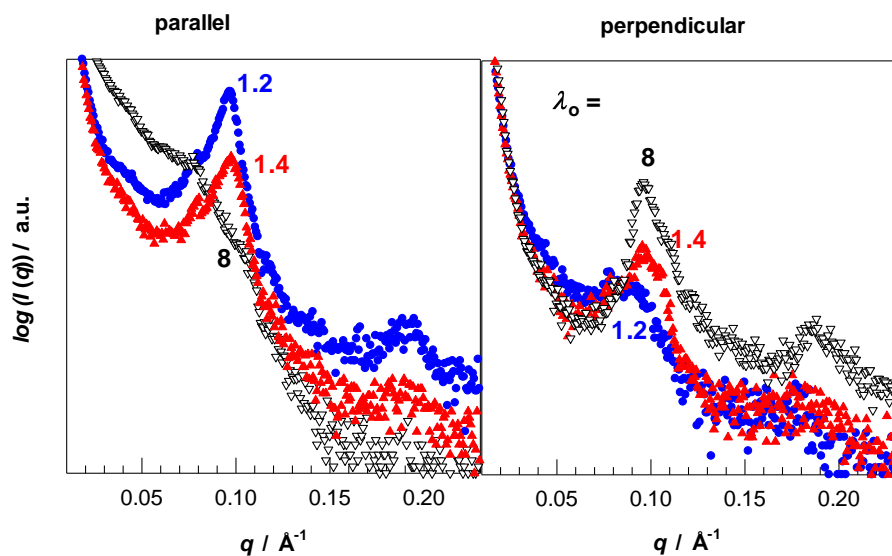
Figure S3. SAXS profiles of 0.1LM hydrogels at various prestretch ratios λ_o indicated. The data were recorded in directions parallel (left) and perpendicular (right) to the prestretching direction.
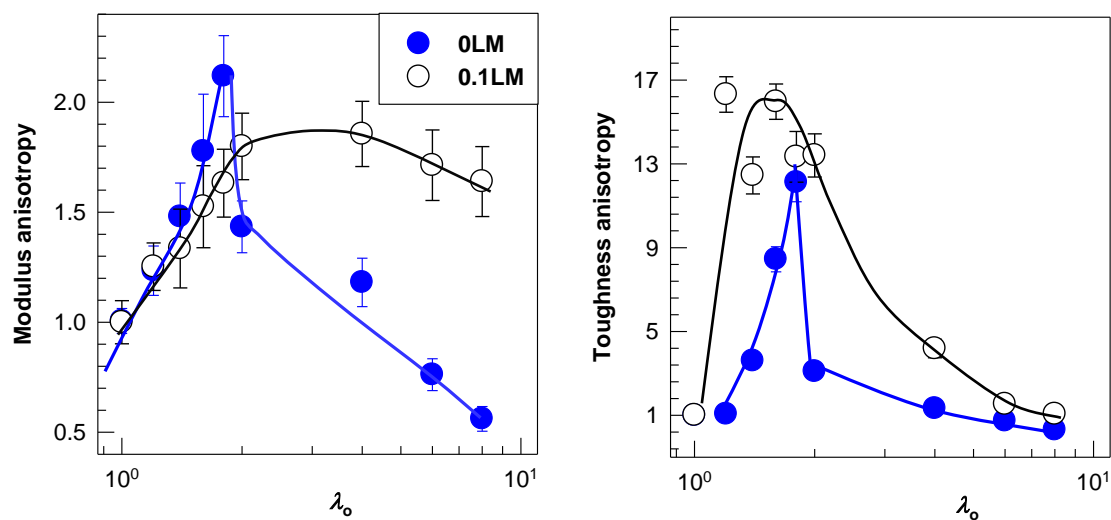

Figure S4. Modulus and toughness anisotropy of 0LM and 0.1LM hydrogels plotted against the prestretch ratio λ_o. The curves show the trend of data.
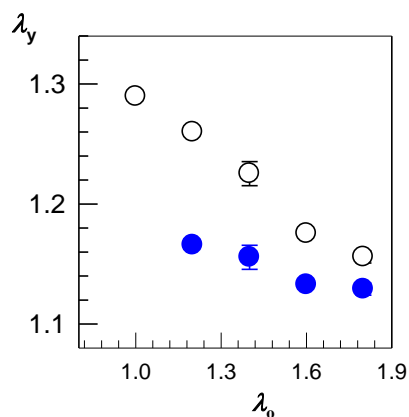
Figure S5. Yield strain λ_y of 0LM (filled symbols) and 0.1LM hydrogels (open symbols) plotted against the prestretch ratio λ_o.
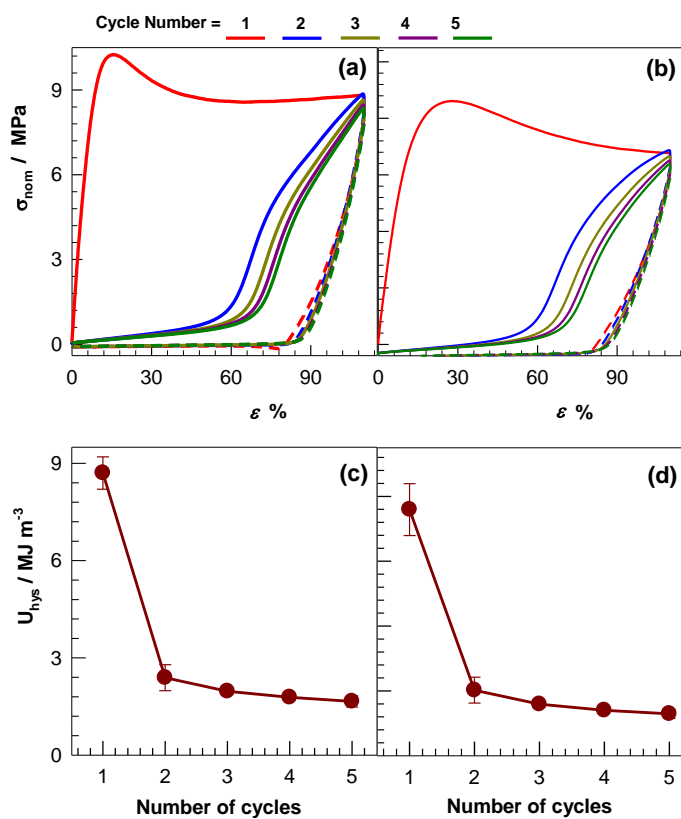

Figure S6. (a, b): Nominal stress σ_{nom} vs strain $\varepsilon\,(=\lambda - 1)$ plots of 0LM hydrogel specimens from five successive tensile cycles up to a maximum strain of 110%. The tests were conducted parallel (a) and perpendicular to the prestretching direction (b). $\lambda_o = 1.8$ (a) and 4 (b). **(c, d):** Hysteresis

energies U_{hys} calculated from the area between the loading and unloading curves of the mechanical cycles in Figures S5a and S5b, respectively, plotted against the cycle number.