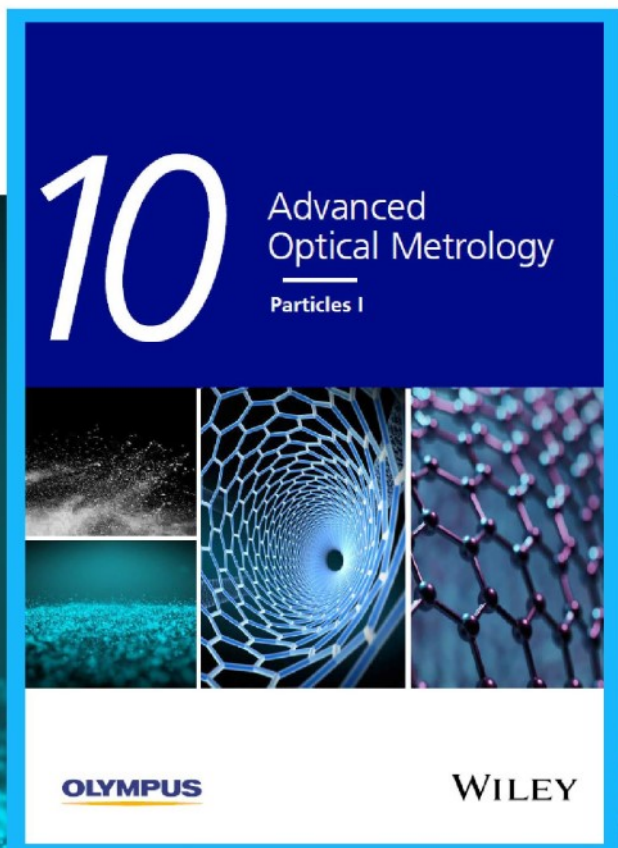




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Facile, Energy-Efficient Microscale Fibrillation of Polyacrylamides under Ambient Conditions

Menandro V. Cruz, Darshil U. Shah, Nina C. Warner, Jade A. McCune, and Oren A. Scherman*

Insight into fiber formation can provide new rationale for the design and preparation of fibers with programmed mechanical properties. While synthetic bioinspired fibers have shown impressive tensile properties, the fiber formation process remains poorly understood. Moreover, these systems are highly complex and their formation is environmentally and economically costly. Controlled fiber formation under ambient conditions from polyacrylamide solutions with properties comparable to natural fibers such as wool and coir is demonstrated. Photopolymerization and subsequent microscale fibrillation of different acrylamides in water/ethanol mixtures yield a simple and energy-efficient route to fiber formation. This strategy reduces required processing energy by two-to-three orders of magnitude. Through extensive experimental elucidation, insight into precise fiber forming conditions of polymeric solutions is achieved. Ethanol is utilized as a chain transfer agent to control the molecular weight of the polyacrylamides, and the entanglement regimes of the solutions are determined through rheological characterization showing fiber formation above the entanglement concentration. Unique from previously reported hydrogel microfibers, it is shown that fibers with good mechanical properties can be obtained without the need for composites or crosslinkers. The reported approach offers a platform for fiber formation under ambient conditions with molecular-level understanding of their assembly.

1. Introduction

The exceptional properties of spider silk have made it an inspiration for the development of synthetic fibers with superior properties, resulting in numerous studies on bioinspired and biomimetic fibers. Among these, spider silk forms fibers with a superb combination of tensile properties at ambient conditions while primarily using water as a solvent.^[1,2] Spiders are difficult to farm for their silk due to their cannibalistic and territorial behavior.^[3] While synthetic biologists have developed ways to address this issue through the expression of recombinant spider silk proteins in different organisms, such as goats, silkworms, and *Escherichia coli*, these methodologies require high production costs as well as a high carbon footprint reaching between 20–200 times that of native spider silk.^[4–6] Alternatively, materials scientists attempted to mimic spider silk through synthetic materials instead of proteins. Attempts to mimic spider silk have resulted in improved fiber tensile properties, however, such synthetic fibers come with disadvantages including

synthetic complexity and high energy requirements for their production, ultimately prohibiting commercial scale-up.

Despite many examples of bioinspired synthetic fibers, only few reports have been of non-peptide-based materials that can be drawn at ambient conditions, all of which have been published within the last 5 years.^[7–13] These polymeric synthetic fibers have displayed excellent properties such as high damping capacity,^[7] moisture-sensitive supercontraction,^[8] anti-freezing,^[9] and environmental-stimuli-responsive behavior^[11] with envisaged applications as shock absorbing ropes,^[10] biomimetic muscles,^[8] textile-based electronic devices,^[9] and smart fibers for sensors, respectively.^[11] Despite the low energy requirements for the drawing process of these synthetic fibers, they all still require multi-step syntheses and processes.

Yarn preparation, which includes spinning of fibers, is the second highest contributor to the overall CO₂ emission in the life cycle of the global apparel industry.^[14] The massive environmental impact of current fiber manufacturing processes presents the need for a more sustainable alternative.^[15]

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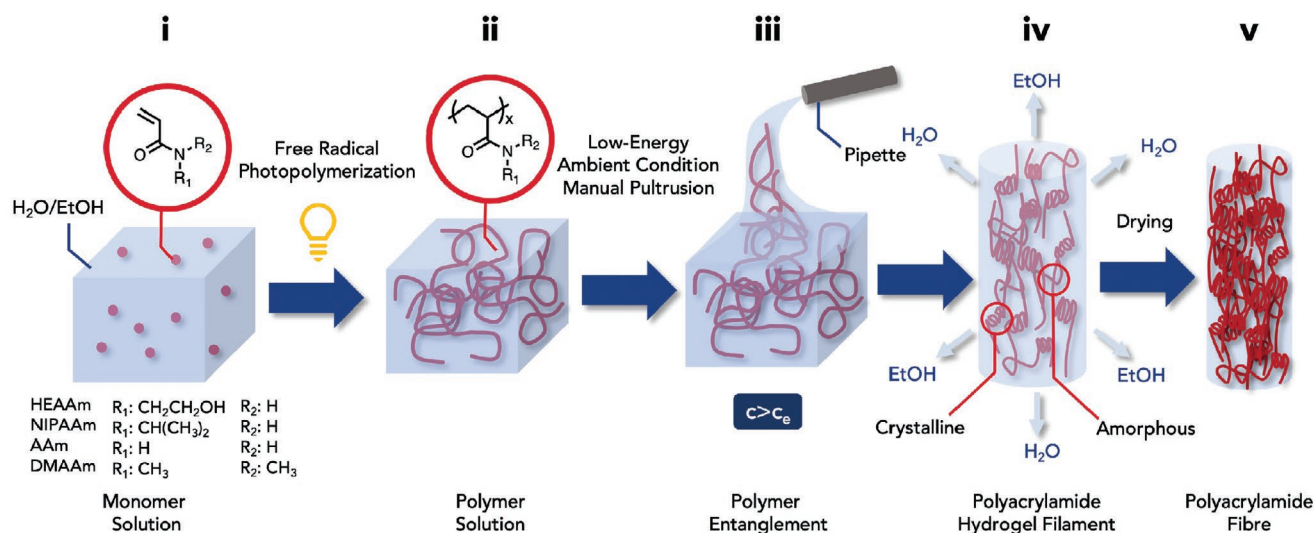


Figure 1. Schematic representation of the fiber formation process under ambient conditions of acrylamides: i) monomer solution of acrylamides in H₂O/ EtOH mixture, ii) polymer solution of polyacrylamide after free radical photopolymerization, iii) low-energy manual pultrusion of polymer solution above the entanglement concentration under ambient conditions, iv) drying of polyacrylamide hydrogel filament, and v) final polyacrylamide fiber.

Natural materials such as silk can be produced using lower energy.^[16] It is estimated that the production of silk fiber at ambient conditions can be up to three orders of magnitude less energy intensive than standard commercial polymers such as high-density polyethylene (HDPE).^[17] While fiber formation of synthetic polymers under ambient conditions remains a challenge, breaking down the problem by investigating the fiber formation process of simple synthetic polymers can help address the gap in this field.

Herein, we report a rapid one-step free radical photopolymerization of different acrylamide monomers and their subsequent fiber-forming capabilities under ambient conditions using a mixture of green solvents water and ethanol (Figure 1-i).^[18,19] Using *N*-hydroxyethylacrylamide (HEAAm) as a model acrylamide monomer, the role of EtOH as a chain transfer agent in the polymerization and its impact on the rheological behavior of the resulting polymer solution was investigated (Figure 1-ii). The effect of concentration on the fiber forming capability of the polymer solutions was explored through determination of its entanglement regimes in the fiber forming solvent system (Figure 1-iii).

2. Polymerization and Fiber-Forming Regime

It is evident from our studies that the amount of ethanol, degree of polymerization, and concentration work synergistically in the fiber formation process. The right combination of the three parameters dictates the “Goldilocks zone” of fiber formation in ambient conditions. The addition of ethanol to water has a dramatic effect on the molecular weight and distribution of chain length as tabulated in Table S1, Supporting Information. Free radical photopolymerization of HEAAm was performed at a 3.3 M monomer concentration using 0.4 mol% of Irgacure-2959 (I-2959) as the photoinitiator in a 50:50 H₂O:EtOH v/v cosolvent system (Table S1, Supporting Information; Figure 2).^[20] The solution was polymerized by exposure to 350 nm light

for 1 h, however, conversion could reach >95% in just 15 min (Figure S2, Supporting Information). This resulted in a polymer with a *M_n* of 180 kDa with a broad dispersity of 3.23. Polymerization of HEAAm in pure H₂O results in a stiff insoluble gel. Polymerization of HEAAm in pure EtOH led to a similar observation (Table S1, Entry 12, Supporting Information). In a H₂O:EtOH mixture (Table S1, Entries 2–11, Supporting Information), a trend was observed, with increasing EtOH content, the resulting *M_n* decreases from ≈2000 to 50 kDa and the PDI increases (Table S1, Supporting Information; Figure 2b,c).

The observation held true for other monomers including acrylamide (AAm), *N*-isopropylacrylamide (NIPAAm), and

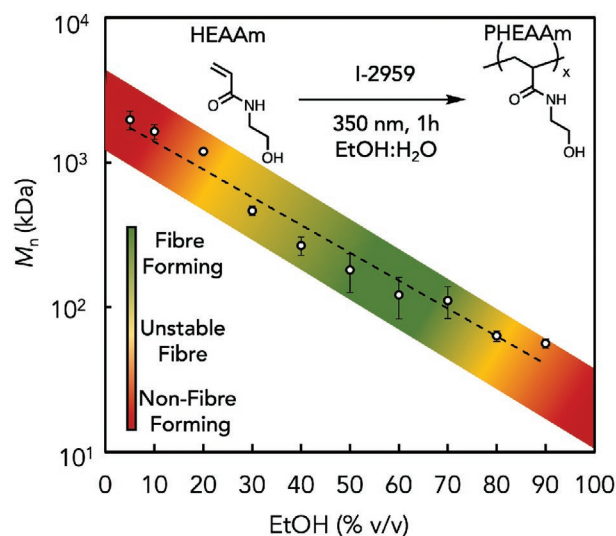


Figure 2. Synthesis of PHEAAm by free radical photopolymerization. (Inset) Reaction conditions for the free radical photopolymerization of HEAAm in H₂O:EtOH mixture using Irgacure-2959 as the photoinitiator. Resulting *M_n* of PHEAAm synthesized in different ratios of H₂O:EtOH with a gradient map showing samples that easily form stable fibers (green) and unstable fibers (yellow), and that do not form fibers (red).

N,N-dimethylacrylamide (DMAAm) (Figure S3 and Table S2, Supporting Information). However, the range of H₂O:EtOH cosolvent system that can be used for these monomers is limited. Poly(*N*-isopropylacrylamide) (PNIPAAm) and poly(acrylamide) (PAAm) exhibit co-nonsolvency at different ranges of H₂O:EtOH, resulting in turbid polymer solutions (20–60% and 60–100% v/v of EtOH, respectively).^[21,22]

The decrease in M_n of the resulting poly(*N*-hydroxyethylacrylamide) (PHEAAm) as the fraction of EtOH increases can be explained by its role as a chain transfer agent, which has been shown previously for acrylamides.^[23–25] This study shows that high-molecular-weight PHEAAm with low dispersity can be obtained by simple free radical photopolymerization in the presence of low concentrations of EtOH as a chain transfer agent in a short amount of time (15 min).

Initial polymerization of HEAAm in 50:50 H₂O:EtOH resulted in a gel which exhibits fiber formation through a qualitative pultrusion test under ambient conditions. In comparison to previously reported fiber-forming polymeric systems under ambient conditions, this system involves a single polymer which contains neither cross-linkers nor colloidal additives. Qualitative manual pultrusion was performed to investigate the fiber forming capabilities of PHEAAm in varying H₂O:EtOH cosolvent ratios (Figure 2). The optimal cosolvent system that results in a fiber formation is 50:50 H₂O:EtOH. However, fibers can still be formed in the range of 30:70 to 50:50 H₂O:EtOH. While gels formed at 20:80, 60:40, and 70:30 H₂O:EtOH could lead to formation of filaments, they were susceptible to breakage and cannot be pulled to greater lengths (>10 cm). The polymers prepared at the extreme ends at this solvent regime (0:100, 10:90, 80:20, 90:10, 0:100 H₂O:EtOH) are stiffer and could not be used for fiber pultrusion. In addition, fibers can also be pulled from PAAm and PNIPAAm solutions, however, not continuously. While the MW of PDMAAm could be controlled, it unfortunately could not form fibers on this range, likely on the account of the absence of hydrogen bonding between monomer units.

3. Polymer Entanglement

To investigate the role of concentration, we needed insight into the entanglement of the polymeric chains (Figure 1-ii). Rheological flow sweep experiments on various polymer concentrations were carried out to determine their corresponding zero-shear viscosity in order to probe their entanglement domain. In Figure S4, Supporting Information, the zero-shear viscosity of PHEAAm solution in 50:50 H₂O:EtOH v/v cosolvent system at different concentrations from 0.1–30 wt% as a function of shear rate is presented.

The zero-shear viscosity increases by five orders of magnitude from 0.38 to ≈16 000 cPa as the concentration increases from 0.1–30 wt% (Figure S4, Supporting Information). PHEAAm solutions start to show non-Newtonian behavior from a concentration of 11.4 wt% and exhibit shear-thinning as seen from the gradual decrease in viscosity as shear rate increases (Figure S4, Supporting Information). Additionally, the shear stress dependence as a function of shear rate clearly depicts the change in slope linearity from 11.4 wt% (Figure 3a). The PHEAAm solutions at different concentration have a similar slope, which represents the flow behavior index or n . This obeys the power law, also known as the Ostwald-de Waele equation, where K is the consistency index:

$$\log \tau = \log K + n(\log \dot{\gamma}) \quad (1)$$

If the flow behavior index has a value of $n = 1$, then it corresponds to a Newtonian fluid. The power law predicts a shear-thinning fluid for $n < 1$, and a shear-thickening fluid for $n > 1$. By fitting Equation (1) to the shear-rate dependence of stress, one can obtain the corresponding flow behavior indices of the samples at different concentrations (Figure 3a). The flow behavior indices at concentrations of 0.1–9.3 wt% decreases from 1.03 to 0.92, roughly corresponding to the behavior of a Newtonian fluid. However, as the concentration increases from

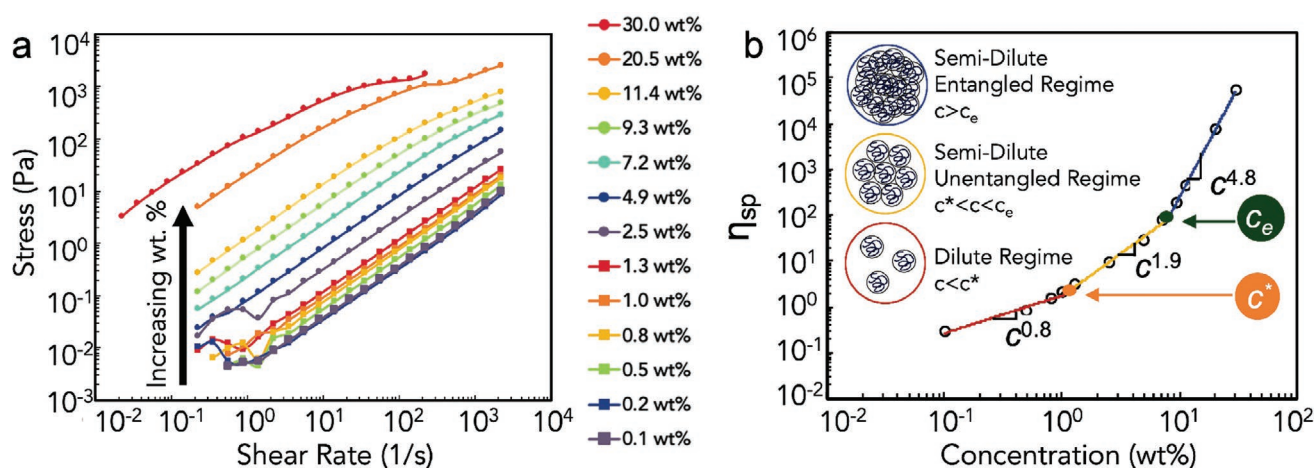


Figure 3. Flow sweep experiment at different concentrations (0.1–30 wt%) to investigate entanglement of PHEAAm in 50:50 H₂O:EtOH v/v cosolvent system. a) Stress as a function of shear rate of different PHEAAm concentration. b) Specific zero-shear viscosity of PHEAAm solution in a 50:50 H₂O:EtOH v/v cosolvent system at 20 °C at different concentrations. The solid lines are power-law fits to the data in the dilute regime (red), semi-dilute unentangled regime (yellow), and semi-dilute entangled regime (blue), with the corresponding power exponent (0.8, 1.9, and 4.8, respectively) for each entanglement regime labeled alongside the fit. The overlap concentration (c^*) and entanglement concentration (c_e) are also labeled at 1.0 (orange arrow) and 8.0 wt% (green arrow), respectively. Inset) Schematic representation of PHEAAm chains at different entanglement regimes.

11.4–30 wt%, PHEAAm solutions transition to a shear-thinning fluids with flow indices decreasing from 0.88 to 0.68.

To further understand the behavior of PHEAAm solutions, an investigation of its entanglement regimes was performed. Graessley has classified polymer solutions into five different regimes based on concentration and molecular weight, namely: dilute, semidilute unentangled, semidilute entangled, concentrated unentangled, and concentrated entangled.^[26] These regimes can be described by different rheological models (see Section S3, Supporting Information).^[27,28] To determine the concentration regimes for the PHEAAm solutions, analysis of flow sweep rheology was performed and the variation of the shear specific viscosity (η_{sp}) of PHEAAm in 50:50 H₂O:EtOH v/v cosolvent system was investigated (Figure 3b), which was determined using the following equation

$$\eta_{sp} = \frac{(\eta_o - \eta_s)}{\eta_s} \quad (2)$$

where η_o is the zero-shear viscosity of the PHEAAm solution determined from the flow sweep and the η_s is the solvent viscosity of 46 wt% aqueous EtOH at 20 °C ($\eta_{sp, EtOH} = 2.98$ mPa s).^[29] Analyzing the concentration dependence of specific zero-shear viscosity of PHEAAm, power-law scalings of $\eta_s \approx c^{0.8}$, $\eta_s \approx c^{1.9}$, and $\eta_s \approx c^{4.8}$ were obtained for the dilute, semidilute unentangled, and semidilute entangled regimes, respectively. The changes in slope of the specific zero-shear viscosity plot mark the onset of a different entanglement regime. The overlap concentration (c^*) is the point of intersection of the dilute and semidilute unentangled regimes and was determined to be 1.0 wt% in this system (Figure 3b, orange arrow). The entanglement concentration (c_e), which is the point of intersection of the semidilute unentangled and semidilute entangled regimes, was determined to be 8.0 wt% as highlighted on Figure 3b (green arrow).

The filament and fiber forming behavior of the PHEAAm solutions at different concentrations was also evaluated. Here, a filament is defined as the point at which the hydrogel solution could be manually drawn to form a high-aspect-ratio material, which still flows back to the mother solution or breaks (Figure 1-iv). Subsequently, when hydrogel filaments can retain their conformation and can be drawn continuously to yield a high-aspect-ratio material, a fiber is formed upon drying in its

elongated state (Figure 1-v). PHEAAm hydrogel solutions from 0.1–9.3 wt% did not form any filaments or fibers. At 11.4 wt%, the PHEAAm hydrogel solutions begin to form filaments, however, they are fragile. Above this value of 11.4 wt%, the PHEAAm solutions were able to continuously form fibers when manually drawn under ambient conditions. It is worth noting that filament and fiber formation were only observed for PHEAAm solutions at concentrations in the entangled regimes.

4. Fiber Characterization

The fibers drawn from PAAm, PNIPAAm, and PHEAAm are cylindrical in shape and maintain consistent widths as seen in the optical microscopy (Figure 4a; Figures S5–S8, Supporting Information) and scanning electron microscopy (SEM) images (Figure 4b,c; Figure S9, Supporting Information). The cross-sectional image of the PHEAAm fiber shows signs of brittle fracture with a rough and wrinkled surface (Figure 4b,c).

Tensile properties of PHEAAm fibers were then investigated as shown in Figure 5. The stress–strain profile of the PHEAAm fibers (Figure 5a–d), which are typical for polymer glasses have five distinct features: 1) a linear stress growth in the low-strain elastic regime; 2) an “anelastic” regime where the growth of stress is relatively slower; 3) a “yield peak” local maximum with subsequent drop in stress also known as “strain softening”; 4) a plateau also known as the plastic-flow regime where chain reorientation and extension occur, followed by 5) “strain hardening” or the increase in stress due to chain deformation and increased alignment.^[30,31] An initial linear region up to a yield point of 1–2% strain could be seen, wherein elastic moduli of similar values among four samples were observed around 2.0 GPa (Figure 5h). Conversely, when the polymerization was performed in a lower EtOH content, a higher M_n was obtained, resulting in stronger pulled fibers. From the set of samples tested, PHEAAm fibers with significant differences in strength were obtained, varying from 28.1 ± 11.9 to 75.7 ± 28.3 MPa (Figure 5g). There was no significant difference observed for the failure strain of the four different PHEAAm fibers (Figure 5f). Last, the toughness of PHEAAm fibers was calculated and varied between 3.3 ± 2.4 and 13.1 ± 8.2 MJ m^{−3}, with the fiber from 53 kDa PHEAAm being significantly less tough than the rest (Figure 5e). The

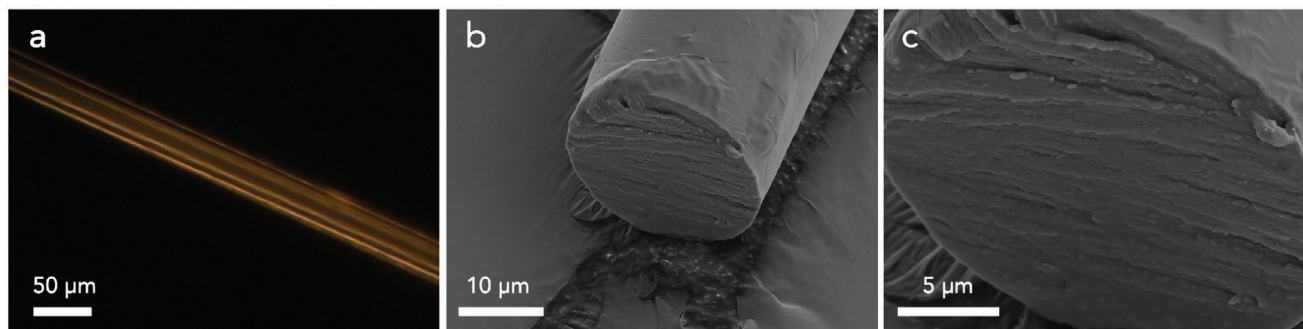


Figure 4. Microscopy images of PHEAAm fiber drawn from polymer solution in 50:50 H₂O:EtOH v/v solution in ambient condition. a) Representative optical microscopy image, b) SEM image of the cross-section, and c) higher magnification of the cross-section SEM image of the PHEAAm fiber.

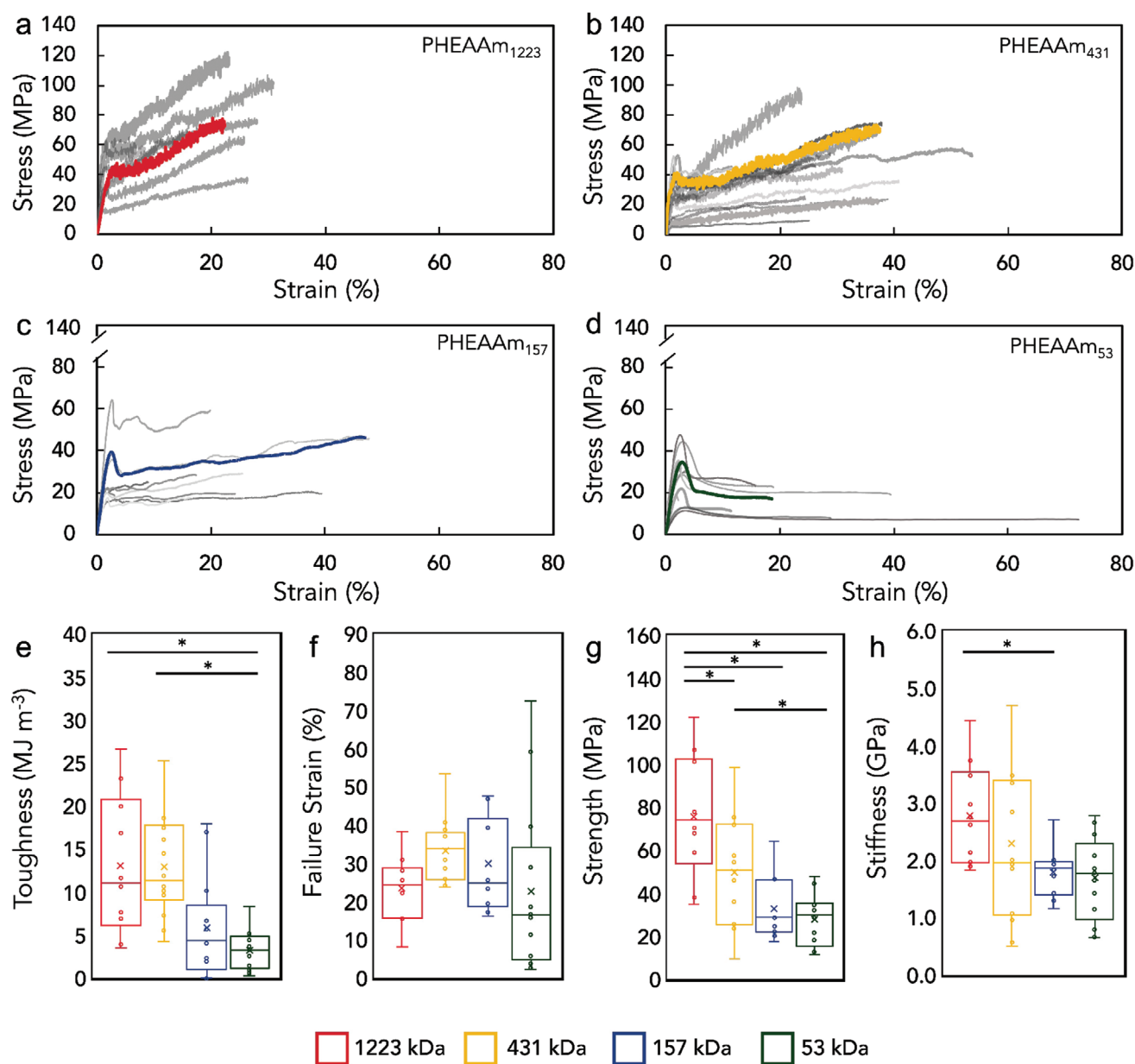


Figure 5. Tensile test of PHEAAm fibers of varying M_n . a–d) Stress–strain curves of PHEAAm with M_n : a) 1223 kDa, b) 431 kDa, c) 157 kDa, and d) 53 kDa. e–h) Box plots of fiber toughness (e), failure strain (f), strength (g), and stiffness (h) of PHEAAm fibers (M_n : 1223 kDa = red, 431 kDa = yellow, 157 kDa = blue, 53 kDa = green). One-way ANOVA and Tukey–Kramer posthoc analysis were performed to determine statistical significance. ns = $p > 0.05$ and * $p < 0.05$.

combination of the tensile properties of these PHEAAm fibers are comparable to those of natural fibers such as wool and coir (Figure S11, Supporting Information). Remarkably, the combination of tensile properties of PHEAAm fibers compares favorably to those of other hydrogel microfibers previously reported in literature despite not containing crosslinkers or composites (Table S3 and Figure S12, Supporting Information). Additionally, thermal analysis by DSC was performed on PHEAAm fibers (Figure S10, Supporting Information), yielding a glass transition temperature at 104 °C (Figure S10d, Supporting Information) and an onset of melt at 155 °C (Figure S10b, Supporting Information).

5. Energy Efficiency

Native silk fibrillation is at least three orders of magnitude more energy efficient than synthetic polymer fibrillation.^[17] Since native silk is fibrillated at ambient temperatures and is produced in a pultrusion-dominated process, additional thermal energy used to melt polymers for extrusion dominated processes are not required.^[32] Hence, native silk requires one-tenth of the shearing energy (work input) than that of synthetic polymers for fibrillation.^[17] Inspired by the energy efficiency of native silk fiber formation, energy required for fibrillation of our polyacrylamide system outperforms commercial synthetic polymers by at least

two orders of magnitude. The fiber formation in this system is done through a manual dry-spinning technique which does not require any heating of polymers, nor exposure to hot steam post-pultrusion. As the polyacrylamide fibers form at substantially lower temperatures (100–300 °C lower) than those required to melt synthetic polymers such as viscose, HDPE, poly(ethylene terephthalate), and poly(ether ether ketone), 60–380 MJ less energy per m³ of material is expended (Section S4, Supporting Information). Rheological experiments investigating energy to afford fibrillation may reveal further energy savings as the microscale fibers here are drawn manually. While much of the literature has described multi-step processes in producing fibers in ambient conditions, we have made a substantial progress here by achieving it in a single step.^[7–12] The embodied energy of the fiber materials can be further reduced by using bio-based polymer precursors and sources such as cellulose.^[7,8]

6. Conclusions

We have shown that fiber formation under ambient conditions is possible from polymeric solutions of PHEAAm, PNIPAm, and PAAm. EtOH can act as a cosolvent and chain transfer agent for photopolymerization of HEAAm to control the molecular weight. The different entanglement regimes of PHEAAm solutions in 50:50 H₂O:EtOH *v/v* were identified, showing that fiber formation was only observed at concentrations well above entanglement ($c_e = 8.0$ wt%). The exceptional simplicity of the polymer synthesis and fiber drawing process makes this system easily accessible for most chemical laboratories. In the future, we aim to modify these fiber forming polyacrylamide systems to include different cross-linkers and a variety of different nanoparticles, resulting in composite fibers with emergent chemical and mechanical properties previously inaccessible. Establishing a platform for the formation of fibers with tailorable properties unveils a new paradigm for sustainable fiber development and smart fiber technologies to meet the ever increasing material demands of our evolving society.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

entanglement, free-radical photopolymerization, low-energy processes, polyacrylamide, synthetic fibers

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