Electronic Supplementary Information (ESI)

Assembly of Emulsion Droplets into Fibers by Microfluidic Wet Spinning

R. V. Bell,[ab] C. C. Parkins,[a] R. A. Young,[a] C. M. Preuss,[a] M. M. Stevens,[b] and S. A. F. Bon*[a]

[a]Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK.

[b]Department of Materials, Department of Bioengineering and Institute for Biomedical Engineering, Imperial College London, Exhibition Road, London SW7 2AZ, UK.

*Email: S.Bon@warwick.ac.uk Web: www.bonlab.info

Contents

1. Materials

Poly(ethylene glycol) methyl ether methacrylate (PEGMA, M_n = 1100 g·mol^{-1}, Sigma-Aldrich), methacrylic acid (MAA, 99 %, Sigma-Aldrich), ethyleneglycol dimethacylate (EGDMA, 98 %, Sigma-Aldrich), 1-dodecanethiol (DDT, ≥98 %, Sigma-Aldrich) and (trimethylsilyl)diazomethane (2 M in hexane, Sigma-Aldrich). Azobis(isobutyronirile) (AIBN, BDH) was recrystallized from methanol prior to use. Deuterated chloroform and methanol were purchased from Sigma-Aldrich. All organic solvents were standard laboratory grade. Laponite RD (BYK), dodecane (≥99 %, Sigma-Aldrich), oil blue N (96 %, Sigma-Aldrich), oil red O (Sigma-Aldrich), ferrofluid (Reference code: EFH1, Ferrotec), D-(+)-Gluconic acid δ-lactone (≥99 %, Sigma-Aldrich), mowiol 8-88 (poly(vinyl alcohol), PVA, M_w ~67,000 g·mol^{-1}, Sigma-Aldrich), calcium chloride dihydrate (Analar normapur), ammonium hydroxide (35 %, Fisher chemical), hydrochloric acid (37 %, Analar Normapur), and sodium hydroxide pellets (Fisher chemical).

2. Synthesis and Characterization of pH-Responsive Branched Copolymer

The pH-responsive branched copolymer (pH-BCP) was synthesized via thiol-regulated free radical polymerization. A round bottom flask was charged with PEGMA (3 g, 2.73 mmol), MAA (4.456 g, 51.80 mmol), EGDMA (1.080 g, 5.45 mmol), DDT (1.102 g, 5.45 mmol) and ethanol (96 mL). The reaction mixture was degassed with nitrogen gas for 20 minutes, and subsequently immersed into a preheated oil bath of 70 ^{o}C. The polymerization was initiated by addition of AIBN (0.096 g, 0.59 mmol) and was left stirring for 48 h. The reaction mixture was concentrated under vacuum and the polymer was purified by precipitation in cold diethyl ether (-20 ^{o}C). The polymer was left to dry under vacuum overnight.

The pH-BCP was esterified and the ^{1}H NMR spectrum of the esterified-BCP was used to determine the relative molar ratios of the co-monomers and chain transfer agent in pH-BCP.

The pH-BCP was esterified by firstly dissolving the pH-BCP (50 mg) in methanol (0.2 mL). Toluene (0.2 mL) was added and agitated to obtain a homogeneous solution. (Trimethylsilyl)diazomethane (~0.2 mL) was then added drop wise until a yellow colour appeared and did not become colourless upon agitation. The resulting solution was purified via evaporation, and left to dry in the vacuum oven overnight at 60 ^{o}C. ^{1}H NMR spectra were recorded on 1 wt% polymer solutions in deuterated solvents using Bruker Specrospin 400 UltrashieldTM operating at 400 MHz. The ^{1}H NMR spectra of the pH-BCP and the esterified pH-BCP are shown in **Figure S1A and Figure S1B**, respectively. The target and actual compositions of the pH-BCP are depicted in **Table S1**.

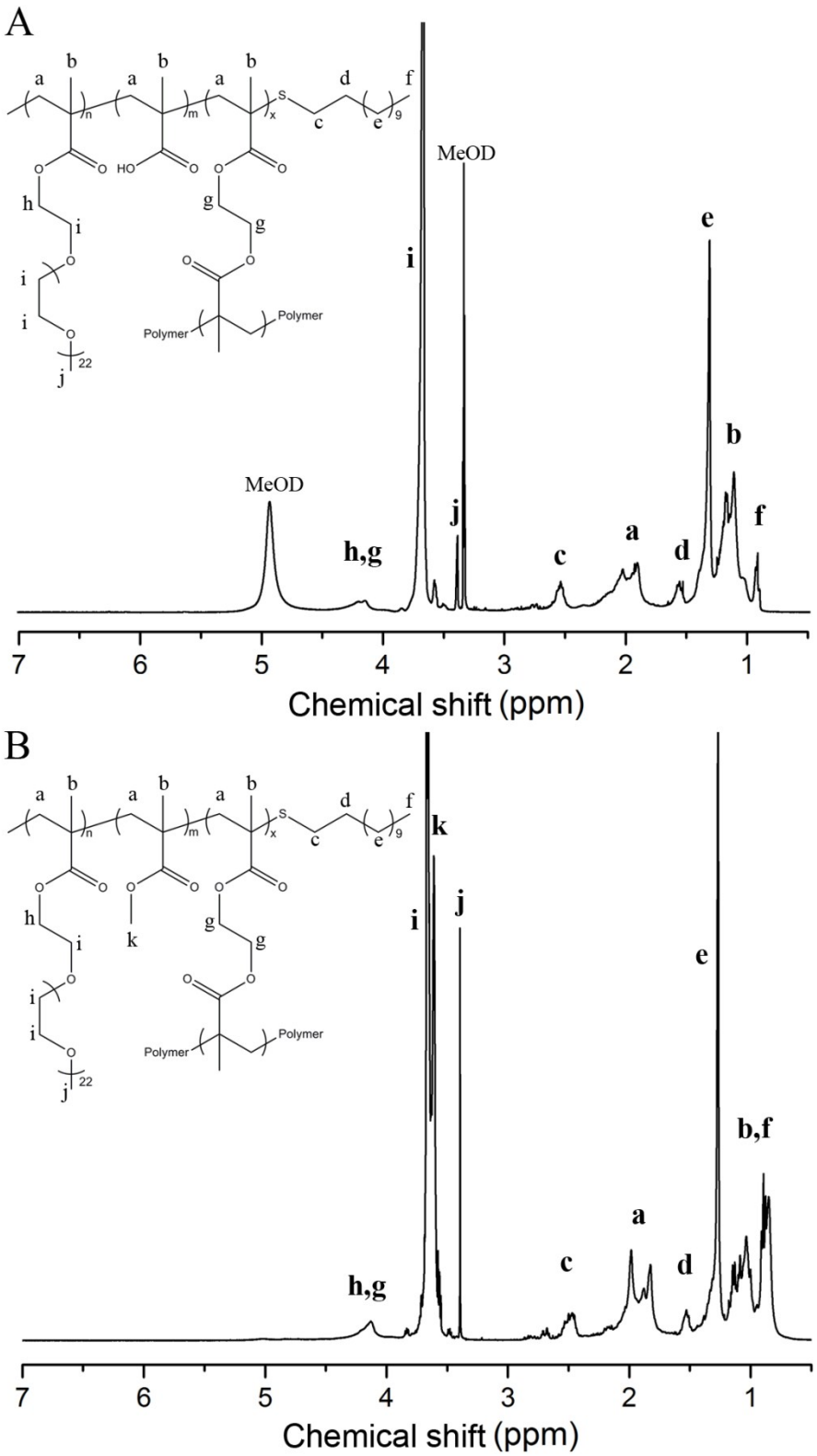

Figure S1. ^{1}H NMR spectra of (A) pH-BCP in CD_3OD, and (B) esterified pH-BCP in $CDCl_3$. The appearance of peak 'k' (methyl from the ester group) confirms esterification of the pH-BCP.

Molar mass, molar mass distribution ($Đ$), and Mark-Houwink (α_η) values were measured by triple detection gel permeation chromatography (TD-GPC) using an Agilent 390-MDS Multi Detector Suite equipped with refractive index, viscometer, and UV detectors. A mobile phase of DMF with 5 mM NH_3BF_4 was employed with a flow rate of 1 mL·min^{-1}. Two PL gel Mixed-D columns and an additional guard column were used with an oven temperature of 50 °C. Specific calibration was carried out using poly(methyl methacrylate) standards. The molecular parameters of the pH-BCP are shown in **Figure S2** and **Table S1**.

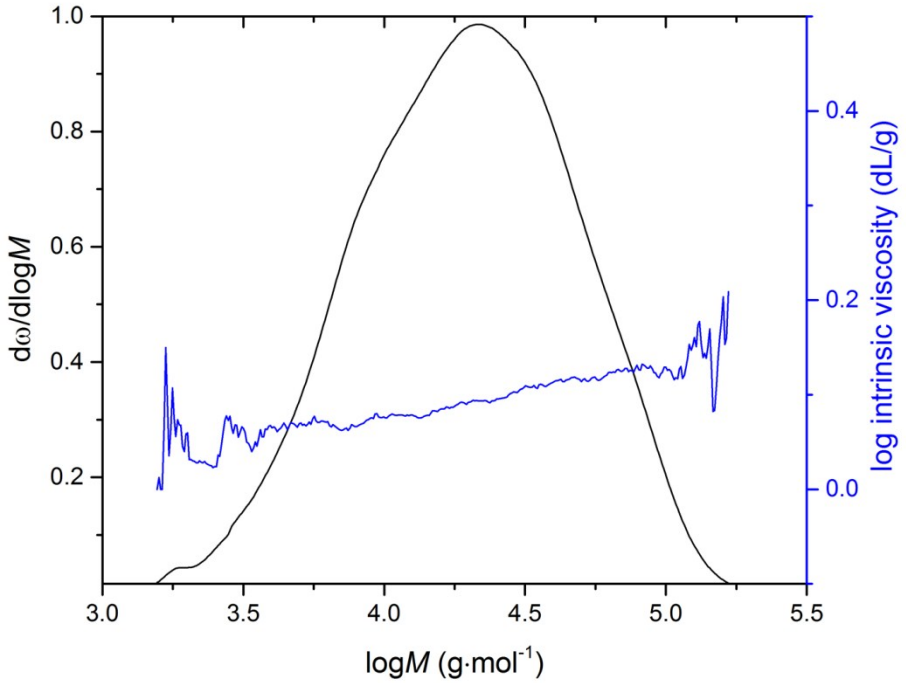

Figure S2. The TD-GPC chromatograms of the pH-BCP. Molar mass distribution of pH-BCP (black line), and molar mass vs. intrinsic viscosity plot of pH-BCP (blue line).

Table S1. Composition and molecular parameters of the pH-BCP.

Target polymer composition[a]	Actual polymer composition[b]	Conversion (%)[c]	M_n ($g \cdot mol^{-1}$)[d]	M_w ($g \cdot mol^{-1}$)[d]	$Đ^d$	α_η^d
$PEGMA_5$/ MAA_{95}-$EGDMA_{10}$-DDT_{10}	$PEGMA_{4.4}$/ $MAA_{95.6}$-$EGDMA_{7.5}$-$DDT_{10.7}$	98	15274	28163	1.84	0.30

[a] Target molar equivalent based on monofunctional monomer nominally set to 100. [b] Polymer composition was calculated from ^{1}H NMR spectrum of the esterified pH-BCP. [c] Polymer conversion was calculated by ^{1}H NMR. [d] Measured by triple-detection GPC in DMF eluent.

3. Potentiometric Titration of the pH-BCP

A potentiometric titration curve of the pH-BCP was generated by dissolving the pH-BCP (0.1 wt%) in a basic solution of pH ~ 11.8 using NaOH (0.5 M). to ensure complete dissolution of the pH-BCP. Changes in pH values were monitored (with an Oakton pH meter) following incremental additions of HCl (0.1 M) to the basic pH-BCP solution (**Figure S3A**). The pH-BCP buffered the solution in the pH range of 10-3.5. The degree of protonation (α) of the pH-BCP with pH was calculated from the Henderson-Hasselbalch equation. At pH 9.68, all of the carboxylic groups of the pH-BCP are deprotonated. The carboxylic groups of the MAA domain are all protonated at pH 3.88. The pK_a of the pH-BCP was determined to be 6.46, and at this instance, 50 % of the carboxylic functional groups are protonated (**Figure S3B**).

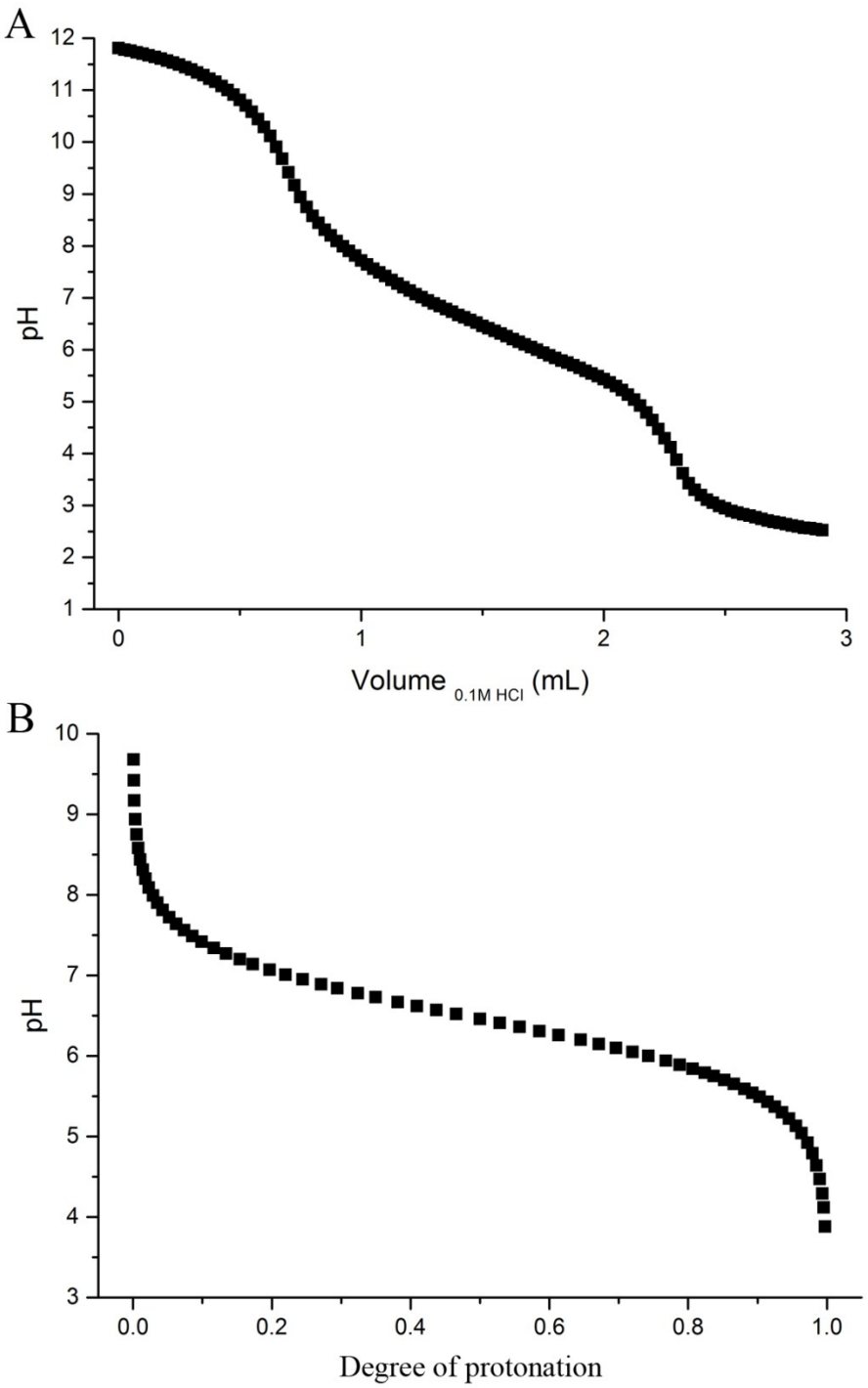

Figure S3. (A) Acid-base titration curve obtained for pH-BCP, and (B) the degree of protonation (α) of pH-BCP with pH. The α of pH-BCP; α = 0 at pH 9.68, α = 0.5 at pH 6.46, and α = 1 at pH 3.88.

4. Fabrication and Characterization of Emulsion

Laponite functionalized with pH-BCP (pH-BCP-Laponite) was prepared by initially preparing an aqueous Laponite dispersion (6.67 w/v%). A physical transition was observed from a flowing aqueous solution to a gel after a few minutes of vigorous mixing. A basic aqueous solution containing 8 w/v% of pH-BCP (the pH was adjusted to 10 with 1 M NH_4OH solution) was added to the Laponite gel with vigorous stirring, and left to stir for 30 minutes to produce a viscous pH-BCP-Laponite aqueous solution (Laponite = 5 w/v%, pH-BCP = 2 w/v%, and pH ~ 9.8). An equal amount of dodecane was added to the viscous pH-BCP-Laponite aqueous solution to give a biphasic mixture. For colored creamed emulsions, oil red O or oil blue N dyes were added to dodecane (0.1 w/v%). Ferro fluid (1 v/v%) was added to dodecane to give magnetic response. This biphasic mixture was homogenized at 24 000 rpm for two minutes to produce an oil-in-water emulsion. The emulsion was left for 48 hours to equilibrate and the resulting emulsion formed a creamed layer. The size and span of the emulsion were recoded using laser diffraction (Mastersizer 2000 equipped with a Hydro 2000S dispersion unit) (**Figure S4**). 10 µL of creamed emulsion was added to the dispersion unit containing 100 mL of basic water (pH adjusted to 11 with 1M NaOH solution) with a stirring rate of 1000 rpm. The volume average droplet diameters ($D_{4/3}$) mentioned were obtained from at least 5 repeat runs ($D_{4/3} = \sum D_{i4}N_i/\sum D_{i3}N_i$). The span is a measure of the distribution of the droplet size distribution and is expressed mathematically as (D(0.9)-D(0.1))/D(0.5), where D(0.9) is the diameter under which 90 % of the particles fall, D(0.5) is the diameter under which 50 % of the particles fall and D(0.1) is the diameter under which 10 % of the particles fall. Light micrographs were taken using a Leica DM 2500M microscope equipped with a Nikon D5·100 digital camera.

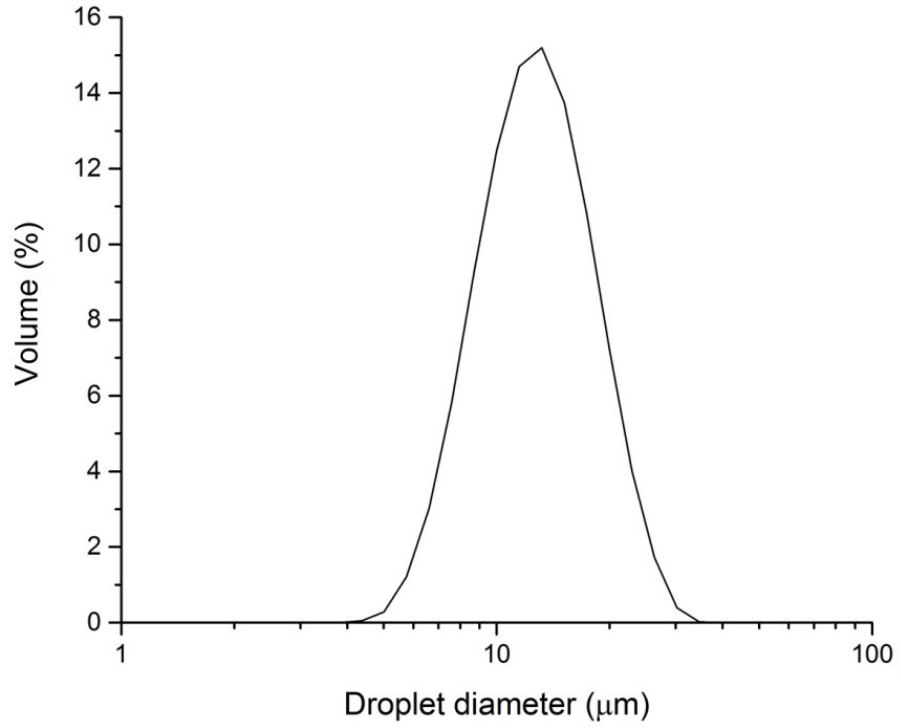

Figure S4. Laser diffraction chromatogram of emulsion droplets stabilized with pH-BCP-Laponite at pH 11.

5. Fabrication of Microfluidic Device and HIPE Fibers

A glass capillary with an inner and outer diameter of 1.16 mm and 2.0 mm, respectively, forms the outer capillary of the device, and contains the sheath fluid. Within the outer capillary, two capillaries (injection and collection inner capillaries) with inner and outer diameters of 0.58 mm and 1.0 mm, respectively, were tapered with a laser puller to allow flow focusing of the concentrated emulsion. The inner injection capillary and inner collection capillary has a diameter of ~110 μm and ~120 μm, respectively. The inner capillaries were aligned to produce a flow-focused junction where the HIPE fibers are fabricated. The optimum flow rates for the HIPE fiber fabrications were 0.1 $mL \cdot min^{-1}$ for the sheath fluid and 0.02 $mL \cdot min^{-1}$ for the concentrated emulsion. Harvard Apparatus PHD 2000 Infusion was used as the pumping system. The sheath fluid was acidified by adding gluconic acid δ-lactone (3 w/v%). All HIPE fibers were collected in an acidic aqueous solution reservoir (pH 3,

adjusted by addition of 1 M HCl). HIPE fiber was disintegrated in basic aqueous solution (pH 11, adjusted by addition of 1 M NaOH).

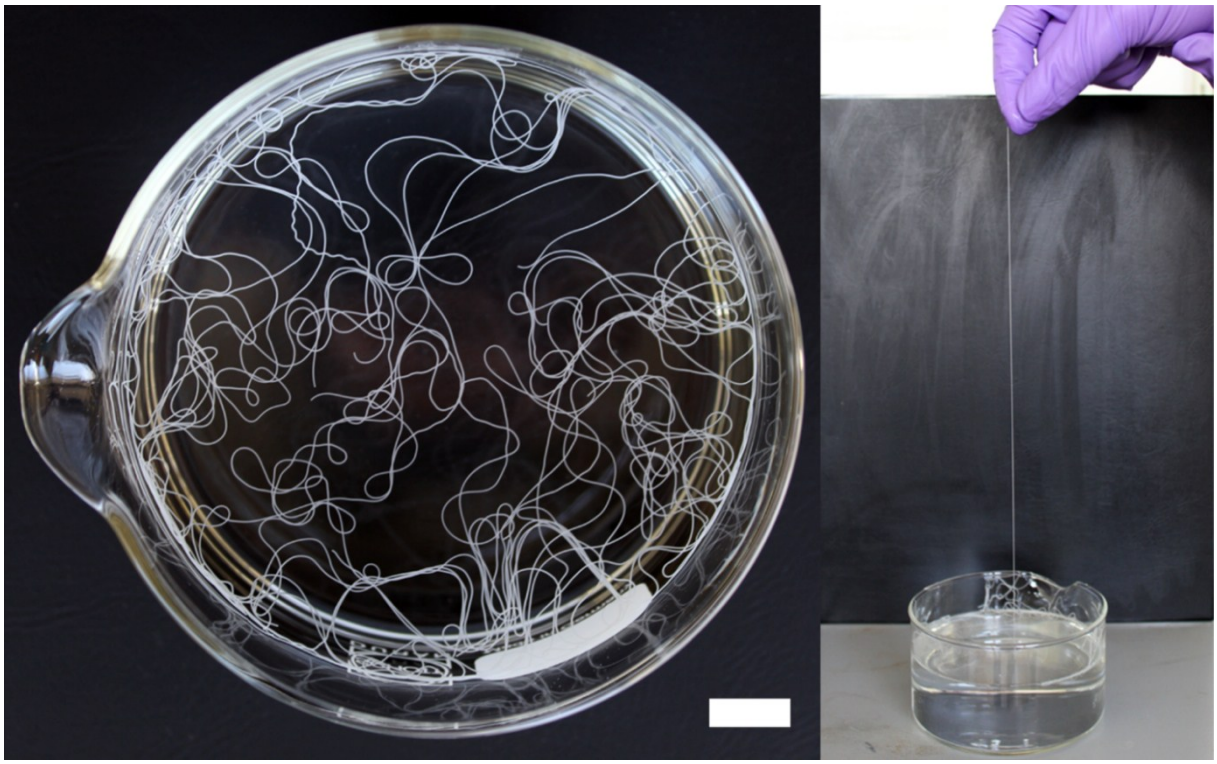

Figure S5. HIPE fiber fabricated with acidic sheath fluid containing no poly(vinyl alcohol). Scale bar represents 1 cm. Several fragmented fibers arise from capillary clogging and viscosity mismatch of the concentrated emulsion and sheath fluid.

The fabrication of HIPE fiber was optimized by adding poly(vinyl alcohol) in the acidic sheath fluid (3 w/v%).

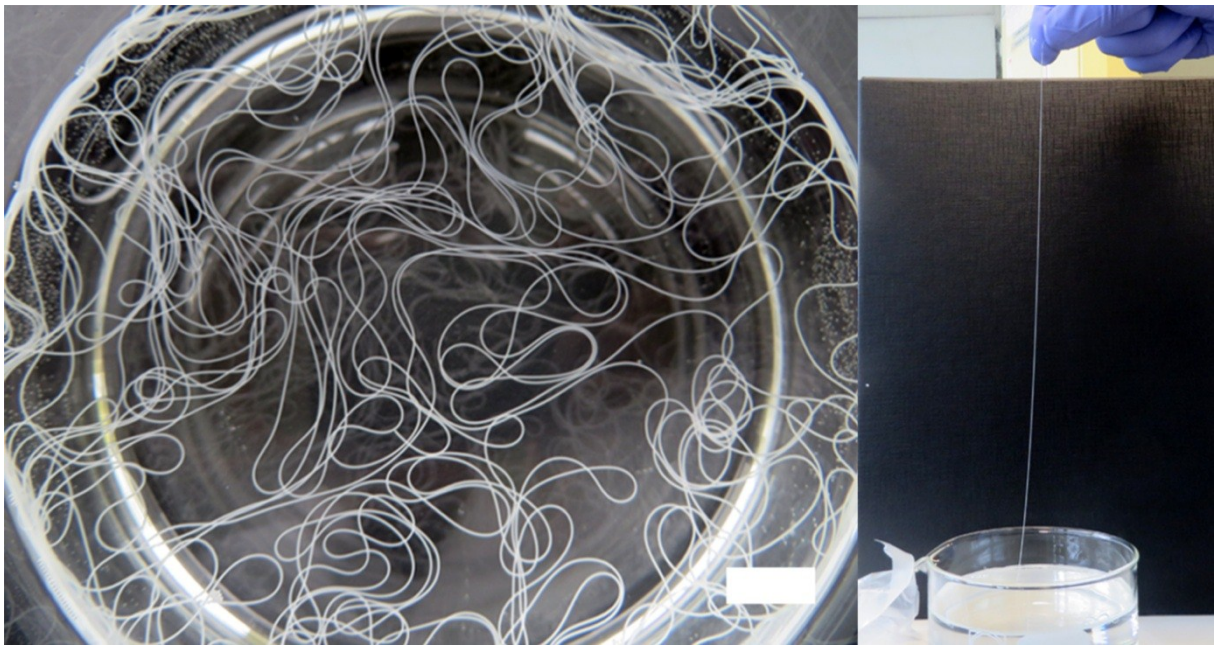

Figure S6. Photograph of continuous long HIPE fibers fabricated with sheath fluid containing poly(vinyl alcohol). Scale bar represents 1 cm.

HIPE fiber was permanently cross-linked with calcium ion by incubating the HIPE fiber in acidic aqueous solution containing calcium ions for 1 hour (pH 3, adjusted by addition of 1 M HCl, $[Ca^{2+}]$ = 1 M).

6. Thermogravimetric Analysis of HIPE Fiber

Thermogravimetric analysis was recorded using a Mettler Toledo TGA/DSC1 STAR^e System instrument. The HIPE fiber was heated from 30 ^oC to 1000 ^oC at10 $^oC \cdot min^{-1}$ in a flow of dry air at 50 $mL \cdot min^{-1}$

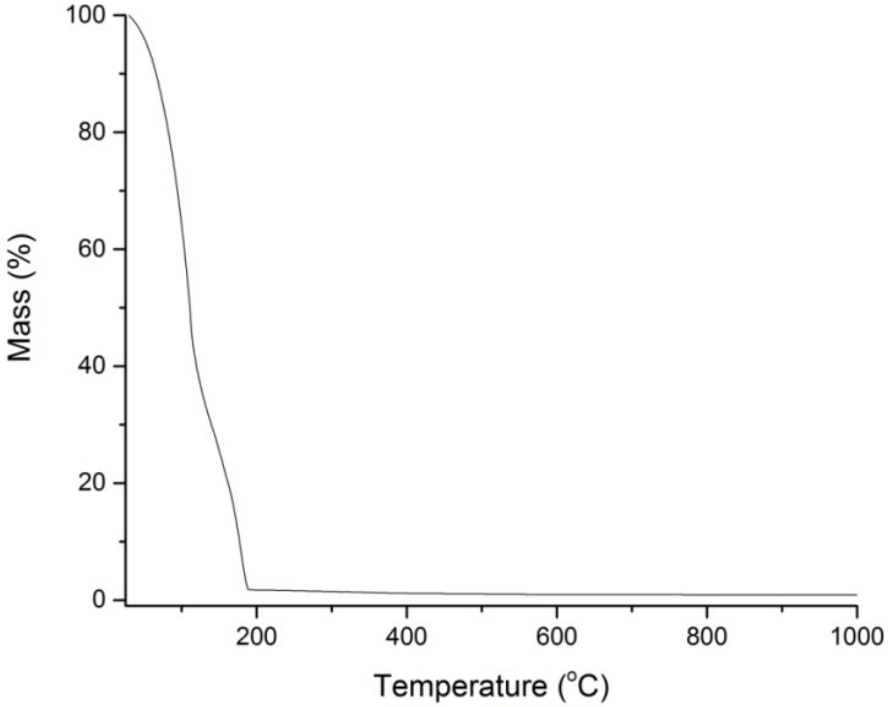

Figure S7. Thermogravimetric (TG) curve of the HIPE fiber. There are two regions of mass losses on the TG curve of the HIPE fiber. The mass loss of 98.32 % between 30 – 220 ^oC is due to the evaporation of dodecane and water. Therefore, the solid content of the HIPE fiber is 1.68 %, which is a combination of Laponite and polymer. The mass loss of 0.69 % between 220 ^oC – 550 ^oC represents decomposition of the polymer (pH-BCP and poly(vinyl alcohol)). This means there is 0.99 % Laponite and 0.69 % polymer in the HIPE fiber (polymer 0.70 : 1 Laponite).

7. Fabrication of Various Types of HIPE Fiber by Microfluidics

HIPE fibers with uniform length and asymmetric fibers were fabricated by having multiply inlets to the injection inner capillary. The Table S2 shows the flow parameters to fabricate these various HIPE fibers.

Table S2. The flow parameters to fabricate various HIPE fibers.

	Outer capillary	**Inner injection capillary**		
		Inlet 1	**Inlet 2**	**Inlet 3**
HIPE fiber with uniform length (1 cm)	0.1 mL·min^{-1} *Acidic PVA solution*	0.02 mL·min^{-1} *Unloaded concentrated emulsion*	0.002 mL·min^{-1} *Air*	
Janus	0.1 mL·min^{-1} *Acidic PVA solution*	0.01 mL·min^{-1} *Red concentrated emulsion*	0.01 mL·min^{-1} *Blue concentrated emulsion*	
'Toothpaste'	0.1 mL·min^{-1} *Acidic PVA solution*	0.007 mL·min^{-1} *Red concentrated emulsion*	0.007 mL·min^{-1} *Blue concentrated emulsion*	0.007 mL·min^{-1} *Unloaded concentrated emulsion*

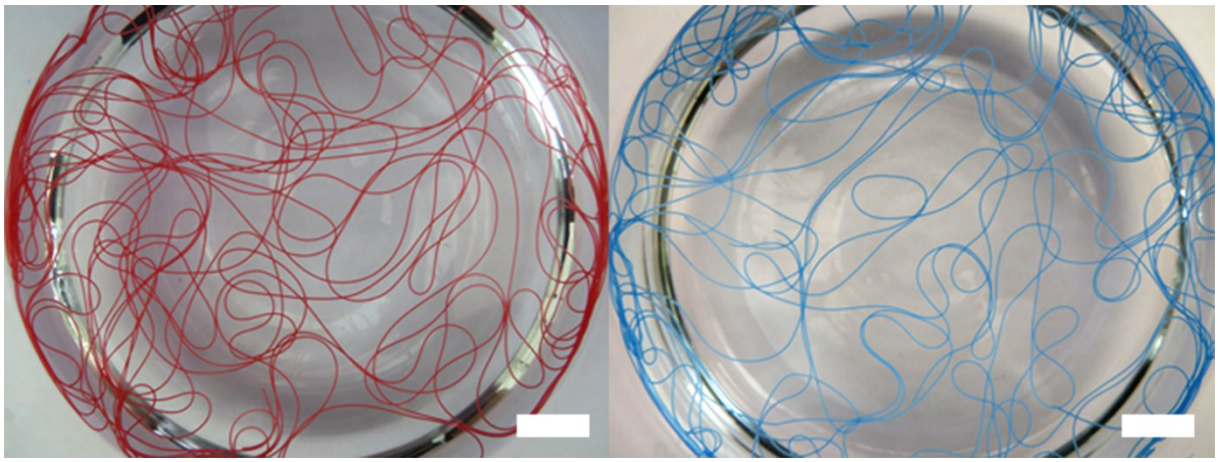

Figure S8. Photographs of HIPE fibers loaded with hydrophobic materials. Red and blue HIPE fibers loaded with hydrophobic red and blue dyes, respectively. Scale bars represent 1 cm.

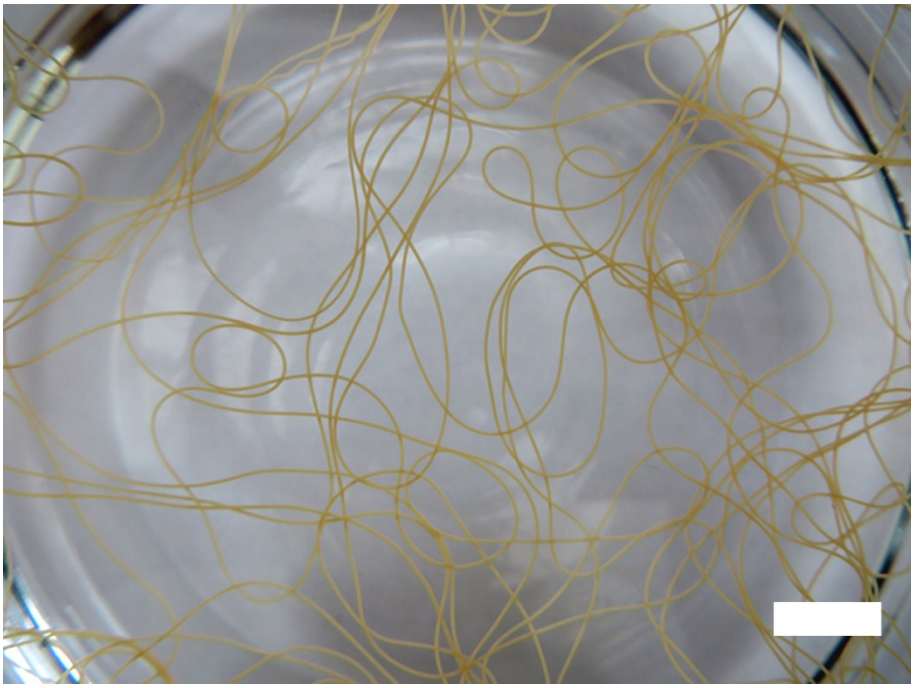

Figure S9. Photograph of magnetic HIPE fibers. Scale bar represent 1 cm.

8. Imaging of the Dried HIPE fiber by Focused Ion Beam Scanning Electron Microscopy

The surface morphology and internal structure images of the dried HIPE fiber were obtained using a JEOL 4500 focused ion beam scanning electron microscope. The dried HIPE fiber was coated with carbon prior to imaging. The imaging was performed at 20 kV.

9. Determination of Density of the Dried Nanocomposite Mesh

Density of the sample was measured using a Micrometric AccuPyc II 1340 gas displacement pycnometer with Helium gas. The gas tank's pressure regulator, the purge fill pressure, and cyclic filling pressure were set at 22 psig, 19.5 psig, and 19.5 psig respectively. Before measuring the material's density, the machine was calibrated with a supplied standard of known volume. A 1 cm^3 crucible was used with the sample filling two thirds of it. Prior to the measurement of the sample, the crucible with sample was purged with Helium gas at 19.5 psig for 30 minutes to remove any adsorbed gases from the air.

10. The Fabrication of Solid pH-BCP-Laponite Fiber

The pores of the HIPE fiber can be removed by simply soaking the HIPE fiber in ethanol prior to drying. By doing so, the oil phase of the emulsion (dodecane) diffuses from the HIPE fiber to the ethanol solution as dodecane is miscible with ethanol. The rapid diffusion process causes the voids in the fiber to collapse and form a solid Laponite-pH-BCP fiber. This fiber is more flexible and can sustain some strain compared to analogue porous dried HIPE fiber (Figure S10).

The solid Laponite-pH-BCP was fabricated by firstly incubating the HIPE fiber in acidic aqueous solution containing calcium ions ($[Ca^{2+}]$ = 1 M) for 3 hours. The cross-linked HIPE fiber is then soaked in ethanol for 30 minutes, and air dried. All scanning electron micrographs were obtained with a Zeiss Supra55VP scanning electron microscope. Samples were coated with gold for imaging. The imaging was performed at 10 kV.

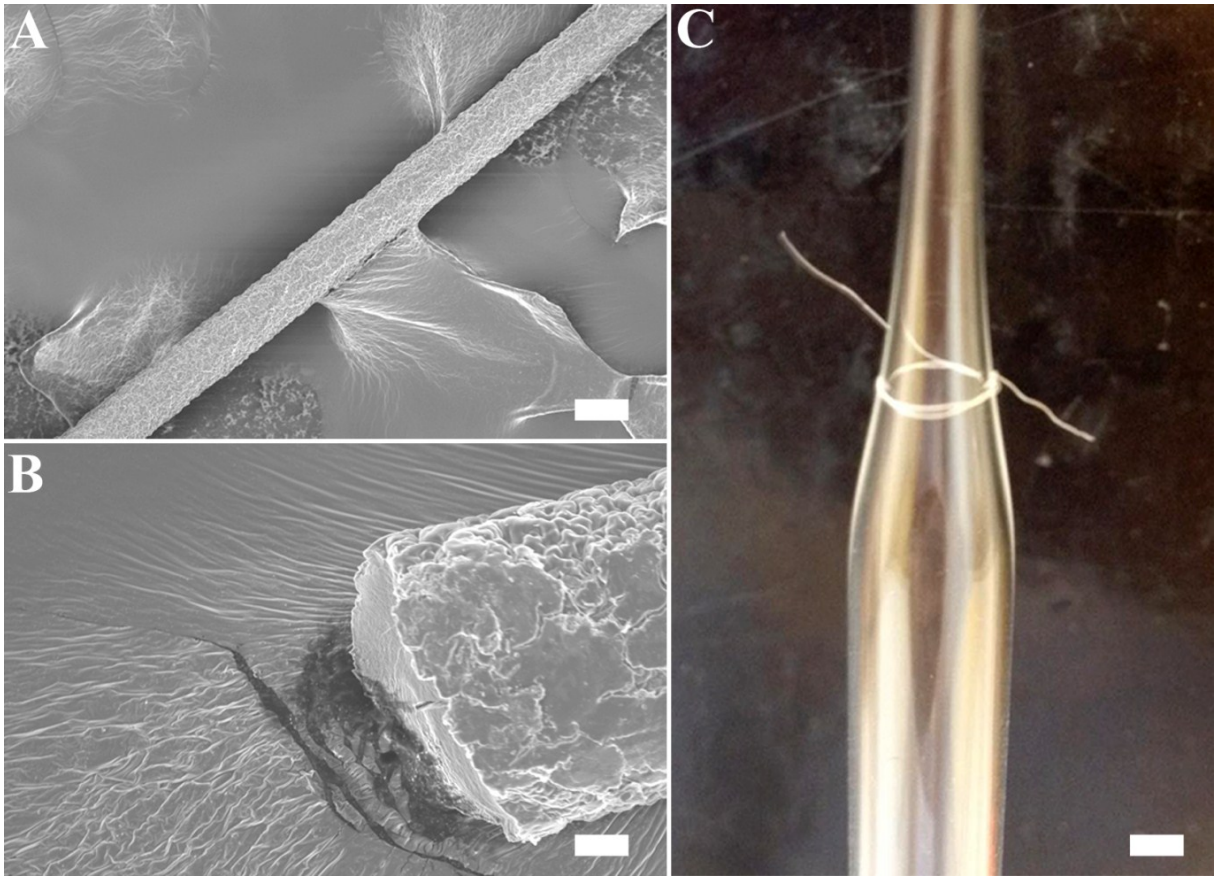

Figure S10. Scanning electron micrographs and photograph of solid pH-BCP-Laponite fiber. (A) Surface morphology of the solid pH-BCP-Laponite fiber. Scale bar represents 51 μm. (B) Non porous internal structure of the solid pH-BCP-Laponite fiber. Scale bar represents 10 μm. (C) The solid Laponite-pH-BCP fiber tied around a glass capillary with multiple loops. Scale bar represents 2.7 mm.

11. Release Study of the Oil Phases of the HIPE Fiber

The evaporation of the liquid phases of the HIPE fiber at ambient temperature was investigated by initially incubating the HIPE fiber (total length = 216 cm) in acidic aqueous solution containing different calcium ion concentrations ($[Ca^{2+}]$ = 0 M, 0.05 M, 0.1 M, 0.5 M, 0.75 M, and 1 M) overnight. The HIPE fibers were collected on a pan. The mass loss of the HIPE fiber was measured over time with a five decimal places weighing balance, Mettler Toledo.