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Supporting Information

Rapid, Green Synthesis of High Performance Viscosifiers via

Photoiniferter Approach for Water-based Drilling Fluid

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Size Exclusion Chromatography with Multi Angle Light Scattering (SEC-MALS)

SEC-MALS measurements are performed in a filtered buffer consisting of either 0.1 M sodium nitrate (NaNO₃), (Buffer 1) or 0.05 M sodium bicarbonate (NaHCO₃), 0.1 M sodium nitrate (NaNO₃), and 0.02 M triethylamine (TEA) with pH 9.656 (Buffer 2). The SEC system consists of Shimadzu modular system with a DGU-20A5R degassing unit, LC20AD LC pump, CBM-20A communications bus module, SPD-20A UV/Vis detector, RID-20A refractive index detector, and CTO-20A column oven equipped with OHpak LB-G 6B guard column (dimensions: 6.0 mm ID x 50 mm) and OHpak LB-806M (dimensions: 8.0 mm ID x 300 mm L, target MW range: 500 - 20,000,000 (estimated maximum) Daltons in pullulan) purchased from Showa Denko America Inc. The MALS consists of a DAWN detector 18 angles of detection providing molar mass detection range of 200 Da-1GDa and molecular size range of 10-500 nm. Normalization, alignment (interdetector delay), and band broadening correction for the DAWN detector is carried out using P-50 Shodex STD P-Series pullulan which is part of Shodex Standard P-82 standard kit using the Astra software (Astra Version 7.3.2.21). Molecular weight analysis is carried out with the Astra software (Astra Version 7.3.2.21). Absolute weight-average molecular weights ($M_{w,SEC-MALS}$), absolute number-average molecular weights ($M_{n,SEC-MALS}$), and polydispersity index (M_w/M_n) were determined by assuming 100% mass recovery for all synthesized samples. A dn/dc value of 0.163 mL g⁻¹ based on literature was applied to commercial PHPA to determine absolute weight-average molecular weights ($M_{w,SEC-MALS}$), absolute number-average molecular weights ($M_{n,SEC-MALS}$), and polydispersity index $(M_{\rm w}/M_{\rm n})$ resulting in $M_{\rm w.SEC-MALS}$ of 11.15 x 10⁶ g/mol, $M_{\rm n.SEC-MALS} = 7.433$ x 10⁶ g/mol, $M_{\rm w}/M_{\rm n} = 1.5$.¹

Nuclear Magnetic Resonance (NMR)

NMR analysis (¹H NMR) is carried out with Bruker Ultrashield 500 MHz operating at 500 MHz for ¹H using DMSO-d₆, D₂O or CDCl₃ as the solvent. Tetramethylsilane (TMS) was used as a reference with chemical shift (δ) of sample measured in ppm downfield from TMS.

Rheometer

Rheological properties (viscosity measurements) of the linear and branched ultra-high molecular weight polymers and partially hydrolyzed polyacrylamide (PHPA) were assessed in an Anton Paar MCR-302 Rheometer fitted with a CC25 Pressure Cell. The solutions were prepared at 0.477 wt% concentrations in water with sodium hydroxide used to provide pH between pH 9 to 10. The viscosities of the different solutions were measured at a constant shear rate of 510 s⁻¹ from 30°C to 150°C at a heating rate of 0.5°C/min under 500 Psi pressure.

Viscometer

Viscometry studies at high temperature (120°F-500°F) and high pressure (10 000 Psi) were carried out with Fann iX77 Rheometer equipped with a Model D4004 Chiller.

<u>Mixer</u>

Fann Five-Spindle Multi-Mixer® Model 9B with No. 9B29X impeller blades was used to generate polymeric nanogels (microgels) from macrogel through mechanical shearing. Each spindle is fitted with a single sine-wave impeller approximately 25 mm in diameter mounted flash side up. This mixer conforms to American Petroleum Institute Specification 13A where all spindles rotate at 11,500 RPM +/- 300 RPM.

Roller Oven

Samples requiring hot rolling at temperatures between 120°F-300°F were rolled in Fann Roller Oven Model 705ES at the desired temperatures in Fann High Temperature Aging Cell pressurized at 500 Psi.

Dynamic light scattering (DLS)

DLS measurements are performed using a Particle Analyzer Litesizer 500 running Kalliope software (40mW, semiconductor laser, $\lambda = 658$ nm). The temperature is stabilized to ± 0.1 °C of the set temperature 25 °C. All samples are prepared in Milli-Q water at concentrations of ~ 0.477 wt% with pH adjusted between pH 9 - 10 with sodium hydroxide. Hydrodynamic radii are calculated by the non-negative least squares (NNLS) algorithm using the Kalliope software.

Thermal Gravimetric Analysis (TGA)

Thermogravimetric analyses (TGA) of the synthesized products are performed on a TA Thermogravimetric Analyzer (SDT Q600). All samples tested are heated from room temperature at a constant rate of 10 °C min⁻¹ using air as the furnace gas to 1000 °C. Heating is carried out at a ramp rate of 10°C/min to 1000°C in air to ensure complete removal of residual water and organic content.

<u>Photopolymerization</u> was carried out using UV LED ($\lambda_{max} = 365 \text{ nm}$, intensity = 7.2 mW/cm²) nail lamp (Melodysusie nail light) purchased from Amazon.

EXPERIMENTAL SECTION

SECTION I – Synthesis of Xanthate

Thiocarbonylthiol compound: methyl 2-(ethoxycarbonothioylthio)propanoate (Xanthate) was synthesized according to literature procedures as described.^{2, 3} Potassium ethyl xanthogenate (3.21 g, 20 mmol) was slowly added in a round bottomed flask with 50 mL of dry acetone under stirring. The mixture was continuously stirred at ambient temperature with nitrogen bubbling for 30 minutes. The potassium ethyl xanthogenate solution was then cooled to 0°C in an ice bath for 15 minutes. In a separate vial, methyl 2-bromopropionate (2mL, 18 mmol) was dissolved in 10 mL acetone. The diluted methyl 2-bromopropionate was then added drop-by-drop for 20 minutes into potassium ethyl xanthogenate followed by vigorous stirring for 30 minutes to yield a white solution. The ice bath was then removed, and nitrogen bubbling stopped. The reaction was stirred for 8 hours. The reaction mixture was filtered to remove potassium bromide precipitate and the remaining acetone was then evaporated off. The resultant liquid was then dissolved in diethyl ether (100 mL) and washed with water (50 mL) at least four times. The organic phase was then collected and dried to yield a yellow liquid. Xanthate was obtained with 67% yield and analyzed with ¹H NMR.



Figure S1. 500 MHz ¹H NMR of xanthate in CDCl₃.

SECTION II – Synthesis of Poly(acrylic acid) with Xanthate



Figure S2. 500 MHz ¹H NMR of poly(acrylic acid) in DMSO-d₆. (Monomer conversion of ~99% and $M_{n,NMR} = 2520 \text{ g/mol}$)



Figure S3. SEC-MALS analysis of poly(acrylic acid) in Buffer 2.

Poly(acrylic acid) synthesized in UV-mediated RAFT/MADIX polymerization was then used as a macromolecular chain transfer agent (PAA-MacroCTA) to synthesize ultra-high molecular weight linear block copolymer – UHMW-LCP-1 and UHMW-LCP-2 – and to synthesize ultra-high molecular weight branched block copolymer – UHMW-BCP-1 and UHMW-BCP-2.

SECTION III – Synthesis of UHMW-LCP-1

A reaction stock solution consisting of water (30 mL), DMA (52.4 mmol, 5.194 g, 5.4mL), AMPS (6.29 mmol, 1.297 g), and PAA-MacroCTA (22 μ L pipetted from the final reaction mixture of poly(acrylic acid) described above provided a dry mass of 11 mg and $M_{n,SEC-MALS}$ of 4800 g/mol which was used as the polymer molecular weight leading to a molar composition of 2.292 μ mol) was prepared in 50 mL round bottomed flask with a stir bar covered in aluminum foil (DMA : AMPS : PAA = 22 860 : 2731 : 1). After 10 minutes of stirring, the reaction mixture was distributed into four 20 mL sample vials with stir bars. One of the vials was then sealed with septa before being sparged under nitrogen for 20 minutes. The mixture was then irradiated in a UV photoreactor (λ_{max} = 365 nm, 7.2 mW/cm²). The reaction was carried out for 30 minutes. Aliquots of the reaction mixture were taken at specific time points (5, 10, 20, and 30 minutes) during the reaction to determine monomer conversions through ¹H NMR analysis, and to determine number average molecular weights (M_n) and polydispersities (M_w/M_n) through SEC-MALS analysis using Buffer 1 (Figure S4A-C & Table S1).



Figure S4. Synthesis of UHMW-LCP-1. (A) Plot of $\ln([M_o]/[M]_t)$ vs. exposure time; (B) Differential refractive index (dRI) traces from SEC-MALS analysis; (C) Light scattering (LS) traces for SEC-MALS analysis; and (D) Overlap of dRI and LS traces of UHMW-LCP-1 synthesized after 60-min irradiation.

The reaction was then repeated without performing any kinetic analysis with the sample being irradiated for 60 minutes to ensure complete monomer conversion. The final sample was then analyzed through gravimetric analysis to determine monomer conversion, followed by SEC-MALS analysis in Buffer 2 to determine polymer molecular weight and molecular weight distributions (Figure S4D), and FTIR analysis (Figure S5) to determine the chemical composition.

Table S1. Kinetics for linear chain polymerization of *N*,*N*-Dimethylacrylamide (DMA) and 2-Acrylamido-2methyl-1-propanesulfonic acid (AMPS) under UV light mediated by poly(acrylic acid) terminated with xanthate as the macro chain transfer agent (PAA-macroCTA).^{*a*}

no.	Exp. Cond. ^{<i>a</i>}	[DMA] :	Time	α^b	$M_{ m n,th.}{}^c$	$M_{\mathrm{n,SEC-MALS.}}^{d}$	$M_{\rm w}/M_{\rm n}^{d}$
	[AMPS] : [PAA-Xant	hate]	(min)	(%)	(g/mol)	(g/mol)	
1	22860 : 2731 : 1		5	17	486 300	901 300	1.59
2	22860 : 2731 : 1		10	33	939 400	1 428 000	1.46
3	22860 : 2731 : 1		20	68	1 931 000	1 706 000	1.43
4	22860 : 2731 : 1		30	83	2 355 000	1 780 000	1.47

Note: *a*Reactions were performed in the absence of oxygen at ambient temperature with monomer concentrations of 1.656 M in water. Polymerization was carried out under mild UV light (λ_{max} = 365 nm, intensity = 7.2 mW/cm²). *b* Overall monomer conversion was determined by using ¹H NMR spectroscopy. *c*Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[Macro-CTA]_0 \times MW^M \times \alpha + MW^{PAA-Xanthate}$, where [M]₀, [Macro-CTA]₀, MW^M, α , and MW^{PAA-Xanthate} correspond to initial monomer concentration, initial PAA-Xanthate concentration, molar mass of monomer, conversion determined by ¹H NMR, and absolute molar mass of PAA-Xanthate determined in SEC-MALS. Conversions determined by ¹H NMR were based on the disappearance of vinyl protons of both DMA and AMPS with the average monomer consumption assumed to be similar for both DMA and AMPS for any given time. *d*Absolute number-average molecular weights ($M_{n,SEC-MALS}$) and polydispersity index (M_w/M_n) were determined by SEC equipped with multi-angle light-scattering detector assuming 100% mass recovery.



Figure S5. FTIR spectra of UHMW-LCP-1 and the different vibrational modes of various functional groups.

Based on Figure S5, the broad absorption band at 3450-3500 cm⁻¹ corresponds to N-H stretching from amide group and hydrogen bonding between carbonyl groups and hydroxyl groups of water, the absorption band at 2927 cm⁻¹ corresponds to C-H stretch, the absorption bands at 1630 and 1723 cm⁻¹ correspond to C=O stretch, the absorption bands at 1612 and 1400 cm⁻¹ correspond to amide bands, bands at 1498 and 1355 cm⁻¹ correspond to CH₃ deformation vibration, and the absorption band at 1035 cm⁻¹ correspond to S=O groups of sulfonic acid.⁴⁻⁶

SECTION IV – Synthesis of UHMW-LCP-2

A reaction stock solution consisting of water (30 mL), DMA (52.4 mmol, 5.194 g, 5.4mL), AMPS (6.29 mmol, 1.297 g), 2-HEA (3.145 mmol, 0.365g, 0.361 mL), and PAA-MacroCTA (22 μ L pipetted from the final reaction mixture of poly(acrylic acid) described above provided a dry mass of 11 mg and $M_{n,SEC-MALS}$ of 4800 g/mol which was used as the polymer molecular weight leading to a molar composition of 2.292 μ mol) was prepared in 50 mL round bottomed flask with a stir bar covered in aluminum foil (DMA : AMPS : HEA : PAA = 22 860 : 2731 : 1371 : 1). After 10 minutes of stirring, the reaction mixture was distributed into four 20 mL sample vials with stir bars. One of the vials was then sealed with septa before being sparged under nitrogen for 20 minutes. The mixture was then irradiated in a UV photoreactor ($\lambda_{max} = 365$ nm, 7.2 mW/cm²). The reaction was carried out for 30 minutes. Aliquots of the reaction mixture were taken at specific time points (5, 10, 20, and 30 minutes) during the reaction to determine monomer conversions through ¹H NMR analysis, and to determine number average molecular weights (M_n) and polydispersities (M_w/M_n) through SEC-MALS analysis using Buffer 1 (Figure S6A-C & Table S2).



Figure S6. Synthesis of UHMW-LCP-2. (A) Plot of $\ln([M_o]/[M]_t)$ vs. exposure time; (B) Differential refractive index (dRI) traces from SEC-MALS analysis; (C) Light scattering (LS) traces for SEC-MALS analysis; and (D) Overlap of dRI and LS traces of UHMW-LCP-2 synthesized after 60-min irradiation.

The reaction was then repeated without performing any kinetic analysis with the sample being irradiated for 60 minutes to ensure complete monomer conversion. The final sample was then analyzed through gravimetric analysis to determine monomer conversion, followed by SEC-MALS analysis in Buffer 2 to determine polymer molecular weight and molecular weight distributions (Figure S6D), and FTIR analysis (Figure S7) to determine the chemical composition.

Table S2. Kinetics for linear chain polymerization of *N*,*N*-Dimethylacrylamide (DMA), 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS), and 2-hydroxyethyl acrylate (2-HEA) under UV light mediated by poly(acrylic acid) terminated with xanthate as the macro chain transfer agent (PAA-macroCTA).^{*a*}

no.	Exp. Cond. ^{<i>a</i>}	[DMA] :	Time	α^b	$M_{ m n,th.}{}^c$	$M_{n, \text{SEC-MALS.}}^{d}$	$M_{ m w}/M_{ m n}^{d}$
	[AMPS] : [2-HEA] : [PAA	-Xanthate]	(min)	(%)	(g/mol)	(g/mol)	
1	22860 : 2731 : 137	1:1	5	4	105 905	2 393 000	1.60
2	22860 : 2731 : 137	1:1	10	27	812 500	3 690 000	1.63
3	22860 : 2731 : 137	1:1	20	39	1 171 400	4 472 000	1.55
4	22860 : 2731 : 137	1:1	30	54	1 620 000	4 959 000	1.53

Note: *a*Reactions were performed in the absence of oxygen at ambient temperature with monomer concentrations of 1.727 M in water. Polymerization was carried out under mild UV light (λ_{max} = 365 nm, intensity = 7.2 mW/cm²). *b* Overall monomer conversion was determined by using ¹H NMR spectroscopy. *c*Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[Macro-CTA]_0 \times MW^M \times \alpha + MW^{PAA-Xanthate}$, where [M]₀, [Macro-CTA]₀, MW^M, α , and MW^{PAA-Xanthate} correspond to initial monomer concentration, initial PAA-Xanthate concentration, molar mass of monomer, conversion determined by ¹H NMR, and absolute molar mass of PAA-Xanthate determined in SEC-MALS. Conversions determined by ¹H NMR were based on the disappearance of vinyl protons of both DMA, AMPS, and 2-HEA with the average monomer consumption assumed to be similar for both DMA, AMPS, 2-HEA for any given time. *d*Absolute number-average molecular weights ($M_{n,SEC-MALS}$) and polydispersity index (M_w/M_n) were determined by SEC equipped with multi-angle light-scattering detector assuming 100% mass recovery.



Figure S7. FTIR spectra of UHMW-LCP-2 and the different vibrational modes of various functional groups.

Based on Figure S7, the broad absorption band at 3450-3500 cm⁻¹ corresponds to N-H stretching from amide group and hydrogen bonding between carbonyl groups and hydroxyl groups of water, the absorption band at 2927 cm⁻¹ corresponds to C-H stretch, the absorption bands at 1630 and 1723 cm⁻¹ correspond to C=O stretch, the absorption bands at 1612 and 1400 cm⁻¹ correspond to amide bands, bands at 1498 and 1355 cm⁻¹ correspond to CH₃ deformation vibration, and the absorption band at 1035 cm⁻¹ correspond to S=O groups of sulfonic acid.⁴⁻⁶

SECTION V – Synthesis of UHMW-BCP-1

A reaction stock solution consisting of water (30 mL), DMA (52.4 mmol, 5.194 g, 5.4mL), AMPS (6.29 mmol, 1.297 g), MBA (16.22 µmol, 0.0025 g) and PAA-MacroCTA (22 µL pipetted from the final reaction mixture of poly(acrylic acid) described above provided a dry mass of 11 mg and $M_{n,SEC-MALS}$ of 4800 g/mol which was used as the polymer molecular weight leading to a molar composition of 2.292 µmol) was prepared in 50 mL round bottomed flask with a stir bar covered in aluminum foil (DMA : AMPS : MBA : PAA = 22 860 : 2731 : 7 : 1). After 10 minutes of stirring, the reaction mixture was distributed into four 20 mL sample vials with stir bars. One of the vials was then sealed with septa before being sparged under nitrogen for 20 minutes. The mixture was then irradiated in a UV photoreactor ($\lambda_{max} = 365$ nm, 7.2 mW/cm²). The reaction was carried out for 8 minutes. Aliquots of the reaction mixture were taken at specific time points (2, 4, 6, and 8 minutes) during the reaction to determine monomer conversions through ¹H NMR analysis, and to determine number average molecular weights (M_n) and polydispersities (M_w/M_n) through SEC-MALS analysis using Buffer 1 (Figure S8A-C & Table S3).



Figure S8. Synthesis of UHMW-BCP-1. (A) Plot of $\ln([M_o]/[M]_t)$ vs. exposure time; (B) Differential refractive index (dRI) traces from SEC-MALS analysis; (C) Light scattering (LS) traces for SEC-MALS analysis.

Table S3. Kinetics for polymerization of N,N-Dimethylacrylamide (DMA), 2-Acrylamido-2-methyl-1propanesulfonic acid (AMPS), and N,N'-methylenebis(acrylamide) (MBA) under UV light mediated by poly(acrylic acid) terminated with xanthate as the macro chain transfer agent (PAA-macroCTA).^{*a*}

no.	Exp. Cond. ^{<i>a</i>}	DMA]: Tim	ne α^b	$M_{n,SEC-MALS}^{c}$	$M_{\rm w}/M_{\rm n}^{c}$
	[AMPS]: [MBA]: [PAA-Xa	anthate] (min	n) (%)	(g/mol)	
1	22860 : 2731 : 7 : 1	2	5	1 784 000	1.46
2	22860:2731:7:1	4	20	2 167 000	1.47
3	22860 : 2731 : 7: 1	6	25	3 564 000	1.55
4	22860 : 2731 : 7 :1	8	37	4 656 000	1.68

Note: ^{*a*}Reactions were performed in the absence of oxygen at ambient temperature with monomer concentrations of 1.656 M in water. Polymerization was carried out under mild UV light (λ_{max} = 365 nm, intensity = 7.2 mW/cm²). ^{*c*}Absolute number-average molecular weights ($M_{n,SEC-MALS}$) and polydispersity index (M_w/M_n) were determined by SEC equipped with multi-angle light-scattering detector assuming 100% mass recovery.

The reaction was then repeated without performing any kinetic analysis with the sample being irradiated for 60 minutes to ensure complete monomer conversion, which resulted in the formation of a macrogel. The macrogel was then mechanically sheared to generate polymeric nanogels (microgels). The final sample was then analyzed through gravimetric analysis to determine monomer conversion (>99%), followed by SEC-MALS analysis in Buffer 2 to determine polymer molecular weight and molecular weight distributions (Figure 3C), ¹H NMR analysis (Figure S9) and FTIR analysis (Figure S10) to determine the chemical composition, DLS analysis

(Figure S11) to determine the hydrodynamic volume of the polymeric nanogels (microgels), and TGA analysis on the dry polymer to determine the thermal stability (Figure S12).



Figure S9. 500 MHz 1 H NMR of UHMW-BCP-1 in D₂O.



Figure S10. FTIR spectra of UHMW-BCP-1 and the different vibrational modes of various functional groups.

Based on Figure S10, the broad absorption band at 3450-3500 cm⁻¹ corresponds to N-H stretching from amide group and hydrogen bonding between carbonyl groups and hydroxyl groups of water, the absorption band at 2927 cm⁻¹ corresponds to C-H stretch, the absorption bands at 1630 and 1723 cm⁻¹ correspond to C=O stretch, the absorption bands at 1612 and 1400 cm⁻¹ correspond to amide bands, bands at 1498 and 1355 cm⁻¹ correspond to CH₃ deformation vibration, and the absorption band at 1035 cm⁻¹ correspond to S=O groups of sulfonic acid.⁴⁻⁶



Figure S11. DLS analysis of UHMW-BCP-1 polymeric nanogels (microgels) generated from mechanically sheared macrogel synthesized after 60 minutes of irradiation.

Based on Figure S11, DLS analysis was carried out on UHMW-BCP-1 which was mechanically sheared to generate microgels. The UHMW-BCP-1 was then diluted in water to generate a concentration of 0.477 wt% with the pH adjusted between pH 9 - 10 with sodium hydroxide. The microgel has a particle diameter of 290 nm and moderate particle dispersity of 23.9%.



Figure S12. TGA curve for UHMW-BCP-1.

Based on Figure S12, initial mass loss of up to 100°C can be attributed to the loss of water trapped in the dry polymer and water hydrating the surface of the dry polymer. The polymer then remains temperature stable, without any mass loss, from 100°C to 225°C. Heating the dry UHMW-BCP-1 above 225°C led to continuous loss of mass due to degradation of functional moiety on the pendant groups.



Figure S13. UHMW-BCP-1 with concentration of 0.477wt% (right) prepared by mechanical shearing and hot rolling (150°C for 16 hours at 500 Psi in a pressure cell) of macrogel (left) synthesized after 1 hr mild UV irradiation.

SECTION VI – Synthesis of UHMW-BCP-2

A reaction stock solution consisting of water (30 mL), DMA (52.4 mmol, 5.194 g, 5.4mL), AMPS (6.29 mmol, 1.297 g), 2-HEA (3.145 mmol, 0.365g, 0.361 mL), MBA (16.22 µmol, 0.0025 g) and PAA-MacroCTA (22 µL pipetted from the final reaction mixture of poly(acrylic acid) described above provided a dry mass of 11 mg and $M_{n,SEC-MALS}$ of 4800 g/mol which was used as the polymer molecular weight leading to a molar composition of 2.292 µmol) was prepared in 50 mL round bottomed flask with a stir bar covered in aluminum foil (DMA : AMPS : 2-HEA: MBA : PAA = 22 860 : 2731 : 1371 : 7 : 1). After 10 minutes of stirring, the reaction mixture was distributed into four 20 mL sample vials with stir bars. One of the vials was then sealed with septa before being sparged under nitrogen for 20 minutes. The mixture was then irradiated in a UV photoreactor (λ_{max} = 365 nm, 7.2 mW/cm²). The reaction was carried out for 8 minutes. Aliquots of the reaction mixture were taken at specific time points (2, 4, 6, and 8 minutes) during the reaction to determine monomer conversions through ¹H NMR analysis, and to determine number average molecular weights (M_n) and polydispersities (M_w/M_n) through SEC-MALS analysis using Buffer 1 (Figure S14A-C & Table S4).



Figure S14. Synthesis of UHMW-BCP-2. (A) Plot of $\ln([M_o]/[M]_t)$ vs. exposure time; (B) Differential refractive index (dRI) traces from SEC-MALS analysis; (C) Light scattering (LS) traces for SEC-MALS analysis.

Table S4. Kinetics for polymerization of N,N-Dimethylacrylamide (DMA), 2-Acrylamido-2-methyl-1propanesulfonic acid (AMPS), 2-hydroxyethyl acrylate (2-HEA) and N,N'-methylenebis(acrylamide) (MBA) under UV light mediated by poly(acrylic acid) terminated with xanthate as the macro chain transfer agent (PAAmacroCTA).^{*a*} Data from Table S1 used to plot (below) kinetics of MW vs conversion for Figure S4.

no.	Exp. Cond. ^{<i>a</i>}	[DMA] :	Time	α^b	$M_{n,SEC-MALS}^{c}$	$M_{\rm w}/M_{\rm n}^{c}$
	[AMPS]: [2-HEA]: [MI	BA] : [PAA-	(min)	(%)	(g/mol)	
	Xanthate]					
1	22860 : 2731 : 1371	: 7 : 1	2	13	1 925 000	1.54
2	22860 : 2731 : 1371	: 7 : 1	4	23	2 741 000	1.59
3	22860 : 2731 : 137	: 7: 1	6	39	4 227 000	1.69
4	22860 : 2731 : 137	: 7 :1	8	51	6 218 000	1.45



Note: *^a*Reactions were performed in the absence of oxygen at ambient temperature with monomer concentrations of 1.728 M in water. Polymerization was carried out under mild UV light (λ_{max} = 365 nm, intensity = 7.2 mW/cm²). *^c*Absolute number-average molecular weights ($M_{n,SEC-MALS}$) and polydispersity index (M_w/M_n) were determined by SEC equipped with multi-angle light-scattering detector assuming 100% mass recovery.

The reaction was then repeated without performing any kinetic analysis with the sample being irradiated for 60 minutes to ensure complete monomer conversion, which resulted in the formation of a macrogel. The macrogel was then mechanically sheared to generate polymeric nanogels (microgels). The final sample was then analyzed through gravimetric analysis to determine monomer conversion (>99%), followed by SEC-MALS analysis in Buffer 2 to determine polymer molecular weight and molecular weight distributions (Figure S15), ¹H NMR

analysis (Figure S16) and FTIR analysis (Figure S17) to determine the chemical composition, DLS analysis (Figure S18) to determine the hydrodynamic volume of the polymeric nanogels (microgels), and TGA analysis on the dry polymer to determine thermal stability (Figure S19).



Figure S15. Overlap of dRI and LS traces of UHMW-BCP-2 synthesized after 60-min irradiation followed mechanical shearing in Fann Five-Spindle Multi-Mixer® and hot rolling (150°C for 16 hours at 500 Psi in a pressure cell) before analyzing with Buffer B.



Figure S16. 500 MHz ¹H NMR of UHMW-BCP-2 in D₂O.



Figure S17. FTIR spectra of UHMW-BCP-2 and the different vibrational modes of various functional groups.

Based on Figure S15, the broad absorption band at 3450-3500 cm⁻¹ corresponds to N-H stretching from amide group and hydrogen bonding between carbonyl groups and hydroxyl groups of water, the absorption band at 2927

 cm^{-1} corresponds to C-H stretch, the absorption bands at 1630 and 1723 cm^{-1} correspond to C=O stretch, the absorption bands at 1612 and 1400 cm^{-1} correspond to amide bands, bands at 1498 and 1355 cm^{-1} correspond to CH₃ deformation vibration, and the absorption band at 1035 cm^{-1} correspond to S=O groups of sulfonic acid.⁴⁻⁶



Figure S18. DLS analysis of UHMW-BCP-2 polymeric nanogels (microgels) generated from mechanically sheared macrogel synthesized after 60 minutes of irradiation.

Based on Figure S16, DLS analysis was carried out on UHMW-BCP-2 which was mechanically sheared to generate microgels. The UHMW-BCP-2 was then diluted in water to generate a concentration of 0.477 wt% with the pH adjusted between pH 9 - 10 with sodium hydroxide. The microgel has a particle diameter of 198 nm and moderate particle dispersity of 23.6%.



Figure S19. TGA curve for UHMW-BCP-2.

Based on Figure S18, initial mass loss of up to 100°C can be attributed to the loss of water trapped in the dry polymer and water hydrating the surface of the dry polymer. The polymer then remains temperature stable, without any mass loss, from 100°C to 225°C. Heating the dry UHMW-BCP-2 above 225°C led to continuous loss of mass due to degradation of functional moiety on the pendant groups.



Figure S20. UHMW-BCP-2 with concentration of 0.477wt% (right) prepared by mechanical shearing and hot rolling (150°C for 16 hours at 500 Psi in a pressure cell) of macrogel (left) synthesized after 1 hr mild UV irradiation.



Figure S21. Viscosifiers synthesized in Sections III-VI after 1-hour irradiation under mild UV light.

SECTION VII – Shale Inhibition Studies

Salts	g/L	Ion types	g/L
CaCl ₂	1.71	Chloride	933.39
MgCl ₂	8.26	Sodium	802.57
KC1	1.13	Magnesium	86.73
NaCl	41.72	Potassium	15.22
NaHCO ₃	0.21	Sulfate	43.12
Na_2SO_4	6.12	Bicarbonate	2.46

Table S5. Composition of the synthetic Arabian sea water.

Synthetic Arabian Sea Water, g	210	210	210	210
Xanthan Gum, g	0.43	0.43	0.43	0.43
Inhibitors	No Inhibitor (70 g water)	UHMW-BCP-1 (1 g in 70 g water)	UHMW-BCP-2 (1 g in 70 g water)	PHPA (1 g in 70 g water)
Pierre II shale, g	17.5	17.5	17.5	17.5

Table S6. Fluid formulations in synthetic Arabian sea water for shale stability studies.



Data from Table S2 used to plot (above) kinetics of MW vs conversion for Figure S6

Fluid Formulations (lb/bbl)	UHMW-BCP-1	UHMW-BCP-2	PHPA	Control
Water	324 g	324 g	324 g	324 g
Sodium hydroxide (caustic soda)	0.1 g	0.1 g	0.1 g	0.1 g
Sodium chloride	36 g	36 g	36 g	36 g
Xanthan gum	1 g	1 g	1 g	1 g
Modified Starch	4 g	4 g	4 g	4 g
PAC LV	1 g	1 g	1 g	1 g
Shale Inhibitor	2 g	2 g	2 g	0 g

Table S7. Water-based fluids formulated and used in dynamic linear swelling test.

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