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Amphoteric, Sulfonamide-Functionalized "Polysoaps": CO_2-Induced Phase Separation for Water Remediation

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S *Supporting Information*

ABSTRACT: Amphoteric polysoaps have been prepared via statistical RAFT copolymerization using either methacryloyl sulfacetamide (mSAC) or methacryloyl sulfmethazine (mSMZ) and 4-hexylphenyl methylacrylamide (4HPhMA). These copolymers form pH- and CO_2-responsive polymeric micelles capable of sequestering hydrophobic molecules in water. The composition and structure of the respective copolymers can be changed to tailor the onset and extent of CO_2-dependent phase behavior. When CO_2 is introduced into the system, resulting in carbonic acid formation, the pH drops below the pK_a of the sulfonamide units along the copolymer backbone, and phase separation occurs. Purging with N_2 results in an increase in pH and redissolution of the polysoap; this process can be repeated multiple times. The mSMZ polysoaps, which show complete phase transitions using this reversible process, were especially efficient in removing the model contaminants pyrene and 9-anthracenemethanol from water. The feasibility of recovering and reusing these copolymers is demonstrated, pointing to the potential utility of such CO_2-responsive systems in water treatment and related environmental remediation applications.

pH- and CO_2-responsive "polysoaps" for removal of hydrocarbon impurities from water
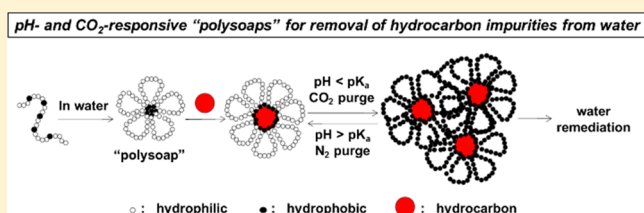
INTRODUCTION

Assuring the quality and availability of clean drinking water is a major global objective, spurred recently by well-documented reports of contamination by pollutants including pharmaceuticals, pesticides, and polycyclic aromatic hydrocarbons (PAHs).[1−7] These types of chemicals typically enter water sources through sewer drainage and water runoff or from industrial waste disposal.[6−9] The presence of PAHs and related hydrophobic compounds in water sources has been linked to cancer and birth defects.[9−11] Unfortunately, removal of these harmful chemicals has proven to be challenging due to the low efficiency and high cost of commercial purification techniques.[12−14]

Stimuli-responsive, amphiphilic copolymers have become increasingly important for environmental and biological applications due to their unique phase separation in aqueous media. For example, micelles, vesicles, and other ordered structures can result from induced self-assembly of a wide range of structural types including statistical, block, graft, star, and hyperbranched copolymers.[15−20] Amphiphilic copolymers, or polysoaps, that reversibly form multimeric or unimeric micelles are of particular interest for water remediation since they potentially combine surfactant-like behavior and hydrophobe capture/sequestration capabilities at high dilution.[20−27]

Seminal work by Strauss,[21,22] who coined the term polysoap, demonstrated that surfactant analogues placed strategically along a hydrophilic polymer backbone could yield soap-like characteristics. Studies to date on an extensive number of amphiphilic polymer types exhibiting polysoap behavior have shown that the corona can have nonionic,[28] cationic,[29−32] anionic,[30,31,33−35] or zwitterionic[24,36,37] segments while the core may be composed of hydrophobic entities varying in composition and chain length.[20,26] Functional groups can also be introduced into either the core or corona-forming segments to impart stimuli-responsiveness.[32,38−40] Prior to the development of reversible deactivation radical polymerization (RDRP) techniques,[41−43] control over molecular weight and polymer architecture was quite limited. Previously, our group utilized reversible addition−fragmentation chain transfer (RAFT) copolymerization to synthesize polysoaps with controlled molecular weights and low dispersities for oil-spill remediation applications.[25] We demonstrated that copolymers prepared from hydrophobic dodecyl acrylamide and hydrophilic 2-acrylamido-2-methylpropanesulfonic acid (AMPS) form both unimeric and multimeric micelles based on composition. The former have no concentration dependence on micelle formation and are especially promising since each copolymer forms its own micelle capable of hydrocarbon (foulant) sequestration, even at high dilution. These first-generation polysoaps rely on indigenous bacteria present in the environment for remediation.

A second generation of polymeric micelles based on stimuli-responsive polysoaps can be envisioned that allow hydrocarbon capture/sequestration, followed by subsequent recovery and release of both the foulant and polymer. Recently, our group has taken a step in this direction by demonstrating the tunable pH- and CO_2-responsive behavior of sulfonamide-based homopolymers achieved by varying the sulfonamide substituents (and thus pK_a values) of the constituent monomers (Scheme 1). Most significantly, the corresponding polymers

Scheme 1. Sulfonamide Monomer Structure and Varying R-Groups with Respective pK_a Values[44]
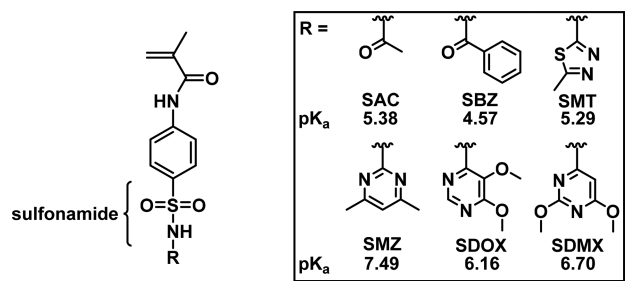

exhibit narrow, reversible pH-dependent solubility transitions with an "on/off" type of behavior.[44] Two reviews regarding advantages and economic feasibility of CO_2-responsive systems have recently been published.[45,46]

In this article, taking advantage of our previous work, we now report the synthesis and CO_2-responsive behavior of two series of statistical copolymers that reversibly undergo phase changes and meet requisites discussed above for the envisioned second-generation polymeric micelles (Scheme 2). These copolymers, based on mSAC and mSMZ, possess pH-responsive coronas and phase-separation behavior that can be controlled through variation of comonomer composition and sulfonamide structure. Hydrophobic molecules can be captured and subsequently removed from solution through precipitation, simply by water acidification via CO_2 addition.

Scheme 2. (top) Conceptual Representation of Second-Generation Polymeric Micelles with pH/CO_2-Responsive Coronas Representing Hydrocarbon Sequestration and Recovery Capabilities; (bottom) Chemical Structure of pH/CO_2-Responsive Sulfonamide-Based Polysoaps
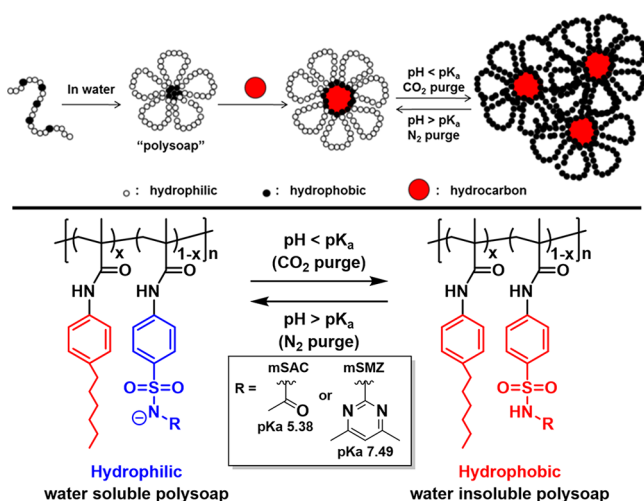
EXPERIMENTAL SECTION

Materials. 4-Cyano-4-(ethylsulfanylthiocarbonylsulfanyl)-pentanoic acid (CEP) was synthesized according to literature procedures.[47] Methacryloyl chloride (Aldrich, 97%) was distilled under vacuum and stored under N_2 at −10 °C prior to use. N,N'-Dimethylformamide (DMF) from Acros (extra dry with sieves) was stirred under vacuum at room temperature for 60 min prior to use to remove traces of dimethylamine. The initiator (96%) 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) from Wako was stored in a sealed container at −10 °C. Sulfonamide precursors (>97%) sulfacetamide (SAC) from Sigma-Aldrich and (99%) sulfamethazine (SMZ) from Acros Organics were used as received. 4-N-Hexylaniline (>98%) was purchased from Alfa Aesar and was distilled immediately prior to use. Trimesic acid (96%) was purchased from Sigma-Aldrich and used as received. Standardized 0.1 N NaOH and 0.05 N HCl solutions were purchased from Fisher Scienctic and used as received. The hydrophobic probes, pyrene (>99%) and 9-anthracenemethanol (97%) from Sigma-Aldrich, were used as received. The detailed synthesis of the RAFT chain transfer agent, CEP, and monomers 4-hexylphenyl methylacrylamide (4HPhMA), methacryloyl sulfacetamide (mSAC), and methacryloyl sulfamethazine (mSMZ) can be found in the Supporting Information.

Statistical Copolymerization of 4HPhMA and mSAC via RAFT. A representative copolymerization procedure for preparing the amphoteric copolymers utilizes 4HPhMA (0.279 g, 1.13 mmol), mSAC (2.89 g, 10.23 mmol), CEP (7.86 mg, 0.006 mmol), DMF (15 mL), and V-70 (1.8 mg, 0.007 mmol) with the molar ratios of $[4HPhMA]_0:[mSAC]_0:[CEP]_0:[V-70]_0$ equal to 38:340:1.0:0.2. Trimesic acid (50 mg) was added as an internal standard. The flask was then sealed and purged with ultrahigh purity N_2 for 60 min in an ice bath. An initial aliquot of 200 μL was taken prior to commencing the polymerization at 30 °C in an oil bath while stirring. Theoretical molecular weights were targeted based on initial monomer to CTA ratios and total monomer conversion (polymerization times varied from 18 to 24 h). Aliquots were taken periodically and analyzed by ^{1}H NMR (DMSO-d_6) to determine monomer conversion by comparing the relative integral areas of the trimesic acid aromatic protons (8.64 ppm, 3H) to the monomer vinyl proton (5.84 ppm, 1H). SEC-MALLS (5% AcOH, 0.02 M LiBr in DMF) was used to monitor the molecular weight and dispersity (Đ) of each polymerization. Polymers isolated for solubility studies were purified by precipitating the reaction mixture into a 10-fold excess of MeOH, followed by isolating the resulting solids by ultracentrifugation. The isolated polymers were then precipitated three times from DMF into MeOH. The resulting solids were removed by vacuum filtration before drying overnight in vacuo.

Dissolution of the Amphoteric Sulfonamide Copolymers. Based on the molar equivalents of sulfonamide monomer in the mSAC (A) and mSMZ (B) series, a 1.25 molar excess of sodium hydroxide was added to the aqueous polymer solutions to deprotonate the sulfonamide units and ensure sample dissolution. For example, a 250 mg sample of the A10 containing 0.971 mmol of −SO_2NH− was solubilized with 1.21 mmol of NaOH into 10 mL of DI water. The sample was then diluted in a volumetric flask to 25 mL to prepare a 10 mg/mL stock solution (pH ∼ 12) for characterization experiments. Sequential dilutions from the stock solution were utilized to prepare concentrations of 0.1, 0.5, 1.25, 2.5, 3.75, 5, 7.5, and 10 mg/mL.

Pyrene Absorbance/Fluorescence Studies. The extent of pyrene uptake and the environment of the micelle core domains in series A and B were studied using UV−vis and fluorescence spectroscopy. Into each well of a 96-well plate was added 5 μL of a 50 mg/mL stock solution of pyrene in acetone. The acetone was then evaporated, and 0.5 mL of the desired polysoap solution was subsequently added. The well plate was covered and placed on a shaker for 24 h to allow the solutions to equilibrate. Then, 200 μL of the polysoap/pyrene solution from each well was transferred to a second 96-well plate for analysis via UV−vis absorbance and fluorescence spectroscopy with a TECAN Safire spectrometer.

Absorbance and Turbidimetric Titration Experiments. Into a 50 mL centrifuge tube was added 50 μL of a 50 mg/mL stock solution of pyrene in acetone. The acetone was then allowed to evaporate; 5 mL of a 10 mg/mL polysoap solution (pH ∼ 12) was added to the tube, and the contents were placed on the shaker for 24 h. The contents of the tube were then centrifuged to remove residual pyrene, and the solution was subsequently transferred to a 20 mL scintillation vial. While stirring, the solution was titrated with 0.01 N HCl at 10 μL increments. The percent transmittance and pyrene absorbance were measured as a function of pH via UV−vis spectroscopy.

Turbidity Measurements during CO_2/N_2 Entrainment Cycles. To a disposable 50 mL centrifuge tube, 10 mL of polysoap solution (10 mg/mL, pH ∼ 12) was added along with a stir bar. The initial % transmittance was measured for the samples. The solution was then purged with CO_2, allowing sufficient time for the solution to become turbid for subsequent measurement of percent transmittance (20 min for the **A** series and 3 min for the **B** series). The sample was then purged with N_2 for a selected period of time (10 min for the **A** series and 60 min for the **B** series); the percent transmittance was again measured. The procedure was repeated for multiple cycles.

Remediation of 9-Anthracenemethanol from Water. The following procedure was utilized to determine behavior of **B10** and **B20** in multiple cycles of remediation of water containing 9-anthracenemethanol (9-AM). To a 1.5 mL microcentrifuge tube were added 10.3 mg of polymer, 1 mL of 0.1 mM 9-AM in water, and 200 μL of 0.2 N NaOH. After vortexing, the contents were equilibrated while shaking for 30 min. The resulting solution (pH ∼ 12) was centrifuged at 10000 rpm, and the absorbance was measured at 388 nm. The solution was then sparged with CO_2 for 3 min, followed by centrifugation at 10000 rpm for 10 min. The supernatant was removed, and the absorbance value was measured at 388 nm. A new 1 mL aliquot of 0.1 mM 9-AM solution and 200 μL of 0.2 N NaOH was added to the centrifuged pellet, allowing it to redissolve while vortexing for 30 min.

Calculating the 9-AM Uptake Capacity for B10 and B20. To determine the uptake capacity for amphoteric polysoaps **B10** and **B20**, the number of moles of polymer was first calculated for each initial solution during the 9-AM remediation experiments (1.53 × 10^{-7} and 2.28 × 10^{-7} mol, respectively). Then the number of moles of 9-AM at the saturation limit was calculated (7.0 × 10^{-7} and 12.0 × 10^{-7} mol for **B10** and **B20**, respectively). These values were then used to determine the moles of 9-AM per mole of copolymer chains. When converted to molecules of each species using Avogadro's number, the result is molecules of 9-AM per polymer chain (4.5 and 5.2 for **B10** and **B20**, respectively).

Characterization of Sulfonamide Polysoaps. Static and dynamic light scattering measurements were conducted at 633 nm utilizing a Research Electro Optics HeNe laser operating at 40 mW. The time-dependent scattering intensities were measured with a Brookhaven Instruments BI-200SM goniometer at 60°, 75°, 90°, 105°, and 120° with an avalanche photodiode detector and TurboCorr correlator.

Gel permeation chromatography (GPC) was performed using a Viscotek TDA 302 equipped with a triple detector array of RI, low, and right-angle light scattering and viscosity detectors. The GPC system was equipped with Tosoh TSKgel Super AW guard column, Super AW3000, and Super AW4000 columns in series. The eluent used for the sulfonamide polysoaps was 5% AcOH, 0.02 M LiBr in DMF.

UV−vis spectroscopy and fluorescence spectroscopy for pyrene absorbance and fluorescence were measured with a TECAN Safire 96-well plate spectrometer running on integrated Microsoft Excel software. Absorbance was measured at 341 nm, and fluorescence was measured via emission scan from 350 to 550 nm with an excitation wavelength of 341 nm. For the pH titrations, CO_2 reversibility, and hydrocarbon removal experiments, percent transmittance and absorbance were determined using an Agilent Technologies Carey Series UV−vis−NIR spectrophotometer run with Carey WinUV software.

RESULTS AND DISCUSSION

Structural Design of Sulfonamide Polysoaps. To study the solution properties of sulfonamide-based, pH- and CO_2-responsive polysoaps, two series of statistical amphoteric copolymers were synthesized via RAFT copolymerization. 4-Hexylphenyl methylacrylamide (4HPhMA) was copolymerized with either sulfonamide-based methacryloyl sulfacetamide (mSAC, pK_a = 5.38) or methacryloyl sulfamethazine (mSMZ, pK_a = 7.49) (Scheme 3). The 4HPhMA structure

Scheme 3. Amphoteric Sulfonamide Polysoap Structure and Synthetic Pathway
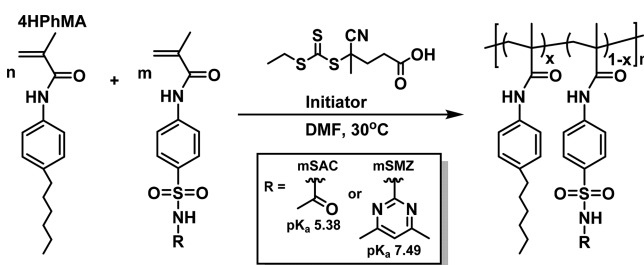
was rationally chosen as the hydrophobic monomer since it comprises the same polymerizable phenyl methacrylamide moiety as the sulfonamide monomers, resulting in similar reactivity ratios between the comonomers. Additionally, the hexyl alkyl chain on 4HPhMA increases the hydrophobicity of the monomer which, by design, will associate into the hydrophobic core domain of the micelles. The sulfonamide-based mSAC or mSMZ monomers were chosen as components of the pH-responsive coronas. When solution pH > sulfonamide pK_a, formation of micelles is expected. Conversely, when solution pH < pK_a, the entire polymer (along with any sequestered hydrocarbon) should form an insoluble coagulate. Mole percentages of 10, 20, 30, and 40 4HPhMA were targeted for this study; pertinent structural data are reported in Table 1. The amphoteric polysoap samples are identified accordingly as follows: **A** or **B** indicates the sulfonamide monomer incorporated (mSAC or mSMZ, respectively) followed by the targeted mole % of 4HPhMA in the copolymer.

Table 1. Structural Data for Amphoteric Sulfonamide Copolymers

sample	sulfonamide monomer	ρ^a (%)	4HPhMA content^a (%)	$M_{n,exp}$^{b} (kDa)	$Đ^b$
A0^c	mSAC	79	0	57.1	1.34
A10	mSAC	51	8	77.3	1.36
A20	mSAC	86	17	79.4	1.39
A30	mSAC	56	27	53.4	1.28
A40	mSAC	76	43	52.2	1.30
B0^c	mSMZ	87	0	21.6	1.39
B10	mSMZ	52	10	67.2	1.35
B20	mSMZ	44	20	45.0	1.40
B30	mSMZ	61	29	60.0	1.35
B40	mSMZ	42	42	51.1	1.35

^{a}Total monomer conversion (ρ) and mol % composition determined by ^{1}H NMR. ^{b}Determined by SEC-MALLS. ^{c}Homopolymer samples are used as controls for the CO_2/N_2 purge and remediation experiments.
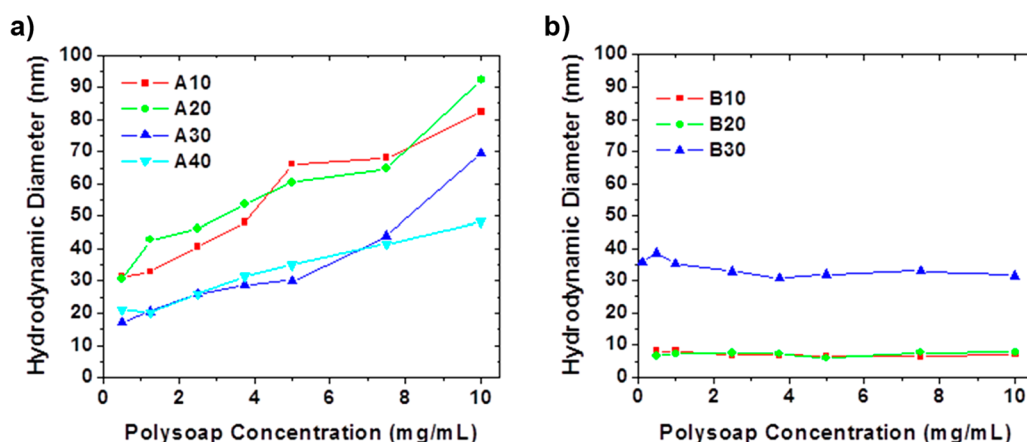
Figure 1. Hydrodynamic diameter (D_h) vs polysoap micelle concentration as measured by dynamic light scattering: (a) **A** series; (b) **B** series.
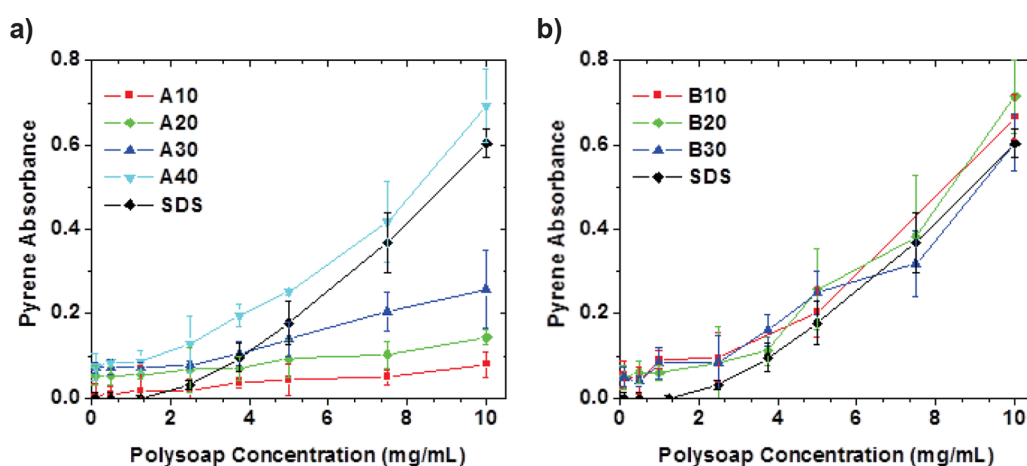

Figure 2. Pyrene sequestration as measured by UV absorbance at 341 nm as a function of polysoap concentration: (a) **A** series; (b) **B** series.
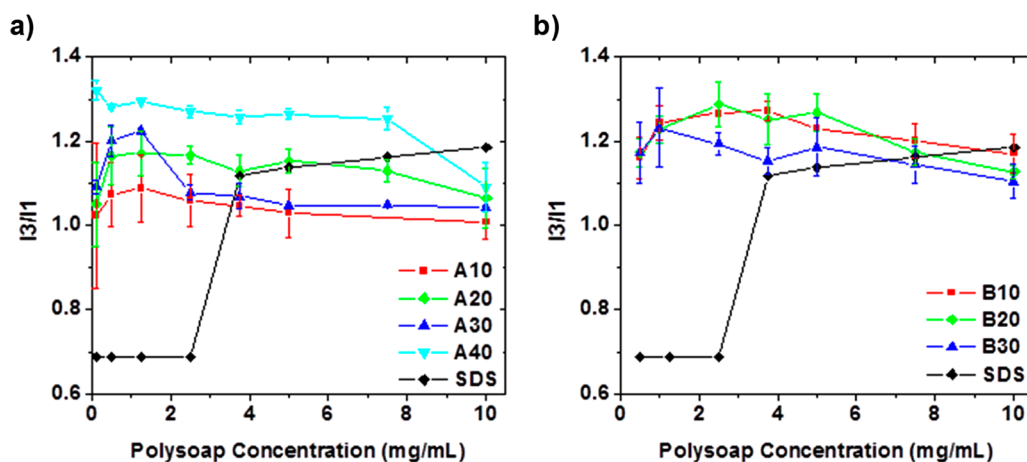

Figure 3. Pyrene I_3/I_1 values of the polysoaps at varying polymer concentrations: (a) **A** series; (b) **B** series.

Micellar Properties of Amphoteric Sulfonamide Polysoaps in Water. Dynamic light scattering (DLS) was utilized to determine the hydrodynamic diameter (D_h) values of micelles as a function of concentration for each copolymer in water at pH 12. The experimental data in Figure 1 indicate increases in the D_h values with increasing concentration for each copolymer in the **A** series, consistent with multimer formation. On the other hand, **B10** and **B20** have constant D_h values of ~8 nm across the entire concentration range.

Additionally, Zimm analysis (Figures S11 and S12) for **B10** and **B20** indicates weight-average molecular weights of 83.8 and 55.8 kDa, respectively, consistent with single chain micelles. **B30**, although exhibiting a near-constant particle size of ~35 nm over the concentration range, obviously contains multiple chains based on SEC-MALLS molecular weight. **B40** is insoluble, even at high pH values, due to increased polymer hydrophobicity. Static light scattering data at
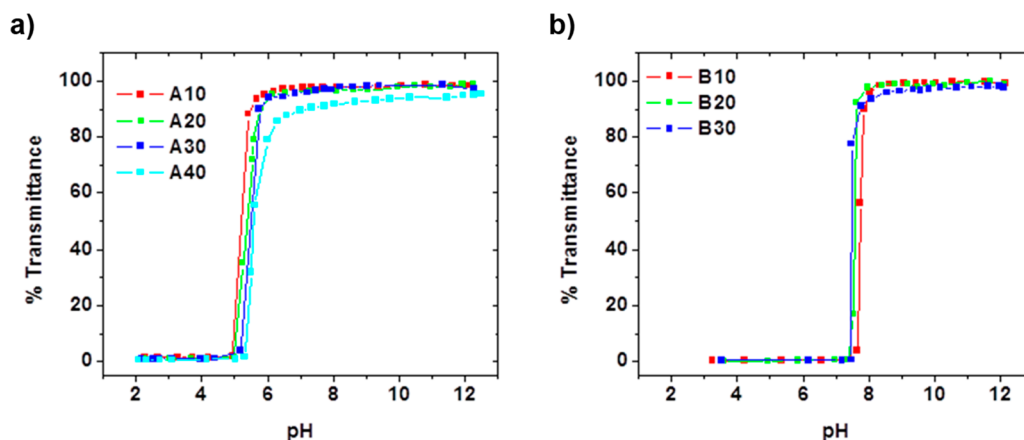
Figure 4. Percent transmittance (533 nm) of amphoteric polysoap series at 10 mg/mL in water as a function of solution pH titrated with HCl: (a) **A** series; (b) **B** series.
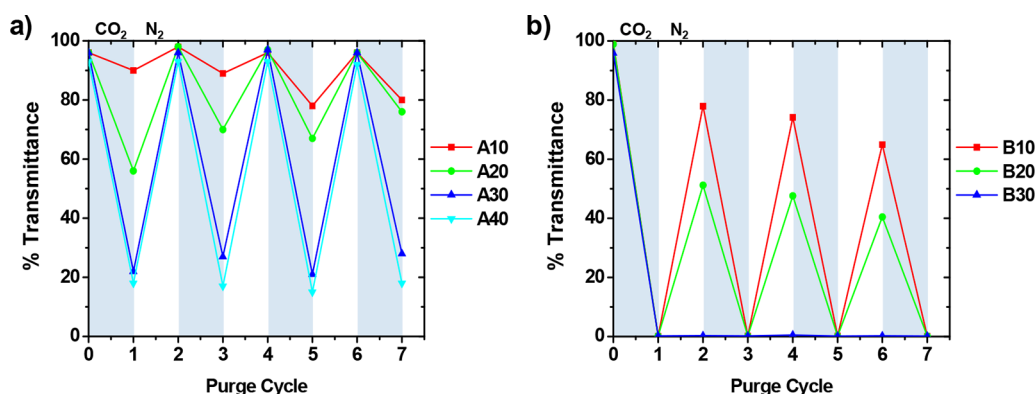

Figure 5. Percent transmittance of amphoteric polysoap solutions showing reversible CO_2-responsiveness in water during CO_2/N_2 purge cycles: (a) **A** series; (b) **B** series.

90° (Figures S9 and S10) further support the DLS observations.

To study the nature of the hydrophobic domains in each sulfonamide series, pyrene was introduced as a probe and its absorbance at 341 nm monitored as a function of increasing copolymer concentration (Figure 2). Sodium dodecyl sulfate (SDS) was employed as a small-molecule surfactant control. For all samples, pyrene absorbance values increase as the number of polysoap domains increase. The entire **B** series and **A40** show sequestration behavior similar or superior to SDS above its critical micelle concentration (CMC). As expected, SDS exhibits virtually no observable pyrene absorbance below its CMC (2.3 mg/mL); however, all samples except for **A10** exhibit noticeable to moderate pyrene absorbance at lower polysoap concentrations (0.1–2.5 mg/mL).

The fluorescence spectrum of pyrene in micellar solution can provide further information about the hydrophobic/hydrophilic microenvironment of core domains. The ratio of the peak intensities I_3/I_1 changes depending on the polarity of the local microenvironment in which the pyrene resides.[48,49] Increasing I_3/I_1 ratios indicate a shift from a polar aqueous environment to a less polar, hydrophobic environment. In Figure 3, measured I_3/I_1 values are plotted as a function of copolymer solution concentration with SDS used as a control. In water, pyrene exhibits an I_3/I_1 value of 0.68 below the CMC of SDS and an I_3/I_1 value of ∼1.1 above the CMC. All polysoap samples tested (**A10–40** and **B10–30**) exhibit I_3/I_1 > 1 over the entire range, even at very low copolymer

concentrations (0.1 mg/mL). Taken together, the light scattering, UV-absorbance, and fluorescence experiments indicate that the **A** series polysulfonamides and **B30** exist as multimeric assemblies while **B10** and **B20** form single-chain micelles. All polymers are capable of sequestering pyrene.

pH-Responsive Behavior of the Sulfonamide-Based Polysoaps. Having studied the micellar nature of the **A** and **B** series of amphoteric polysoaps at pH = 12, the pH-dependent solubility of these copolymers was subsequently examined by turbidimetry while titrating with HCl (Figure 4). As expected, sharp phase transitions are observed at pH values at or near the pK_a of the constituent sulfonamide monomers (**A** series, mSAC, pK_a = 5.38; **B** series, mSMZ, pK_a = 7.49).

CO_2-Responsive Behavior of the Sulfonamide-Based Polysoaps. The concept of "tuning" reversible phase transitions in amphoteric, micelle-forming sulfonamide co-polymers suggests utility in practical applications, including water remediation. For example, the pH of water can be decreased to 3.9 by entraining with CO_2[50] and subsequently returned to its original pH by purging with nitrogen (or air). Series **A** and **B** polysoap solutions were subjected to repeated CO_2/N_2 purge cycles of specific duration and visually inspected for phase separation (Figure S13). To further quantitate the phase behavior of the copolymers, turbidimetric measurements were performed over four purge cycles as shown in Figure 5 (times were chosen to best illustrate the visual differences in phase behavior). The extent of phase separation and redissolution for both series is dependent on the

Scheme 4. Procedure for B10 and B20 Recycle Experiments Involving the Removal of 9-AM from Multiple Batches of Contaminated Water
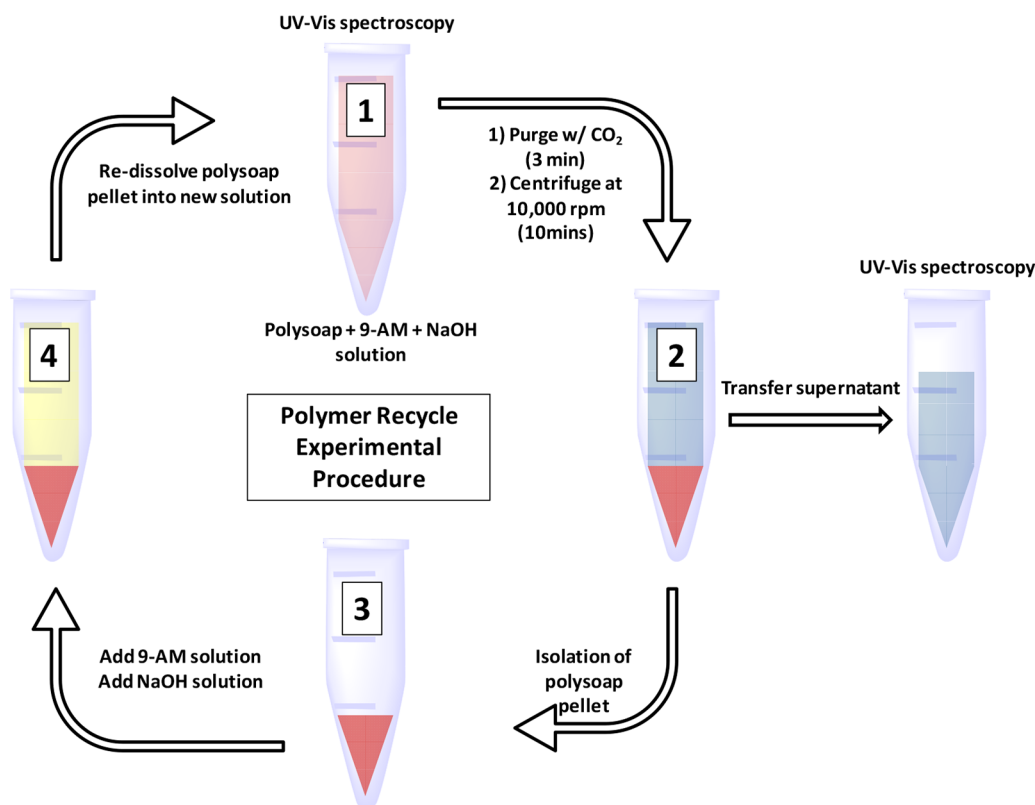
hydrophobic content and proximity of the respective pK_a values of the sulfonamide units to the solution pH (Table S1). Additional experiments reveal a small but noticeable time dependency on copolymer redissolution, which is presented in Figure S14.

Amphoteric Polysoap Remediation of 9-Anthracenemethanol from Water. B10 and B20 were selected for water remediation studies based on our initial observations of phase behavior and an ability to partition the aromatic hydrocarbon pyrene into hydrophobic domains (Figure S15). 9-Anthracenemethanol (9-AM) was chosen as an appropriate model due to its high molar extinction coefficient and moderate water solubility. 9-AM is also a good model for aromatic contaminants found in trace amounts in ground and drinking water.[6,51] Utilizing the procedure outlined in Scheme 4, amphoteric polysoaps B10 and B20 were subjected to multiple dissolution/precipitation cycles to remediate 9-AM from water using CO_2-induced phase separation.

Figure 6 shows 9-AM absorbance values at 388 nm for each copolymer solution and its respective supernatant after remediation. As new solutions of 9-AM are introduced, the polymers continue to sequester 9-AM until saturation of the micelle core domains occurs. Based on calculations described in the Experimental Section, B10 and B20 have the capacity to sequester 4.5 and 5.2 molecules of 9-AM per polymer chain, respectively. Interestingly, at this concentration of 9-AM in the micelle core domains, excimer formation occurs, resulting in a decrease in the measured absorbance values. This is commonly observed when anthracene derivatives associate at high concentrations.[52−55] Further absorbance and fluorescence data are presented in Figures S16−S21, including data of the homopolymer B0 as a control. Overall, this experiment
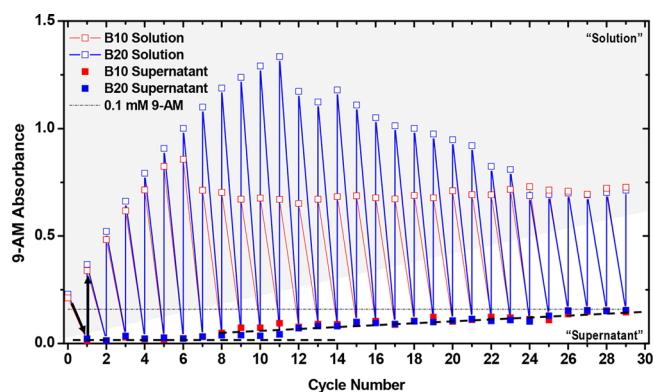

Figure 6. Incremental absorbance values of 9-AM at 388 nm as a function of the number of dissolution/precipitation cycles for B10 and B20. Each cycle shows dissolution followed by CO_2-induced (3 min purge) precipitation of B10 and B20 (10.3 mg) from 1 mL increments of 9-anthracenemethanol solution (0.1 mM).

demonstrates the ability of these amphoteric polysoaps to be reused (recycled) to remediate successive solutions of 9-AM, suggesting utility as sustainable remediating materials.

■ CONCLUSIONS

Amphoteric polysoaps have been prepared utilizing the RAFT copolymerization of sulfonamide-based mSAC or mSMZ and permanently hydrophobic 4HPhMA. At high pH values the copolymers are water-soluble and exist as micelles; below a critical pH value, phase separation occurs, and the polymers become water insoluble. These amphoteric sulfonamide polysoaps have pK_a values in a range allowing for CO_2-

responsive behavior. The **A** series of polysoaps (mSAC derivatives) has minimal responsiveness as demonstrated by limited increases in solution turbidity. On the other hand, the **B** series (mSMZ derivatives) exhibits excellent CO_2-responsiveness with sharp phase separation. The amphoteric nature of these copolymers allows sequestration of hydrocarbon impurities from water. Specifically, **B10** and **B20** were efficient at removing the model foulant 9-AM from aqueous solutions via CO_2-induced phase-separation. We believe the demonstrated potential of these pH/CO_2-responsive amphoteric sulfonamide polysoaps will have future implications in deriving commercially feasible water remediation technologies.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01613.

> Experimental synthesis: CEP: ^{1}H NMR, ^{13}C NMR; 4HPhMA: ^{1}H NMR, ^{13}C NMR; mSAC: ^{1}H NMR, ^{13}C NMR; mSMZ: ^{1}H NMR, ^{13}C NMR; additional results and discussion; Figures S9−S21; Tables S1 and S2 (PDF)

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Notes

The authors declare no competing financial interest.

Paper 161 in a series entitled "Water-Soluble Polymers."

■ ACKNOWLEDGMENTS

■ ABBREVIATIONS

mSAC, methacryloyl sulfacetamide; mSMZ, methacryloyl sulfamethazine; 4HPhMA, 4-hexylphenyl methylacrylamide; PAHs, polycyclic aromatic hydrocarbons; RDRP, reversible deactivation radical polymerization; RAFT, reversible addition−fragmentation chain transfer; AMPS, 2-acrylamido-2-methylpropanesulfonic acid; DMF, N,N'-dimethylformamide; CEP, 4-cyano-4-(ethylsulfanylthiocarbonylsulfanyl)pentanoic acid; V-70, 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile); SAC, sulfacetamide; SMZ, sulfamethazine; DLS, dynamic light scattering; D_h, hydrodynamic diameter; SDS, sodium dodecyl sulfate; CMC, critical micelle concentration; 9-AM, 9-anthracenemethanol.

■ REFERENCES

(1) Stackelberg, P. E.; Furlong, E. T.; Meyer, M. T.; Zaugg, S. D.; Henderson, A. K.; Reissman, D. B. Persistence of Pharmaceutical Compounds and Other Organic Wastewater Contaminants in a Conventional Drinking-Water- Treatment Plant. *Sci. Total Environ.* **2004**, *329*, 99−113.

(2) Stehle, S.; Schulz, R. Agricultural Insecticides Threaten Surface Waters at the Global Scale. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 5750−5755.

(3) Ying, G.; Kookana, R. S.; Ru, Y. Occurrence and Fate of Hormone Steroids in the Environment. *Environ. Int.* **2002**, *28*, 545−551.

(4) Meyer, B.; Pailler, J.-Y.; Guignard, C.; Hoffmann, L.; Krein, A. Concentrations of Dissolved Herbicides and Pharmaceuticals in a Small River in Luxembourg. *Environ. Monit. Assess.* **2011**, *180*, 127−146.

(5) Celino, J. J.; Corseuil, H. X.; Fernandes, M.; Garcia, K. S. Geociências Distribution and Sources of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: A Multivariate Analysis. *REM, Rev. Esc. Minas* **2010**, *63*, 211−218.

(6) Niño, L. R.; Torres, R. J.; Mozeto, A. A.; Fadini, P. S. Using Urban Streams as Drinking Water: The Potential Risk in Respect to Polycyclic Aromatic Hydrocarbons (PAHs) Content in Sediments. *Polycyclic Aromat. Compd.* **2014**, *34*, 518−531.

(7) Hartmann, J.; Beyer, R.; Harm, S. Effective Removal of Estrogens from Drinking Water and Wastewater by Adsorption Technology. *Environ. Process* **2014**, *1*, 87−94.

(8) Ciesielczuk, T.; Kusza, G.; Poluszynska, J.; Kochanowska, K. Pollution of Flooded Arable Soils with Heavy Metals and Polycyclic Aromatic Hydrocarbons (PAHs). *Water, Air, Soil Pollut.* **2014**, *225*, 2145.

(9) Von Lau, E.; Gan, S.; Ng, H. K.; Poh, P. E. Extraction Agents for the Removal of Polycyclic Aromatic Hydrocarbons (PAHs) from Soil in Soil Washing Technologies. *Environ. Pollut.* **2014**, *184*, 640−649.

(10) Brette, F.; Shiels, H. A.; Galli, G. L. J.; Cros, C.; Incardona, J. P.; Scholz, N. L.; Block, B. A. A Novel Cardiotoxic Mechanism for a Pervasive Global Pollutant. *Sci. Rep.* **2017**, *7*, 41476.

(11) Flotron, V.; Delteil, C.; Bermond, A.; Camel, V. Remediaiton of Matrices Contaminated by Polycyclic Aromatic Hydrocarbons: Use of Fenton's Reagent. *Polycyclic Aromat. Compd.* **2003**, *23*, 353−376.

(12) Andersen, H.; Siegrist, H.; Halling-Sorensen, B.; Ternes, T. A. Fate of Estrogens in a Municipal Sewage Treatment Plant. *Environ. Sci. Technol.* **2003**, *37*, 4021−4026.

(13) Gogate, P. R.; Pandit, A. B. A Review of Imperative Technologies for Wastewater Treatment II: Hybrid Methods. *Adv. Environ. Res.* **2004**, *8*, 553−597.

(14) Sonune, A.; Ghate, R. Developments in Wastewater Treatment Methods. *Desalination* **2004**, *167*, 55−63.

(15) Zhang, L.; Eisenberg, A. Formation of Crew-Cut Aggregates of Various Morphologies from Amphiphilic Block Copolymers in Solution. *Polym. Adv. Technol.* **1998**, *9*, 677−699.

(16) Rodriguezhernandez, J.; Checot, F.; Gnanou, Y.; Lecommandoux, S. Toward 'Smart' Nano-Objects by Self-Assembly of Block Copolymers in Solution. *Prog. Polym. Sci.* **2005**, *30*, 691−724.

(17) York, A. W.; Kirkland, S. E.; McCormick, C. L. Advances in the Synthesis of Amphiphilic Block Copolymers via RAFT Polymerization: Stimuli-Responsive Drug and Gene Delivery. *Adv. Drug Delivery Rev.* **2008**, *60*, 1018−1036.

(18) Riess, G. Micellization of Block Copolymers. *Prog. Polym. Sci.* **2003**, *28*, 1107−1170.

(19) Dai, S.; Ravi, P.; Tam, K. C. PH-Responsive Polymers: Synthesis, Properties and Applications. *Soft Matter* **2008**, *4*, 435.

(20) Laschewsky, A. Molecular Concepts, Self-Organisation and Properties of Polysoaps. *Adv. Polym. Sci.* **1995**, *124*, 1−86.

(21) Strauss, U. P.; Jackson, E. G. Polysoaps. I. Viscosity and Solubilization Studies on an n-Dodecyl Bromide Addition Compound of Poly-2-Vinylpyridine. *J. Polym. Sci.* **1951**, *6*, 649−659.

(22) Jackson, E. G.; Strauss, U. P. Polysoaps. II. Effect of Added Hydrocarbon on Reduced Viscosity of an n-Dodecyl Bromide Addition Compound of Poly-2-Vinylpyridine ″. *J. Polym. Sci.* **1951**, *7*, 473−484.

(23) Borisov, O. V.; Halperin, A. Self-Assembly of Polysoaps. *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 415−421.

(24) Armentrout, R. S.; Mccormick, C. L. Water-Soluble Polymers. 77. Amphoteric Cyclocopolymers with Sulfobetaine Units: Phase Behavior in Aqueous Media and Solubilization of p-Cresol in Microdomains. *Macromolecules* **2000**, *33*, 2944−2951.

(25) Wan, W.-M.; Pickett, P. D.; Savin, D. A.; McCormick, C. L. Structurally Controlled "Polysoaps" via RAFT Copolymerization of AMPS and n-Dodecyl Acrylamide for Environmental Remediation. *Polym. Chem.* **2014**, *5*, 819−827.

(26) Yamamoto, H.; Morishima, Y. Effect of Hydrophobe Content on Intra- and Interpolymer Self-Associations of Hydrophobically Modified Poly (Sodium 2- (Acrylamido) −2-Methylpropanesulfonate) in Water. *Macromolecules* **1999**, *32*, 7469−7475.

(27) Hashidzume, A.; Kawaguchi, A.; Tagawa, A.; Hyoda, K.; Sato, T. Synthesis and Structural Analysis of Self-Associating Amphiphilic Statistical Copolymers in Aqueous Media. *Macromolecules* **2006**, *39*, 1135−1143.

(28) Smith, G. L.; McCormick, C. L. Water-Soluble Polymers. 80. Rheological and Photophysical Studies of Ph-Responsive Terpolymers Containing Hydrophobic Twin-Tailed Acrylamide Monomers. *Macromolecules* **2001**, *34*, 5579−5586.

(29) Chang, Y.; McCormick, C. L. Water-Soluble Copolymers. 49. Effect of the Distribution of the Hydrophobic Cationic Monomer Dimethyldodecyl(2-Acrylamidoethy1)Ammonium Bromide on the Solution Behavior of Associating Acrylamide Copolymers. *Macromolecules* **1993**, *26*, 6121−6126.

(30) Chang, Y.; McCormick, C. L. Water-Soluble Copolymers: 57. Amphiphilic Cyclocopolymers of Diallylalkoxybenzyl- Rnethylammonium Chloride and Diallyl- Dimethylarnmonium Chloride. *Polymer* **1994**, *35*, 3503−3512.

(31) McCormick, C. L.; Lowe, A. B. Aqueous RAFT Polymerization: Recent Developments in Synthesis of Functional Water-Soluble (Co)Polymers with Controlled Structures. *Acc. Chem. Res.* **2004**, *37*, 312−325.

(32) Morikawa, H.; Morishima, Y.; Motokucho, S.; Morinaga, H.; Nishida, H.; Endo, T. Synthesis and Association Behavior of Cationic Amphiphilic Copolymers Consisting of Quaternary Ammonium and Nonionic Surfactant Moieties. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5022−5030.

(33) McCormick, C. L.; Chen, G.-S.; Hutchinson, B. H. Water-Soluble Copolymers. V. Compositional Determination of Random Copolymers of Acrylamide with Sulfonated Comonomers by Infrared Spectroscopy and C13 Nuclear Magnetic Resonance. *J. Appl. Polym. Sci.* **1982**, *27*, 3103−3120.

(34) Mccormick, C. L.; Elliott, D. L. Water-Soluble Copolymers. 14. Potentiometric and Turbidimetric Studies of Water-Soluble Copolymers. *Macromolecules* **1986**, *19*, 542−547.

(35) Neidlinger, H. H.; Chen, G.-S.; McCormick, C. L. Water-Soluble Copolymers. VI. Dilute Solution Viscosity Studies of Random Copolymers of Acrylamide with Sulfonated Comonomers. *J. Appl. Polym. Sci.* **1984**, *29*, 713−730.

(36) Wever, D. a. Z.; Picchioni, F.; Broekhuis, A. A. Polymers for Enhanced Oil Recovery: A Paradigm for Structure−property Relationship in Aqueous Solution. *Prog. Polym. Sci.* **2011**, *36*, 1558−1628.

(37) Richardson, M. F.; Armentrout, R. S.; McCormick, C. L. Amphipathic Polymers with Stimuli-Responsive Microdomains for Water Remediation: Binding Studies Withp-Cresol. *J. Appl. Polym. Sci.* **1999**, *74*, 2290−2300.

(38) Branham, K. D.; Snowden, H. S.; McCormick, C. L. Water-Soluble Copolymers. 64. Effects of PH and Composition on Associative Properties of Amphiphilic Acrylamide/Acrylic Acid Terpolymers. *Macromolecules* **1996**, *29*, 254−262.

(39) Anghel, D. F.; Alderson, V.; Winnik, F. M.; Mizusaki, M.; Morishima, Y. Fluorescent Dyes as Model ' Hydrophobic Modifiers " of Polyelectrolytes: A Study of Poly (Acrylic Acid) s Labelled with Pyrenyl and Naphthyl Groups. *Polymer* **1998**, *39*, 3035−3044.

(40) Smith, A. E.; Xu, X.; McCormick, C. L. Stimuli-Responsive Amphiphilic (Co)Polymers via RAFT Polymerization. *Prog. Polym. Sci.* **2010**, *35*, 45−93.

(41) Wang, J.; Matyjaszewski, K. Control1ed "Living" Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615.

(42) Lowe, A. B.; McCormick, C. L. Reversible Addition−fragmentation Chain Transfer (RAFT) Radical Polymerization and the Synthesis of Water-Soluble (Co)Polymers under Homogeneous Conditions in Organic and Aqueous Media. *Prog. Polym. Sci.* **2007**, *32*, 283−351.

(43) Moad, G.; Rizzardo, E.; Thang, S. H. Living Radical Polymerization by the RAFT Process − A Second Update. *Aust. J. Chem.* **2009**, *62*, 1402.

(44) Abel, B. A.; Sims, M. B.; Mccormick, C. L. Tunable PH- and CO_2 - Responsive Sulfonamide-Containing Polymers by RAFT Polymerization. *Macromolecules* **2015**, *48*, 5487−5495.

(45) Yan, Q.; Zhao, Y. Block Copolymer Self-Assembly Controlled by the "Green" Gas Stimulus of Carbon Dioxide. *Chem. Commun.* **2014**, *50*, 11631−11641.

(46) Liu, H.; Lin, S.; Feng, Y.; Theato, P. CO_2-Responsive Polymer Materials. *Polym. Chem.* **2017**, *8*, 12−23.

(47) Thomas, D. B.; Convertine, A. J.; Hester, R. D.; Lowe, A. B.; McCormick, C. L. Hydrolytic Susceptibility of Dithioester Chain Transfer Agents and Implications in Aqueous RAFT Polymerizations †. *Macromolecules* **2004**, *37*, 1735−1741.

(48) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press, Inc.: Orlando, FL, 1987.

(49) Winnik, F. M. Photophysics of Preassociated Pyrenes in Aqueous Polymer Solutions and in Other Organized Media. *Chem. Rev.* **1993**, *93*, 587−614.

(50) Peng, C.; Crawshaw, J. P.; Maitland, G. C.; Martin Trusler, J. P.; Vega-Maza, D. The PH of CO_2-Saturated Water at Temperatures between 308 and 423 K at Pressures up to 15 MPa. *J. Supercrit. Fluids* **2013**, *82*, 129−137.

(51) Qiao, M.; Qi, W.; Liu, H.; Qu, J. ScienceDirect Occurrence, Behavior and Removal of Typical Substituted and Parent Polycyclic Aromatic Hydrocarbons in a Biological Wastewater Treatment Plant. *Water Res.* **2014**, *52*, 11−19.

(52) Chandross, E. A.; Ferguson, J.; McRae, E. G. Absorption and Emission Spectra of Anthracene Dimers. *J. Chem. Phys.* **1966**, *45*, 3546−3553.

(53) Chandross, E. A.; Ferguson, J. Absorption and Excimer Fluorescence Spectra of Sandwich Dimers of Substituted Anthracenes. *J. Chem. Phys.* **1966**, *45* (10), 3554−3564.

(54) Abdel-Mottaleb, M. S. A.; Galal, H. R.; Dessouky, A. F. M.; El-Naggar, M.; Mekkawi, D.; Ali, S. S.; Attya, G. M. Fluorescence and Photostability Studies of Anthracene-9-Carboxylic Acid in Different Media. *Int. J. Photoenergy* **2000**, *2*, 47−53.

(55) Ferguson, J.; Mau, A. W. Molecular Physics: An International Journal at the Interface Between Chemistry and Physics A New Gradient-Corrected Exchange Functional. *Mol. Phys.* **1974**, *27* (2), 377−387.