



universität
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DISSERTATION / DOCTORAL THESIS

Titel der Dissertation / Title of the Doctoral Thesis

„Poly(Acrylamide-co-Styrene) as Model to Test
Macromolecular Associations“

verfasst von / submitted by

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angestrebter akademischer Grad / in partial fulfilment of the requirements for the degree of
Doktorin der Naturwissenschaften (Dr.rer.nat)

Wien, 2023 / Vienna, 2023

Studienkennzahl lt. Studienblatt /
degree program code as it appears on
the student record sheet:

UA 796 605 419

Studienrichtung lt. Studienblatt /
degree program as it appears on
the student record sheet:

Chemie

Betreut von / Supervisor:

Univ.-Prof. Dr Alexander Bismarck

Abstract

Nature-inspired macromolecular associations of hydrophobically modified copolymers are appealing systems for materials, biological and medical sciences, chemistry, and physics. The hypothesis that high molecular weight M_w assemblies created by lower M_w amphiphilic water-soluble copolymers can be efficient drag reducing agents (DRAs) was tested. Hydrophobic interactions holding the macromolecular associations together might behave as a “physical fuse” and protect the polymer backbone from fast degradation prolonging the lifetime of polymer DRA. Amphiphilic copolymers of poly(acrylamide-co-styrene) (P(AAm-co-St)) having $M_w \leq 1000$ kg/mol containing increasing amounts of hydrophobic styrene moieties, ranging from 0 to 11 mol.% relative to hydrophilic acrylamide molar ratio, were synthesised using micellar copolymerisation. The drag reduction (DR) effectiveness in pipe flow of hydrophobically modified copolymers when compared to corresponding unmodified polyacrylamide (PAAm) reference with similar M_w were as follows: amphiphilic copolymers having $M_w \approx 1000$ kg/mol showed improved DR by a factor of ~ 2 , while DR effectiveness of copolymers with $M_w < 1000$ kg/mol was not improved. Foam formation during DR experiments led to reduced effective polymer concentration in solution, which negatively affected the DR performance but inspired to test ‘self-removal’ of P(AAm-co-St) from aqueous solutions. About 55% of the higher M_w fractions of P(AAm-co-St) with ~ 4 mol.% of styrene could be recovered from aqueous solution. The subtracted liquid copolymer foams exhibited high stability and could be dried without collapse offering the potential to reuse the polymer for instance in templating techniques for production of porous polymers. The possibility to use P(AAm-co-St) as an amphiphilic “macrosurfactant” to stabilise oil/water high or medium internal phase emulsion (H/MIPE) templates was explored. Concentrations as low as $c = 0.1$ wt.% of as-synthesised P(AAm-co-St) still containing 0.01 wt.% cetyltrimethylammonium bromide was sufficient to effectively stabilise cyclohexane-in-water H/MIPEs. Cyclohexane-in-water H/MIPE templates containing 2-hydroxyethyl methacrylate (HEMA) and N,N-methylenebis(acrylamide) (MBAm) in the aqueous phase were successfully polymerised. Obtained macroporous poly(HEMA-co-MBAm)M/HIPEs exhibited superior swelling capabilities and mechanical properties compared to poly(HEMA-co-MBAm)HIPEs described in the literature.

Zusammenfassung

Von der Natur inspirierte makromolekulare Assoziationen hydrophob modifizierter Polymere sind vielversprechend für Anwendungen in Materialwissenschaften, Biologie, Medizin, Chemie und Physik. Es wurde getestet, ob hochmolekulare Assoziationen von amphiphilen, wasserlöslichen Polymeren mit relativ niedrigem M_w als effektive *drag reduction agents* (Wirkstoffe zur Verringerung des Fließwiderstands in turbulenten Strömungen von Flüssigkeiten) eingesetzt werden können. Die makromolekularen Assoziationen werden durch hydrophobe Wechselwirkungen zusammengehalten, die als Sollbruchstelle die kovalenten Bindungen in den Polymeren in turbulenter Strömung schützen können. Amphiphiles Poly(acrylamid-co-styrol) (P(AAm-co-St)) mit $M_w \leq 1000$ kg/mol und variablem Anteil hydrophober Styrolblöcke (0 bis 11% relativ zur Masse des hydrophilen Acrylamids) wurde mittels Co-Polymerisation in Mizellen synthetisiert. Die *drag reduction* in turbulenter Rohrströmung verhielt sich für die modifizierten Polymere im Vergleich zu den unmodifizierten wie folgt: *Drag reduction* amphiphiler Polymere mit $M_w \approx 1000$ kg/mol war um einen Faktor ~ 2 erhöht; bei amphiphilen Polymeren mit $M_w \leq 1000$ kg/mol gab es keine Verbesserung. Schaumbildung während der Experimente verringerte die effektive Konzentration der Polymere in Lösung was einen negativen Effekt auf die *drag reduction* hatte. Dies gab den Anstoß P(AAm-co-St) als selbst-entfernenden Zusatzstoff zu testen. Ungefähr 55% des gelösten P(AAm-co-St) mit ~ 4 mol.% Styrol konnten aus wässriger Lösung zurückgewonnen werden. Im Schaum wurden die Polymere mit hohem M_w angereichert. Der stabile entnommene Schaum eröffnet die Möglichkeit, die zurückgewonnenen Polymere als Schablone in der Synthese poröser Polymere einzusetzen. Die Verwendung von P(AAm-co-St) als amphiphiles „Makrotensid“ zur Stabilisierung von Emulsionen wurde untersucht. Konzentrationen von 0.1 wt.% unaufbereitetem P(AAm-co-St) waren ausreichend um Cyclohexan als *H/MIPE templates* (Emulsionen als Polymersiationsschablone mit mittleren bis hohem Anteil der Ölphase) in Wasser zu stabilisieren. Diese Schablonen wurden mit 2-Hydroxyethyl Methacrylat (HEMA) und N,N-Methylenbis-(acrylamid) (MBAm) in der wässrigen Phase polymerisiert. Die *Poly(HEMA-co-MBAm)M/HIPEs* hatten ein größeres Quellvermögen und bessere mechanische Eigenschaften als *Poly(HEMA-co-MBAm)HIPEs* welches bisher in der Literatur beschrieben wurde.

Acknowledgment

I would like to express my deepest appreciation to my supervisor, or as I prefer to say *Doktorvater*, Prof. Alexander Bismarck for his guidance, continuous support, and endless patience throughout my PhD. Your enthusiasm and constructive feedback encouraged me to develop scientific skills and confidence for future challenges.

I would also like to thank Dr Hans Werner Müller for his support and who, together with Alexander, believed in me and gave me the opportunity to pursue my PhD in the PaCE group. It is inevitable to acknowledge the importance of support Dr Angelika Menner provided to me with her understanding and willingness to listen and help—thank you, Angelika! My gratitude extends to Dr Qixiang Jiang whose expertise allowed me to gain know-how in producing emulsion templated macroporous polymers. I highly appreciate Ass. Prof. Robert Woodward for giving me the opportunity to work with him on pH-responsive nanoparticles and, thus, being able to broaden my knowledge in polymer science. I also thank Dr Andriy Grytsiv for his assistance enabling me to proceed with my research when our laboratory burnt down.

I am deeply grateful to all members in the PaCE group for their support and wonderful time we spent together. Special thanks goes to my girls Dr Hande Barkan, Dr Neptun Yousefi and Amy Ho for all the fun and cherished moments we shared together. This gratitude extends to Lukas Brandfellner for the amazing teamwork, as well as to Nadine Barna for her support at the beginning of my PhD! Last but not least, I would like to acknowledge all students who contributed to the success of my PhD work, especially to Jana Schöffmann, Samuel Hartmann and Stanislaus Breitwieser for the significant contribution with their hard work and dedication.

To my parents and brothers: *Veliko hvala mojim roditeljima i braći na njihovoj konstantnoj, nesebičnoj ljubavi i podršci koju su mi pružali tokom mog obrazovanja, kao i cjelokupnog života.*

Words are not sufficient to express the gratitude I feel towards my husband Dr Edin Muratspahić who I shared my PhD moments the most with. It is your endless understanding, encouragement and enthusiasm that inspired me to keep driving in tough moments. *Hvala ti za sve! Volim te!*

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List of Scientific Publications

Publication 1: Muratspahić, E.; Brandfellner, L.; Schöffmann, J.; Bismarck, A.; Müller, H. W. Aqueous Solutions of Associating Poly(Acrylamide-co-Styrene): A Path to Improve Drag Reduction? *Macromolecules*. **2022**, *55* (23), 10479–10490. DOI 10.1021/acs.macromol.2c01219

All authors contributed to conceptualisation of the work, EM performed most synthetic and characterisation work and analysed the data; LB and EM performed ViEDRA experiments and analysed the data; JS performed the rheological characterisation. EM and AB wrote the manuscript and designed the figures. HWM and AB supervised the work. All authors contributed to manuscript review and editing.

Publication 2: Muratspahić, E.; Schöffmann, J.; Jiang, Q.; Bismarck, A. Micellar Aggregation of Poly(Acrylamide-co-Styrene): Towards ‘Self-Removing’ Polymers from Solution. Submitted 2023.

EM and AB conceptualised the work. EM and JS performed all experimental work, EM and JS analysed the data. EM, QJ and AB wrote the manuscript and designed the figures. AB supervised the work. All authors contributed to manuscript review and editing.

Publication 3: Muratspahić, E.; Schöffmann, J.; Jiang, Q.; Bismarck, A. Poly (Acrylamide-co-Styrene): A Macrosurfactant for Oil/Water Emulsion Templating toward Robust Macroporous Hydrogels. *Macromolecules*. **2023**, *56* (8), 3213–3223. DOI 10.1021/acs.macromol.2c02504

EM, QJ and AB conceptualised the work, EM and JS performed all experimental work, EM analysed the data, and JS analysed the SEM data. EM, QJ and AB wrote the manuscript and designed the figures. QJ and AB supervised the work. All authors contributed to manuscript review and editing.

Oral presentations and papers at conferences:

Muratspahić, E., Müller, H. W., Bismarck, A., Understanding polymer degradation in pipe flows as first step in the evolution of drag reducing agents. 1st Vienna Polymer-Group Symposium (ViP). Vienna, 2018.

Muratspahić, E., Müller, H. W., Bismarck, A., Hydrophobically modified copolymer associations—a promising path to improve drag reduction? Polymer Meeting 14 (PM14). Graz, 2021.

Muratspahić, E., Brandfellner, L., Schöffmann, J., Müller, H. W., Bismarck, A., Can associating hydrophobically modified copolymers find their application as drag reducing agents in water flows? EPF European Polymer Congress (EPF 2022). Prague, 2022.

Muratspahić, E., Schöffmann, J., Jiang, Q., Bismarck, A., Micellar aggregation of macromolecules: Towards self-removing polymers. Sustainability in a Changing World, ACS Fall 2022. Chicago and virtual, 2022.

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List of Symbols and Abbreviations

Symbols

E_c	Elastic modulus
$\overline{MBA}$	Mean bubble area
M_w	Molecular weight
M_η	Viscosity averaged molecular weight
N_A	Avogadro's number
R_g	Radius of gyration
R_η	Viscosity averaged hydrodynamic radius
V_F	Foam volume
V_T	Total foam/liquid volume
c_m	Mass concentration of polymer
f_p	Fanning friction factors of polymer solution
f_s	Fanning friction factors of pure solvent
m_d	Mass of a dry sample
m_s	Mass of a swollen sample
$\dot{\gamma}$	Shear rate
$[\eta]$	Intrinsic viscosity
η_r	Relative viscosity
η_{sp}	Specific viscosity
σ_c	Crush strength
Δm	Mass change
Δp	Pressure drop along a pipe
$\mathbb{D}$	Polydispersity
DR(%)	Drag reduction percentage
p	Packing parameter

BC	Bubble count
K	Mark–Houwink parameter
LC	Liquid content
Q	Water swelling capacity
Re	Reynolds number
U	Volume averaged velocity
a	Hydrophobic-hydrophilic interfacial area
d	Pipe diameter
f	Fanning friction factor
l_p	Length of a pipe
l	Length of the hydrophobic segments
v	Volume of the hydrophobic segments
α	Mark–Houwink parameter
η	Dynamic viscosity of the fluid
ρ	Density of the fluid

Abbreviations

AAM	Acrylamide
APS	Ammonium persulfate
CMC	Critical micelle concentration
CTAB	Cetyltrimethylammonium bromide
DR	Drag reduction
DRA	Drag reducing agent
GPC	Gel permeation chromatography
HEMA	2-Hydroxyethyl methacrylate
HIPE	High internal phase emulsion
HLB	Hydrophilic-lipophilic balance

HPLC	High-performance liquid chromatography
LIPE	Low internal phase emulsion
MBAm	N,N-Methylenebis(acrylamide)
MIPE	Medium internal phase emulsion
o/w	Oil-in-water
P(AAm-co-St)	Poly(acrylamide-co-styrene)
PAAm	Polyacrylamide
PEO	Poly(ethylene oxide)
pHEMA	Poly(2-hydroxyethyl methacrylate)
PVA	Poly(vinyl alcohol)
RI	Refractive index
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscopy
SLS	Static light scattering
St	Styrene
TEMED	N,N,N',N'-Tetramethyl ethylenediamine
ViEDRA	Vienna Experiment for Drag Reducing Agents
w/o	Water-in-oil

1 Introduction

Polymers became an inevitable component of modern society because of their distinctive features, including low density, mechanical, chemical and barrier properties.¹ “Supramolecular chemistry” embraces development of functional structures formed by non-covalent interactions between (macro)molecular biomimetics.² The supramolecular architectures obtained by self-assembly of amphiphilic copolymers represent one of the major targets of today’s technological processes, which are of interest for controlled manufacturing of hybrid materials³ and biocompatible drug delivery systems,⁴ or for polymers used to control rheological properties of liquids.^{5,6}

Hydraulic fracturing is a powerful technique involving high-pressure injection of water containing additives to increase the extraction of fossil hydrocarbons from fractured reservoir formations.⁷ Fracking operations make use of polymer drag reducing agents (DRAs) to increase water flow efficiency to fracture underground rock formations to extract fossil hydrocarbons from tight reservoirs.⁷ Huge amounts of water (millions of litres per well) are pumped into wells leading to harmful environmental impacts due to lack of effective wastewater management.^{7,8}

Frictional drag arising in fully developed turbulent pipe flows reduces fluid flow efficiency resulting in higher energy demand to drive the flow. Commercial polyacrylamides having molecular weights $M_w > 10^6$ - 10^7 are effective in reducing frictional drag.^{7,9} Drag reduction (DR) saves energy needed to pump a fluid along a pipe (Figure 1); values of saved energy up to 95% were reported.¹⁰ Besides surfactants,¹¹ flexible and long polymer chains are preferred for DR applications as they are very effective in reducing initial flow drag.¹² When used in long-term applications, their flexibility and M_w renders these polymers to be susceptible to degradation in strong turbulent (shear) flows.¹³ Associations of amphiphilic copolymers formed in aqueous solutions govern solution viscosity at different shear rates and, thus, offer the potential to be effective DRAs.^{14,15}

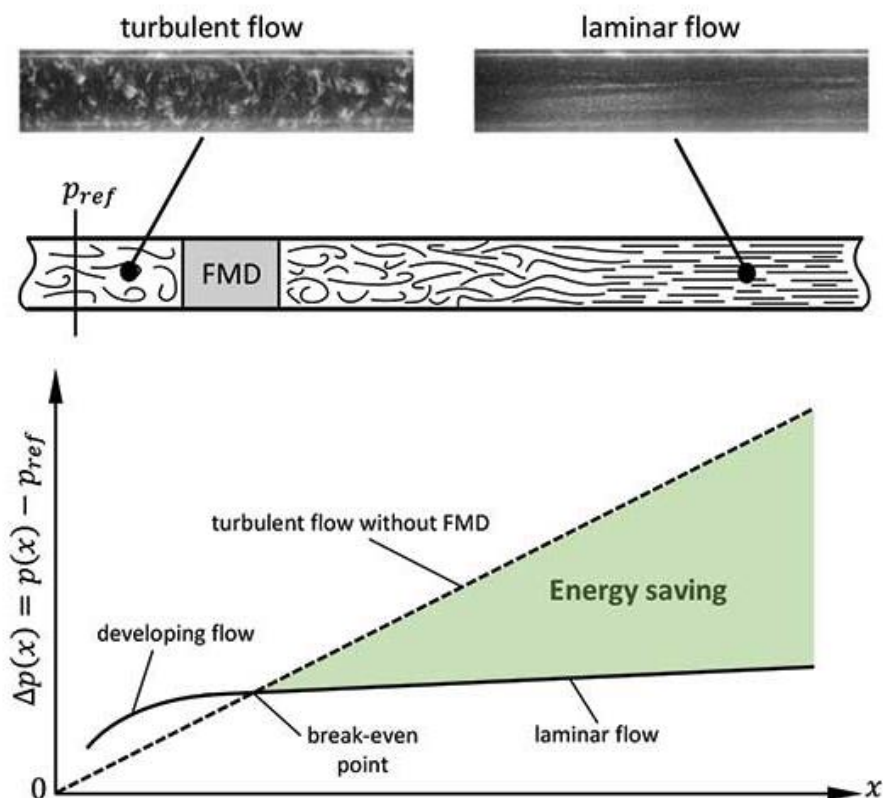


Figure 1. Sketch representing gain in energy by reducing frictional drag expressed as pressure drop (Δp) over travelled distance (x). Turbulent flow is modified using so-called “fluid modification devices” (FMD) to achieve laminar flow. (Thomas F. Armistead “Researchers Develop New Techniques to Calm Pipe Flow”. Link in: <https://www.enr.com/articles/43778-researchers-develop-new-techniques-to-calm-pipe-flow>, assessed on 13.04.2023)

Associations formed by non-covalent hydrophobic interactions between amphiphilic copolymers may offer two benefits: 1) to protect the copolymer backbone from fast degradation,¹⁶ since weaker hydrophobic interactions—acting as “physical fuse”—are more susceptible to degradation than the copolymer backbone, and 2) once broken, associations can re-form¹⁶ leading to long-term DR. Besides surfactants and polymers, other DRAs, such as spherical particles¹⁷ were explored. It is also possible to modify pipe surfaces to reduce drag¹⁸ or to insert a device into the pipe to disturb turbulence offering a new approach to reduce fluid frictional drag.¹⁰

Wide use of polymers in diverse technological processes across the globe led to “plastic pollution” of the environment.¹⁹ Suggested mechanisms to tackle the issue of environmental pollution caused by polymers are reduction of inessential and “single-use” plastics, increase reuse, and recycling but effective waste management procedures have yet to be realised (Figure

2).¹⁹ The reuse strategy is the simplest and preferred option.¹⁹ Polymeric DRAs, precipitating from solution when exposed to an external trigger such as change of pH or temperature, were suggested to offer a potential of polymer reuse in DR applications.²⁰

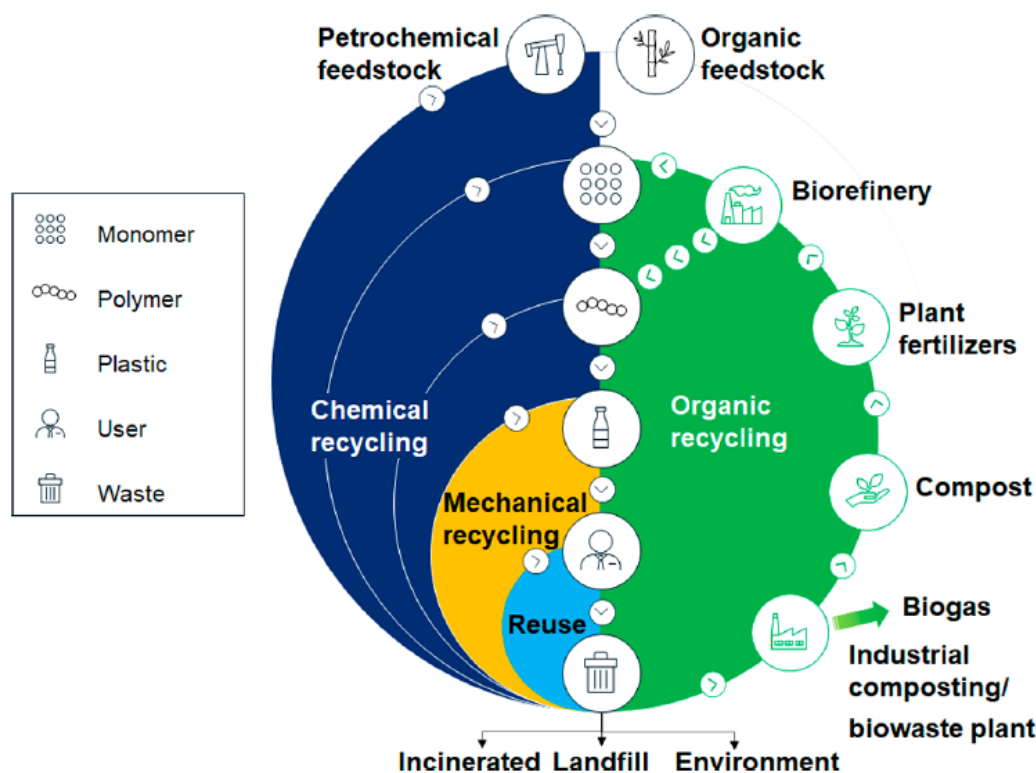


Figure 2. Possible methods for end-of-life options of polymers after their use include reuse and recycling. The reuse approach represents the shortest path. Recycling can be achieved via mechanical, chemical, or organic treatment of polymers. (Reprinted with permission from Millican, J. M. and Agarwal, S.¹⁹ Copyright 2021 American Chemical Society).

Besides potential use in DR applications, amphiphilic copolymers can also be effective “macrosurfactants” offering lower critical micelle concentrations (CMC’s) compared to small-molecule surfactants.²¹ Emulsion templating is an effective method to produce macroporous polymers,²² including hydrogels. Commonly, high (HIPE) or medium internal phase volume emulsions (MIPE) are used as templates,²³ which after polymerisation and removal of the templating (internal) phase result in porous polymers poly(merised)H/MIPEs. Emulsion templating offers effective control over properties of the final porous polyH/MIPEs, such as mechanical properties, porosity, and degree of interconnectivity.²² However, commonly large amounts of conventional lower M_w surfactants (typically ranging from 6-25%) are required to

stabilise oil/water (or ‘inverse’) H/MIPE templates.^{24, 25} The emulsifier is structurally parasitic^{26,27} and must be removed prior use of such porous polymers. Due to their lower CMC’s, amphiphilic copolymers have the potential to reduce the emulsifier amounts. Hydrogel-based polyH/MIPEs²⁸ are appealing materials exhibiting significant water sorption and retention capabilities,²⁹ which in combination with high porosity and pore interconnectivity (Figure 3) render porous hydrogels materials of interest for biomedical applications^{30,31} over micromixers²⁵ to adsorbers.³²

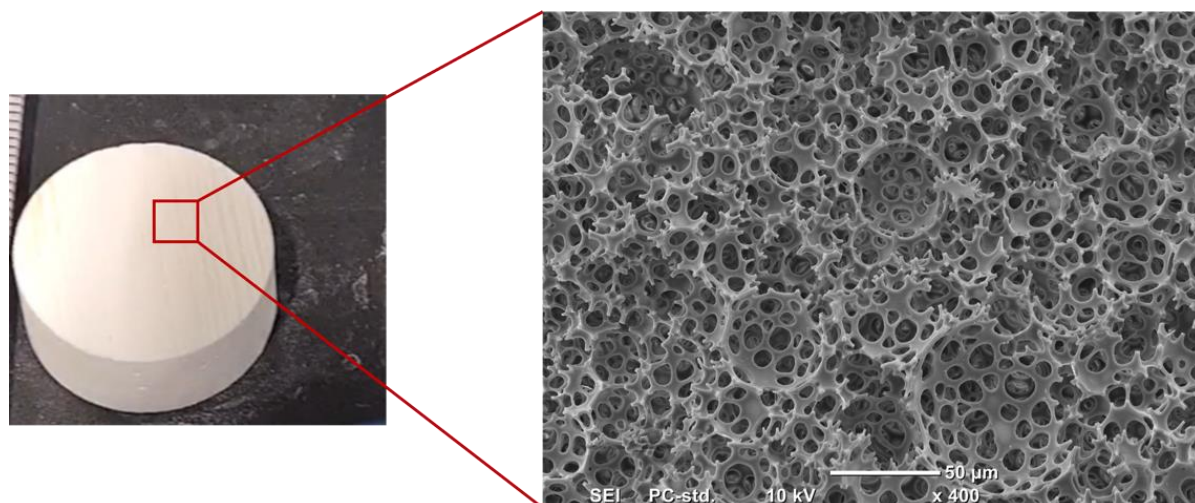


Figure 3. An example of a macroporous hydrogel produced using emulsion templating and a SEM micrograph of its porous structure.

1.1 Aims & objectives

The initial aim of my PhD thesis was to test the hypothesis that high M_w associations of macromolecules, formed by lower M_w amphiphilic hydrophobically modified polyacrylamide (PAAm), provide DR effectiveness in aqueous solutions in turbulent pipe flow. Aqueous solutions of these copolymers exhibited pronounced foaming behaviour during DR experiments, which resulted in a reduced copolymer concentration in solution. The observation of foam formation further led to new research ideas aiming to test the amphiphilic character of acrylamide-based copolymers. The amphiphilic nature of poly(acrylamide-co-styrene) was explored for ‘self-removal’ of polymers after DR applications and to stabilise H/MIPE templates to produce porous polymers.

To accomplish these aims, the following objectives were defined:

1. to identify a synthesis route enabling control over chemical composition of amphiphilic copolymers and M_w to optimise copolymer association behaviour for DR application,
2. to quantify DR effect of the macromolecular associations, produced by amphiphilic copolymers, in turbulent pipe flow facility and a rotating ‘disc’ apparatus,
3. to prove and quantify ‘self-removal’ of amphiphilic copolymers during DR experiments in turbulent pipe flow,
4. to assess the stability of produced copolymer foams,
5. to demonstrate the effectiveness of amphiphilic copolymers to stabilise H/MIPE templates which can be polymerised to yield “superporous” hydrogels, and to quantify swelling capacities and mechanical properties of resulting porous hydrogels.

1.2 Structure of the thesis

Following the brief introduction and aims & objectives, the structure of my thesis will be as follows: Chapter 2 is a detailed literature review describing the advance of amphiphilic copolymers, especially of those produced by micellar copolymerisation, and their application areas. The literature review is followed by a brief summary of materials and characterisation methods (Chapter 3) and an executive summary of my main results (Chapter 4) highlighting the key findings reported in the appended publications I to III. Chapter 5 deals with drawn conclusions and suggestions for future work. The appended publications describe my research findings: **Publication I** reports DR capabilities of hydrophobically modified poly(acrylamide-co-styrene) copolymers and corresponding unmodified polyacrylamide homopolymers. Challenges when using amphiphilic copolymers produced via micellar copolymerisation are also addressed. ‘Self-removal’ of poly(acrylamide-co-styrene) from aqueous solutions after DR applications was observed and further investigated to enable reuse of the extracted copolymer (**Publication II**). The use of poly(acrylamide-co-styrene) as amphiphilic “macro surfactant” to stabilise cyclohexane-in-water (inverse) H/MIPE templates for the synthesis of superporous poly(HEMA-co-MBAm)M/MIPE hydrogels is described in **Publication III**.

2 Literature Review

2.1 Polymers

The use of polymers dates back to 1600 BC, when ancient Mesoamericans started to produce rubber balls, figurines, and bands from natural rubber.³³ “*The Classical Age of Polymer Science–1920-1940*”³⁴ began with the seminal discovery of macromolecules—long-chain molecules composed of covalently linked repeating units—by Hermann Staudinger³⁵ who described the nature of polymers and thus provided an incentive for further developments of the emerging discipline of polymer science. Macromolecules can be classified based on their origin into natural, occurring in living organisms, and synthetic polymers.³⁶ The 1940s was “*the golden age for the development of new synthetic polymers*”^{*} both in academia and on industrial scale and henceforth polymers became an inevitable part of humans’ daily lives. The attractive properties of polymers, such as low density, mechanical, chemical and barrier properties, resulted in rapid uptake of these new materials and thus in ever increasing production volumes,¹ which however also resulted in new problems associated with “plastic pollution”.³⁷

Various chemical reactions, i.e., polymerisations, polycondensation, -addition, result in the formation of macromolecules, commonly called polymers.³⁸ The degree of polymerisation—number of monomer units in the chain, having a value >100 —is the determining factor in designating a compound as a polymer.³⁶ The degree of polymerisation can reach values $>10^9$.³⁶ The selection of a vast array of individual molecular building blocks, i.e., monomers, and accompanying structural versatility of the resulting copolymers permit to tune the properties of copolymers and their resulting (nano)materials, such as self-assembly, mechanical, thermal, and viscoelastic properties, among others.^{39 - 43} Macromolecular self-assembly provides a ‘bottom-up’ approach for the synthesis of supramolecular (nano)structures governed by weak dynamic non-covalent bonds, including hydrogen bonds, electrostatic, hydrophobic and van der Waals interactions.⁴⁴ Nature-inspired supramolecular assemblies⁴⁵ paved the way to manufacture advanced materials, such as polymeric membranes,^{46,47} viscosity modifiers,⁵ and photonic crystals,⁴⁸ etc., being valued in multidisciplinary domains such as materials, biological and medical sciences, chemistry, and physics.⁴⁹

* C. Vasilev “A Century of Polymer Science: A Look at the Key Developments”. Link in: <https://www.azom.com/article.aspx?ArticleID=19088>, assessed on 02.04.2023

2.2 Amphiphilic copolymers

Amphiphilic copolymers comprise hydrophilic and hydrophobic monomers. Four common copolymer architectures are distinguished: block, graft, alternating and random copolymer structures (Figure 4),⁵⁰ which can be synthesised using diverse copolymerisation techniques using a range of monomers. A block copolymer consists of the same repeat unit distributed in a linear arrangement as blocks along the copolymer backbone, while in a graft copolymer the polymer (linear) backbone contains identical repeat units onto which polymer side branches were grafted consisting of different repeat units.⁵⁰ Alternating arrangement of two types of monomeric units in a copolymer chain is attributed to alternating copolymers.⁵⁰ In a random copolymer the monomer units used in their synthesis are randomly distributed along the copolymer backbone.⁵⁰

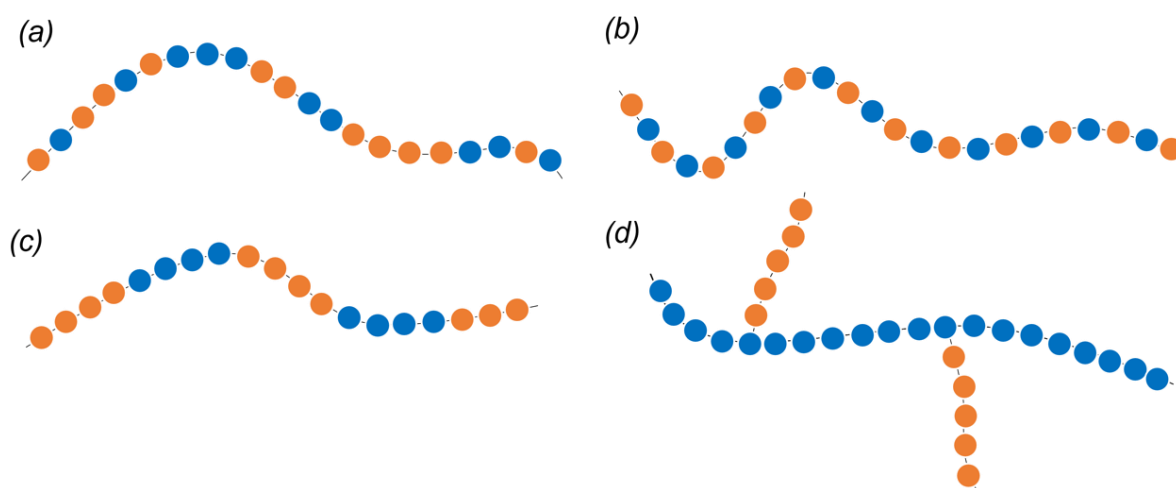


Figure 4. Graphic illustration of copolymer structure (a) random, (b) alternating, (c) block, and (d) graft. Blue and orange circles represent two different monomer repeat units. (Adapted from “Materials Science and Engineering: An Introduction”, Callister, W. D., 7th edition, 2007.⁵⁰ Copyright 2007, with permission from John Wiley & Sons.)

Amphiphilic copolymers, consisting of chemically distinct repeat units, spontaneously self-assemble because of energetically unfavourable interactions of one polymer constituent with surrounding solvent molecules;^{51, 52} copolymer chains aggregate in a solvent selectively dissolving one of the copolymer regions.⁵² Hydrophobic domains present in amphiphilic copolymers aggregate in aqueous solutions driven by attractive, reversible hydrophobic interactions to escape water molecules forming a hydrophobic core region with a hydrophilic shell.⁵³ Hydrophobic interactions as J. Israelachvili put it “*involve the configurational*

rearrangement of water molecules as two hydrophobic species come together".⁵⁴ These physical interactions act together and govern the structural conformation of macromolecular associations similar to those naturally formed in association of colloids, such as spherical, cylindrical or worm-like micelles, vesicles, and lamellar (bilayer) structures formed by surfactants (Figure 5).^{55,56}

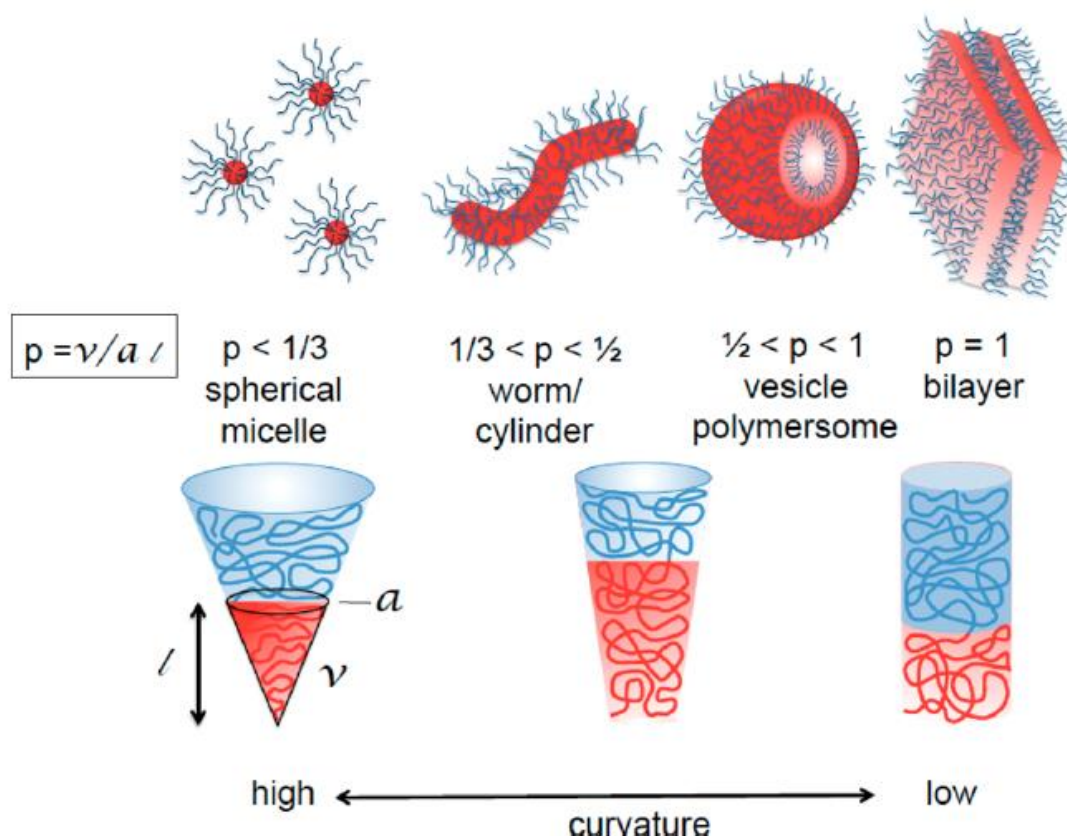


Figure 5. Illustration of possible copolymer self-assembled structures in solution and influence of hydrophobic-hydrophilic interface curvature on the packing parameter p determining structure of macromolecular self-assemblies. (Reprinted with permission from Pereira Nunes, S.⁵⁶ Copyright 2016 American Chemical Society)

The structure development of thermodynamically stable macromolecular associations is driven by influence of the following factors on the free energy of the system: stretching extent of repeating units creating the association core, interfacial tension of the association core and surrounding solvent, and repulsive forces between copolymer chains forming the core.⁵⁵ The factors influencing morphology of macromolecular associations can be adjusted by addition of e.g., ions or homopolymers, varying copolymer concentration and chemical composition, or solvent quality.⁵⁵ The state of the system is generally governed by the intrinsic molecular

curvature of the copolymer, or the hydrophobic-hydrophilic interface curvature determining the arrangement of copolymer chains described by the dimensionless packing parameter p :^{51,57}

$$p = \frac{v}{a \cdot l} \quad (1)$$

where v and l are the volume and the length of the hydrophobic segments, and a the hydrophobic-hydrophilic interfacial area. The structure of self-assembled copolymers can be predicted based on values of the packing parameter;^{51,55,56} if the packing parameter is $p < 1/3$ spherical micelles, $1/3 < p < 1/2$ cylinders, $1/2 < p < 1$ vesicles, or for $p = 1$ lamellae form.⁵⁶ The morphologies of self-assemblies mentioned here are among the simplest examples but more complex structures were reported.⁵⁶

Diverse synthesis techniques to tailor amphiphilic copolymers for particular structure-property relationships were developed. Synthesis routes include micellar,^{16,58,59} emulsion,^{60,61} reversible addition-fragmentation chain-transfer (RAFT),^{62,63} and ring-opening polymerisation,^{64,65} among others. Françoise Candau's group performed extensive studies on amphiphilic copolymers containing low amounts (typically 0.5-5 mol.%) of hydrophobic comonomers distributed along a hydrophilic backbone in the 1990s until the early 2000s.^{16,66-70} These copolymers were predominantly polyacrylamide-based and synthesised via micellar copolymerisation. Hydrophobically modified copolymers containing low hydrophobe amounts received a lot of attention because of their unique capabilities to form micellar structures in aqueous solutions.⁷¹ These macromolecular associations influence solution viscosity resulting in improved solution rheological properties compared to solutions of corresponding homopolymers.⁷¹

2.2.1 Synthesis of amphiphilic copolymers by micellar copolymerisation

Micellar copolymerisation emerged as a convenient polymerisation method for the synthesis of hydrophobically modified water-soluble polymers.^{72,73} In such copolymers the hydrophobic units are suggested to be incorporated as random blocks.^{16,74} Syntheses of hydrophobically modified hydrophilic polymers tend to be challenging due to the insolubility of the hydrophobic comonomer in aqueous solutions.⁷⁵ In a micellar polymerisation medium hydrophobic comonomers are solubilised in water assisted by water-soluble surfactants, for instance using anionic, such as sodium dodecyl sulphate (SDS)⁷⁶ or cationic surfactants, such as cetyltrimethylammonium bromide (CTAB).⁵⁹ The resulting micellar system is homogeneous and transparent on a macroscopic level since the hydrophobic monomer is solubilised within

surfactant micelles and the hydrophilic monomer is dissolved in the aqueous continuous phase.^{72,75} Micellar copolymerisations are common free-radical polymerisations¹⁶ initiated by addition of water-soluble initiators, such as azo-, or persulfate initiators.⁶⁶ It is noteworthy that the system persists phase separation and retains the homogeneity throughout the reaction, without appearance of a polymer latex.^{72,75} It is this property that renders micellar copolymerisations to be solution copolymerisations (Figure 6).⁷⁵

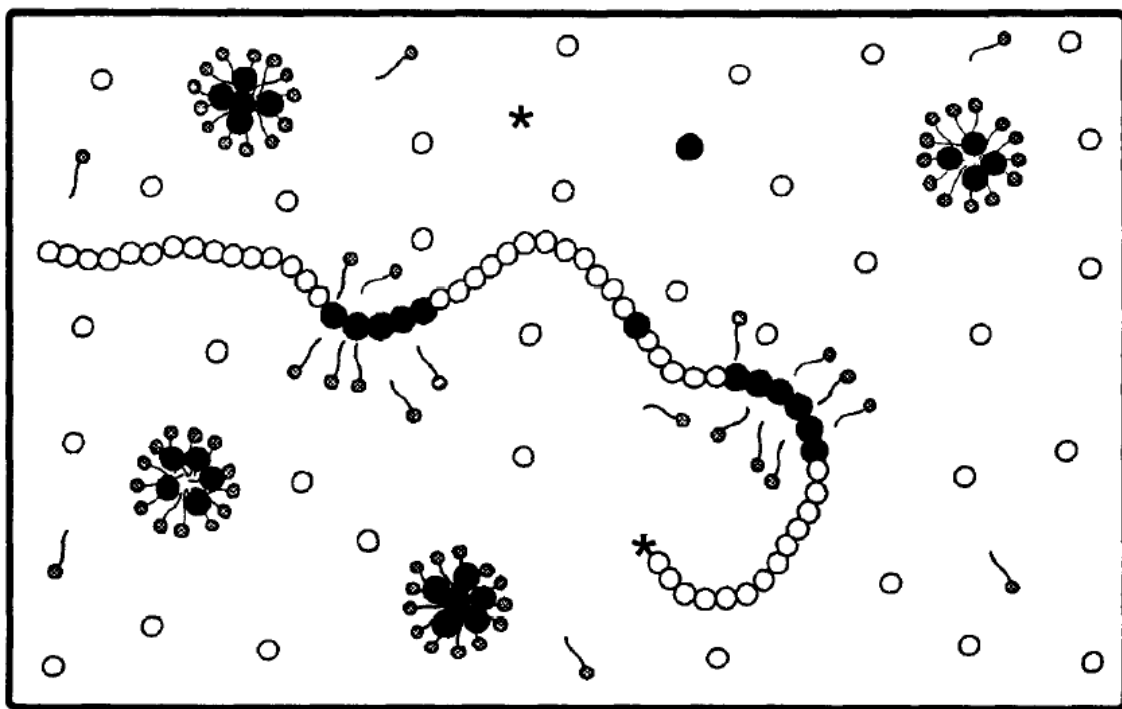


Figure 6. Graphic illustration of the propagating copolymer chain in a micellar copolymerisation reaction medium. Open circles and stars represent hydrophilic monomer and initiator, respectively, dissolved in water, and closed circles hydrophobic monomer dissolved within surfactant molecules. (Reprinted from Candau, F. et al.⁶⁹ Copyright 1994, with permission from Elsevier)

Since the micellar polymerisation was invented, many studies using diverse hydrophobic comonomers that form free radicals were performed; for instance alkylacrylamides,^{67,77,78} alkylarylacrylamides,^{67,79,80} pyrenesulfonamide-based monomers,^{58,81} and styrene^{59,66} were copolymerised with either acrylamide-based monomers and/or acrylic acid. A rational selection of a hydrophilic/hydrophobic monomer system is of utmost importance particularly to lower compositional heterogeneity of the resulting copolymers.⁶⁶ To ensure more homogeneous distribution of hydrophobic blocks in the copolymer structure, monomers having similar reactivities should be used.^{66,71}

One of the essential aspects that determines the association behaviour of these hydrophobically modified copolymers is the nature of the hydrophobic monomer units, primarily their size (length and bulkiness) and structure (e.g., alkyl or aryl molecular groups).⁷¹ For instance, it was demonstrated that copolymers of acrylamide and N,N'-dialkylacrylamide units displayed more prominent associative behaviour than copolymers containing N-alkylacrylamide units.⁶⁷ This behaviour was attributed to greater bulkiness of N,N'-dialkylacrylamide hydrophobic blocks compared to those of N-alkylacrylamide, which leads to closely packed hydrophobic segments exhibiting a stronger hydrophobic effect.⁶⁷

In addition to the nature of the incorporated hydrophobic comonomer, associative properties in an aqueous solution of these amphiphilic copolymers are significantly influenced by their microstructure, i.e., how the hydrophobic comonomers are distributed along the polymer backbone.^{16,67} Following observations by Dowling and Thomas⁸² and McCormick et al.^{79,81,83} for acrylamide-based copolymers having hydrophobic monomers of styrene,⁸² pyrene-,^{81,83} and alkylarylacrylamide-based,⁷⁹ it is now generally accepted that amphiphilic copolymers produced via micellar copolymerisation have hydrophobic monomer units distributed as blocks along the hydrophilic backbone.^{66,67,76} However, the precise block microstructure, i.e., the hydrophobic block length and distribution is difficult to be determined due to low total amount of hydrophobic monomers incorporated into the polymer chains.^{16,67} Candau et al.^{67,68} reported the block microstructure of these copolymers mainly relying on rheological investigations. In their studies^{16,67,68} they showed that in the micellar copolymerisation technique it is relatively straightforward to vary the (theoretical) hydrophobe block length in the copolymer microstructure by adjusting the surfactant to hydrophobic comonomer ratio; increasing the hydrophobe block length results in more pronounced copolymer associative capabilities.⁶⁷ Enhanced association behaviour was also observed for higher hydrophobic to hydrophilic comonomer ratio.⁶⁷

Despite the advantages offered by micellar copolymerisation to synthesise amphiphilic copolymers, several challenges were encountered and reported.^{66,75,80} It is anticipated that the block structure of amphiphilic copolymers synthesised using micellar copolymerisation is due to the high local concentration of hydrophobic comonomer molecules within micelles.⁶⁶ Increasing the hydrophobic monomer concentration in micelles further to vary the copolymer microstructure leads to higher incorporation rates of the hydrophobe into the copolymer backbone.⁸⁰ As a consequence, higher hydrophobe incorporation rates drive two competing processes—preferred block-like incorporation of the hydrophobic comonomer over

incorporation as single units into copolymer microstructure,⁶⁶ while simultaneously depleting the availability of hydrophobic comonomers already at the beginning of the copolymerisation reaction.^{66,67,80} The fast hydrophobe consumption results in inhomogeneous copolymer microstructures, which negatively affects their association, and thus rheological properties.⁶⁶

2.2.2 Applications of amphiphilic copolymers

Amphiphilic copolymers are advantageous macromolecules for diverse biomedical applications, such as drug delivery vehicles,^{84,85} tissue engineering,^{86,87} gene therapy,^{88,89} etc. due to their unique properties to simulate natural systems via self-assembly, e.g., biological membranes.⁹⁰ Furthermore, hydrophobically modified copolymers are also of an immense interest for industrial applications, primarily in water-based systems to modify and govern solution viscosity which is of importance for oil-recovery operations.^{14-16,91} In oil-recovery operations synthetic polymers having M_w in the range of $\geq 10^6$ g/mol are employed as DRAs.^{9,16} Polymeric DRAs are prone to degradation under strong shear flows losing their effectiveness to reduce drag.^{16, 92} In such a case, amphiphilic copolymers forming macromolecular associations could be used as DRAs in which the hydrophobic interactions serve as a sacrificial 'bond' to protect the copolymer backbone.¹⁶ Amphiphilic copolymers are also useful emulsifiers due to their surface activity.⁹³ For instance, amphiphilic branched copolymers containing hydrophilic monomers of poly(ethylene glycol) methacrylate and methacrylic acid with 1-dodecanethiol hydrophobic end-groups were shown to effectively stabilise oil-in-water (o/w) emulsions in basic solution conditions.⁹³ Owing to their chemical structure, i.e., pH dependent degree of dissociation, they showed on/off assembly of emulsion droplets.⁹³ Such responsive emulsions can be used as transient templates to manufacture polymeric colloids.⁹³ Emulsions stabilised by hydrophobically modified copolymers were also used to produce macroporous polymers by polymerisation of emulsion templates following removal of the templating phase.^{94,95} Application areas of hydrophobically modified water-soluble polymers relevant for this dissertation are polymer-based DRAs and production of porous polymers using emulsion templating method, and will be, thus, elaborated in more detail in the following sections.

2.3 Polymer drag reduction

Drag encountered in turbulent pipe-flows is interpreted as frictional resistance of a fluid to flow. Fluid drag is leading to a reduced fluid pumping efficiency resulting in additional energy consumption. In 1948 Toms⁹⁶ reported on a phenomenon, known as polymer DR. He discovered that the addition of small amounts of polymers (10-100 wppm) into the fluid significantly reduced frictional drag.⁹⁶ A beneficial effect of DR is the much lower pressure drop in a pipe flow for a fluid containing polymer DRAs as compared with the pure solvent at the same flow rate. Increasing energy efficiency is of an utmost importance, and thus polymer DR is advantageous for many application areas including fluid pipeline transport,⁹⁷ firefighting,⁹⁸ hydraulic fracturing,⁹⁹ field irrigation¹⁰⁰ and sewerage systems.¹⁰¹ Beside polymers other DRAs were also explored, such as surfactants,¹¹ and spherical particles.¹⁷

To understand drag occurring in turbulent fluid flows it is important to elucidate the main flow regimes—laminar and turbulent—and the transition from one to the other. Laminar flow is characterised by an ordered fluid movement in which fluid layers move linearly and no mixing occurs perpendicular to the flow (Figures 7 and 8).^{102,103} In laminar flow fluid layers at the wall obey no-slip boundary conditions¹⁰² meaning that the velocity of the fluid at the stationary rough wall is zero.¹⁰⁴ The fluid velocity is increasing towards the centre of the pipe resulting in a parabolic flow profile.¹⁰⁴

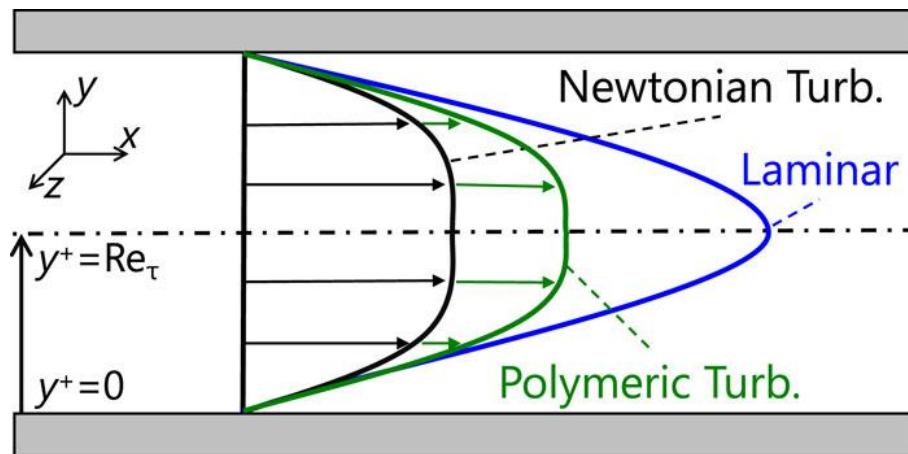


Figure 7. Illustration of fluid flow profile for laminar flow, turbulent flow for pure solvent (Newtonian turbulence) and modified turbulent flow using polymer additives (polymeric turbulence). (Reprinted from Xi, L.,¹⁰⁵ copyright 2019, with permission from AIP Publishing).

In turbulent flow the fluid layers move in an extremely chaotic manner following the development of eddies and vortices (Figures 7 and 8).¹⁰⁶ Turbulent flow prevails when the fluid velocity reaches a critical value defined by the Reynolds number Re describing the competition of inertial and frictional forces:

$$Re = \frac{\text{inertia}}{\text{friction}} = \frac{\rho d U}{\eta} \quad (2)$$

where ρ is the density of the fluid, d the pipe diameter, U the volume averaged velocity, η the dynamic viscosity of the fluid. Turbulence starts developing when $Re \geq 2040$.¹⁰⁷

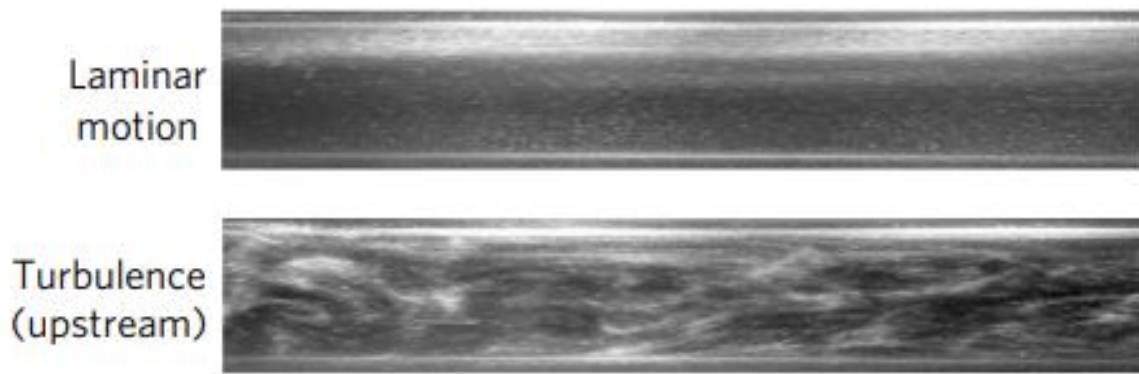


Figure 8. Images showing laminar and fully developed turbulent pipe flow. (Reprinted from Kühnen, J. and Song, B. et al.¹⁰ copyright 2018, with permission from Springer Nature)

The maximum drag reduction possible is defined by the “*maximum drag reduction asymptote*” (see Figure 9).¹⁰⁸ Drag reduction percentage $DR(\%)$ can be calculated using the following relation:

$$DR(\%) = \left(\frac{f_s - f_p}{f_s} \right)_{Re=const.} \cdot 100\% \quad (3)$$

where f_s and f_p are the Fanning friction factors of pure solvent and polymer solution.

The Darcy-Weisbach equation enables to determine the Fanning friction factor f and demonstrates that f is directly proportional to the pressure drop Δp along a pipe:

$$f = \frac{\Delta p}{l_p} \frac{d}{2 \rho U^2} \quad (4)$$

where l_p is the length and d the diameter of the pipe.

2.3.1 Mechanism of polymer drag reduction

Since the discovery of the phenomenon of polymer DR, a myriad of experimental as well as theoretical studies have been performed to identify its cause;^{109 - 111} these studies mainly emphasised the role of individual polymer molecules in interplay with turbulence. The viscous model, proposed by Lumley,^{12,112} states that polymer molecules transform from a coiled to a stretched conformation owing to the elongational component of turbulent flow. Polymer elongation leads to a large increase in effective viscosity.^{12,112} The increased effective viscosity results in the reduction of fluid drag.¹¹² The elastic model suggested by Tabor and de Gennes¹¹³ considers polymer coils to act as small springs, which consume energy from the turbulent flow by stretching polymers affecting the evolution of the vortex cascade. The flow pattern is modified when the elastic and kinetic energies of elongated polymer and the flow field, respectively, reach comparable values.¹¹³ The viscous and elastic models of polymer DR mechanism are the most accepted but an extensive analysis of the subject is elaborated in many reviews.^{13,114,115} The observation of “shear layers” close to the pipe wall, whose average thickness was found to be linked to the extent of drag reduction achieved, made by Zadrazil et al.¹¹¹ are a step further towards unravelling the DR mechanism.

2.3.2 Polymers for drag reduction

Poly(ethylene oxide) (PEO) and PAAm are the most studied water soluble polymeric DRAs, and PAAm is the most commercially utilised synthetic polymer DRA for water systems,^{111,114,116 - 120} but also other water-soluble polymers, such as guar¹²¹ and xanthan¹²² gum, were used. In organic solvents polyisobutylene,¹²³ polystyrene,¹²⁴ poly(methyl methacrylate)¹¹⁴ are utilised to reduce frictional drag. The most important properties of polymers that influence their DR capabilities are their M_w and structure, concentration, and the quality of solvent.^{13,114} Virk¹¹⁴ demonstrated that the M_w is the crucial parameter for flexible polymers to reduce frictional drag. Drag reduction, expressed as reduction in shear wall stress, was shown to be directly proportional to the polymer M_w .¹¹⁴ The minimum required M_w of a polymer DRA to cause drag reduction is $M_w = 5 \times 10^5$ g/mol.¹²⁵ However, the dependence of DR on polymer molecular size is not straightforward, lacking quantitative interpretation to describe discrete contributions of M_w and polymer molecular dimensions in solution, i.e., radius of gyration, hydrodynamic volume, chain length.¹³ The relation between DR and molecular size of polymers becomes more complex when polydispersity $\bar{D}$ of polymer molecules is considered.¹³

Berman¹²⁶ and Hunston and Reischman¹²⁷ demonstrated that small amounts of the highest M_w polymer fractions govern DR.

Virk¹¹⁴ further reported on the influence of polymer concentration on DR showing that the onset of DR is not influenced by polymer concentration. The onset point of DR is defined as the deviation from the Prandtl-Kármán law when the frictional drag is represented in a Prandtl-Kármán plot (Figure 9).¹²⁸ After DR onset, DR is increasing with increasing effective polymer concentration at a fixed Re levelling off at the maximum DR asymptote.^{114,128} In addition, the maximum DR effect is directed towards higher Re ;¹²⁹ at a fixed polymer concentration higher Re leads to greater DR.¹²⁸ It is worth noting that for sufficiently high concentrations or M_w the DR onset vanishes meaning that polymers lower the frictional drag over the whole Re range in turbulent flow.¹¹⁰

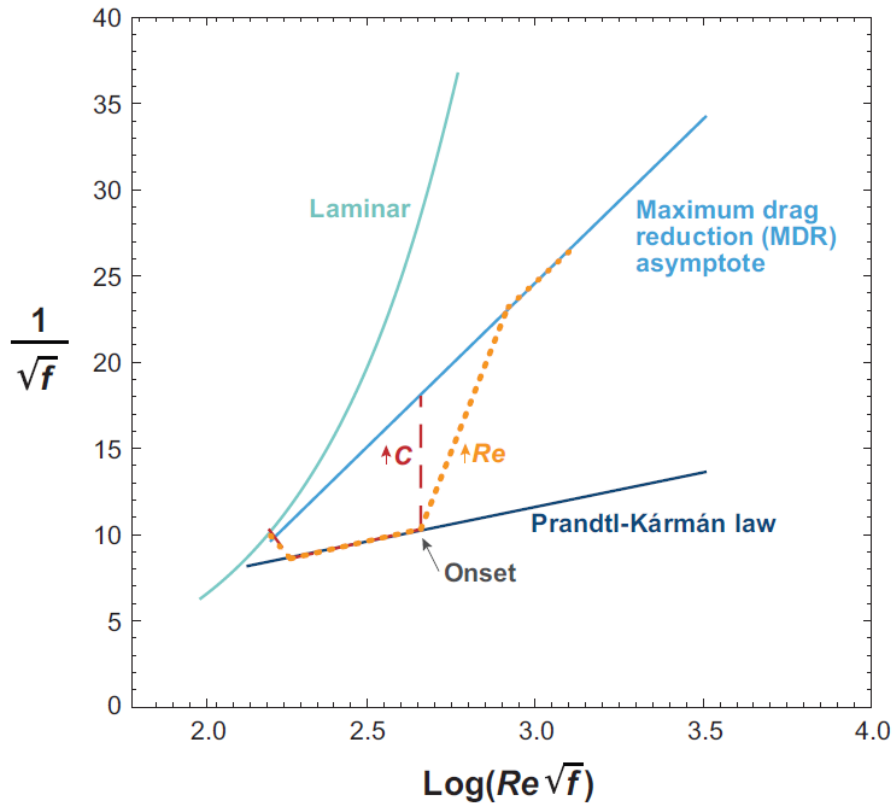


Figure 9. A graphic illustration representing the onset and possible paths for DR by polymers. These DR paths include a scenario when Re is kept constant and polymer concentration c is enhanced (the red dashed line), and when polymer c is constant while Re is enhanced (the orange dotted line). (Reprinted from White, C. M. and Mungal, M. G.¹²⁸ copyright 2008, with permission from Annual Reviews).

Variation of polymer chemical composition, or chain structure, affect polymer DR capability.^{13,14,91,130} The generally accepted notion is that polymers having a linear main chain with few, or no, side branches, and flexible rather than rigid main chain are the most effective frictional drag reducers.^{12,131} Morgan and McCormick¹³ in their review summarised numerous contradictory studies dealing with effects of polymer chain linearity/branching and stiffness. They¹³ showed that the dependence of polymer DR effectiveness on these two factors is not simple; to clarify the effect of polymer structure, contributions of e.g., polymer coil size, flow rate or concentration should be accounted for. The influence of solvent on polymer DR portrays polymer-solvent interactions. Solvent quality affects polymer conformation in a solution meaning that a polymer will exhibit a more extended structure and thus greater hydrodynamic volume in a good solvent compared to a poor solvent.¹³ The more extended the polymer structure in a good solvent the higher the DR.¹³

Polymer DR is more complex as it is affected by polymer mechanical degradation induced by strong shear encountered in turbulent flows.¹³ Degradation of polymer molecules affects the M_w distribution during the fluid flow.¹³ While higher M_w polymer molecules exhibit higher DR, they are also more vulnerable to mechanical scission.¹³ Once broken, polymer DR capabilities decrease resulting in increased frictional drag.⁹² The mechanical degradation of polymer molecules limits their industrial use as DRAs.¹³

A better quantitative interpretation is necessary to elucidate the relation between polymer structure and the properties of fluid flow modified by the presence of dissolved polymers.¹²⁹ Many papers report the loss of polymer DR effectiveness but also lack quantitative descriptions; many findings assigned the reduced polymer DR efficiency to polymer main chain scission,^{109, 132, 133} while others emphasise also the role of macromolecular associations breakage.^{134,135} The influence of macromolecular associations on polymer DR is a long-standing hypothesis stemming from the perception that high M_w polymer DRAs offer the greatest capabilities to lower frictional drag.¹³ Thus, high M_w polymer associations should result in even superior DR effectiveness.¹³ The beauty of this postulate is that the high shear encountered in turbulent flows might break the intermolecular associations preferably to the polymer backbone, i.e., the intermolecular interactions should act as “physical fuse”.^{13,16,136} The result would be “on-off” control of DR–intermolecular interactions can reform in areas of reduced shear flow leading to potential DR recovery.¹³

Cox et al.¹³⁴ reported findings on the time dependent DR exhibited by dilute aqueous solutions of polyethylene oxide and polyacrylamide. Their results point towards the presence of macromolecular associations suggesting that they are more effective in reducing drag than single polymer molecules.¹³⁴ They hypothesised that aggregates can be produced by shear forces in turbulent flow breaking down swollen (yet undissolved) polymer particles.¹³⁴ In such a case, the average association size (swollen polymer particle) reduces continuously with time creating a higher number of associations or free individual molecules.¹³⁴ The dissolution process results in an initial increase in DR followed by a decrease in DR after passing a maximum (Figure 10).¹³⁴ In contrast, when using individual dissolved polymer molecules as DRAs, the initial DR is expected to be highest followed by a steady decrease with flow time or distance. Dunlop and Cox¹³⁷ put forward the idea that even when macromolecular associations are absent in laminar flow, the high shear in turbulent flow might promote association. Warholic et al.¹³⁸ reported observations, which further suggest that the polymer molecules need to associate to be effective in reducing DR. In addition, they¹³⁸ emphasised the idea that insights into macromolecular associations are crucial to understand the phenomenon of polymer DR.

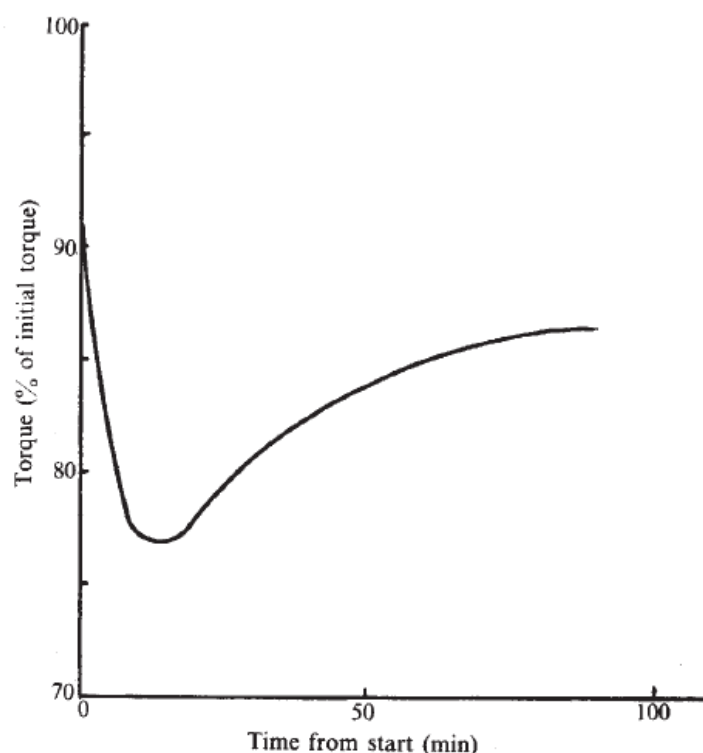


Figure 10. Drag reduction (represented as reduction in measured torque) as a function of time of poly(ethylene oxide) (Polyox Coagulant) at a concentration of 0.86 ppm. (Reprinted from Cox, L. R. et al.,¹³⁴ copyright 1974, with permission of Springer Nature)

Hydrophobically modified PAAm were shown to be effective DRAs due to their ability to associate in aqueous solution into micellar structures.^{14,15,91,139,140} McCormick et al.⁹¹ examined the influence of intermolecular associations on DR efficiency using hydrophobically modified copolymer poly(acrylamide-co-diacetone acrylamide) in different solvents including deionised water, 1 M urea, and 0.514 M NaCl.⁹¹ Reduction of frictional drag was most prominent in aqueous 0.514 M NaCl solution, which was explained by the presence of macromolecular associations as the salt is assumed to enhance hydrophobic interactions compared to pure deionised water and urea.⁹¹

2.4 Polymers in the environment

Favourable properties of polymer materials led to their intensive worldwide use in many advanced applications but resulted in environmental pollution due to the lack of efficient collection and recycling options.^{19, 141} Risks of environmental pollution associated with excessive use of polymers were recognised already in the early 1970s,¹⁴² yet polymer production still kept rising reaching now a worldwide production of more than 400 million tonnes annually.¹⁹ Since their inception, a considerable amount of work was performed to develop technologies and methods allowing to tailor the stability of polymers, rendering them stable during processing, or to resist different environmental factors.¹⁹ This intrinsic stability of polymers results in their long-term retention in water or the ground.¹⁴³ An area of interest for my thesis is polymer induced DR used in hydraulic fracturing processes. Hydraulic fracturing implies injection of water containing additives (so-called fracking fluid) under high-pressure to enhance the extraction of fossil hydrocarbons from fractured reservoir formations (Figure 11).⁷ Even though the concentration of PAAm DRAs commonly used during fracking is approximately 160 ppm,¹⁴⁴ millions of litres of fracturing fluid are used per well.⁸ This process consequently leads to massive wastewater production harming the environment (Figure 11).^{7,8} The frequency of hydraulic operations is only expected to increase in the following years as energy demand keeps rising.⁷ Attempts to deal with the wastewater treatment were reported including electrocoagulation,¹⁴⁵ membrane separation processes,¹⁴⁶ synthesis of (irreversibly) degradable water-soluble PAAm,¹⁴⁷ or thermo-responsive poly(N-isopropylacrylamide) for reversible precipitation offering on-demand DR.²⁰ All these studies are a big step forward to effective routes to treat fracking waste fluids. Polymer molecules adsorb at underground rock formations¹⁴⁸ contributing further to environmental issues. Adsorption of polymer molecules also lowers their effective concentration in solution resulting in reduced effectiveness of

fracking.¹⁴⁸ Thus, when considering applications of polymer DRAs in hydraulic fracturing operations, two factors need to be considered: avoid polymer adsorption and be effective DRA for a flow distance of at least 2130 m¹⁴⁹—an average shale depth.

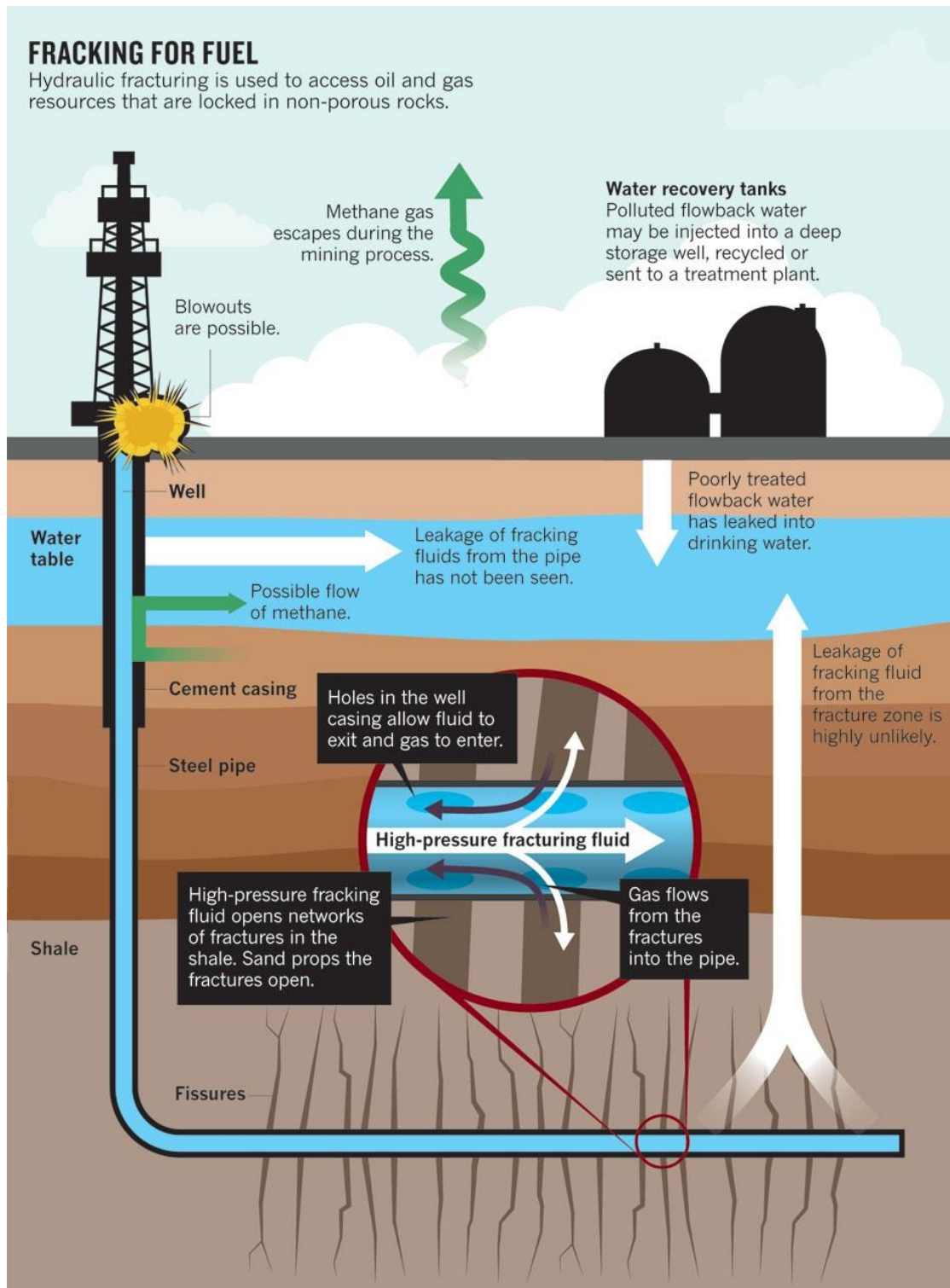


Figure 11. Graphical illustration of the impact of hydraulic fracturing on the environment. (Reprinted from Howarth, R. W. et al.,¹⁵⁰ copyright 2011, with permission of Springer Nature)

2.5 (Super)porous hydrogels

“Hydrophilic gels”,¹⁵¹ or commonly called hydrogels are polymers with a hydrophilic three-dimensional network structure and thus insoluble in water. Due to their hydrophilic nature and crosslinked (porous) structure, hydrogels commonly absorb and retain large quantities of water.¹⁵¹ It is these properties that render hydrogels advantageous for diverse application areas including biomedical applications,¹⁵² food and agriculture,^{153,154} wastewater treatment¹⁵⁵ and chromatography.¹⁵⁶ The crosslinked structure of hydrogels can be fine-tuned to achieve desired material properties tailored for specific applications, such as water sorption capacity, swelling kinetics, mechanical properties, porosity, and toxicity.¹⁵⁴ Over the years biomedical applications of hydrogels, including wound dressings,¹⁵⁷ drug delivery,¹⁵⁸ and (injectable) scaffolds for tissue engineering,¹⁵⁹ were most prominent. Despite the efforts made to tailor their structure for biomedical use, certain properties of conventional hydrogels restrict their application.¹⁶⁰ For instance, in drug delivery applications slow swelling of conventional hydrogels caused by slow water transport through the crosslinked hydrogel structure is preferred.¹⁶¹ In this way, a drug is slowly released from the hydrogel structure enabling controlled drug delivery.¹⁶¹ However, fast swelling hydrogels for gastric retention are more effective.¹⁶¹ To tackle this issue, Chen et al.¹⁶¹ synthesised porous hydrogels with an interconnected pore structure that can reach the equilibrium swollen state in a short period of time—within a couple of minutes. The fast water sorption is attributed to the capillary action through the interconnected open pores.¹⁶¹ These hydrogels are referred to as “superporous” hydrogels.¹⁶¹

Tissue engineering is a biomedical technique which aims to repair or regenerate damaged tissue/organs.¹⁶² Tissue engineering relies on biocompatible, and ideally biodegradable, functional materials, called scaffolds, onto which cells can be seeded and grown in a simulated natural environment.¹⁶² Ideally these scaffolds can also be injected into human/animal bodies to heal/restore the function of damaged tissues or organs.¹⁶² These scaffolds need to comprise porous structure which enables nutrients to reach growing tissue/organ but also to allow for excretion of waste matter.¹⁶² Combined with large surface area which provides a suitable environment for cell growth and proliferation, the interconnected highly porous structure of superporous hydrogels renders them to be a perfect match for tissue engineering applications.^{28,160,162} Beside their porosity, mechanical properties of an implant material are of immense importance.^{159,163} If mechanical properties of the implant deviate (being higher) from

the native tissue to be restored, it can result in damaging of native tissue surrounding the implant leading to additional health issues.¹⁶³ Low biomechanical properties of scaffolds lead to rapid degradation of the injected material.¹⁵⁹ To adjust mechanical properties of hydrogel scaffolds it is often necessary to tailor their chemical composition, such as the total polymer amount in the hydrogel or the crosslinking degree.¹⁶⁴ Altering the formulation of hydrogels influences their physical properties, including pore size and/or distribution, and swelling capabilities, which consequently affect the performance of hydrogel scaffolds in biological processes.¹⁶⁴ Hydrogels that were studied for tissue engineering applications include poly(2-hydroxyethyl methacrylate)-,¹⁶³ chitosan-,¹⁵⁹ polyvinyl alcohol-based hydrogels,¹⁶⁵ among others. Owing to a great biocompatibility of poly(2-hydroxyethyl methacrylate) (pHEMA), it is, together with its copolymers, the most researched hydrogel polymer for tissue engineering.¹⁶³ Although there were efforts made^{29,166} to produce highly porous pHEMA-based hydrogels, this group of materials still remains largely underexplored. Emulsion templating is an effective synthesis route to produce porous polymers offering the possibility to control pore interconnectivity (openness), porosity, pore size, surface area, and mechanical properties of the final polymer.²²

2.5.1 Emulsion templating for production of porous polymers

To understand how emulsion templating works it is necessary to introduce basic principles of emulsions and related phenomena: Emulsions are fine dispersions of droplets of an immiscible liquid dispersed in another ('water' and 'oil').¹⁶⁷ If water is the dispersed phase water-in-oil (w/o) emulsions form or vice versa resulting in oil-in-water (o/w) emulsions.¹⁶⁷ Depending on the internal phase volume ratio emulsions are categorised into high internal phase emulsions (HIPEs) having an internal phase ratio >70 vol.%¹⁶⁸ (more commonly 74.05 vol.% corresponding to the close packing of monodispersed hard spheres),¹⁶⁹ medium internal phase emulsions (MIPEs) with internal phase volumes ranging from 30 to 70 vol.% or low internal phase emulsions (LIPEs) < 30 vol.%.¹⁷⁰ The stability of emulsions formed by mixing pure immiscible liquids are very poor leading to rapid phase separation, which is driven by minimisation of the interfacial energy.¹⁶⁷ Surface-active compounds are added to allow for effective emulsification and to enhance emulsion stability preventing coalescence of the droplets.¹⁶⁷ Emulsifiers commonly used to stabilise emulsions are small molecular and polymeric surfactants, and nano- or microparticles.^{21,26,167,171} Formation of emulsions involves energy input during droplets formation/disruption by applying shear forces originating mainly from mechanical energy.¹⁶⁷ The presence of an emulsifier is essential to reduce the interfacial

tension resulting in lower stress required to deform and break up droplets.¹⁶⁷ Small molecule surfactants are called ‘soaps’.¹⁶⁷ Various factors determine whether o/w or w/o emulsion will be formed, such as emulsifier (surfactant or particles) type, oil/water ratio, electrolyte concentration, temperature, oil type among others.¹⁶⁷ The choice of an appropriate surfactant is important but not the determinant.¹⁶⁷ The rule of thumb (Bancroft’s rule) states that surfactants more ‘soluble’ in water form o/w emulsions, while those more ‘soluble’ in oil form w/o emulsions.¹⁶⁷ The affinity of surfactants to stabilise either o/w or w/o emulsions can be estimated by their hydrophilic-lipophilic balance (HLB);¹⁷² surfactant HLB values in the range 4-6 and 8-18 suggest that w/o and o/w emulsions, respectively, can be created.¹⁷² Emulsions can also be stabilised by amphiphilic copolymers, or “macrosurfactants”.²¹ The major benefit of using macrosurfactants is that lower emulsifier amounts are needed to stabilise emulsions due to their lower CMC (commonly ranging 10^{-9} to 10^{-4} mol/L)²¹ compared to small molecule surfactants (CMC range from $\sim 10^{-5}$ to 1 mol/L).¹⁷³ Polymer-surfactant complexes were also used to stabilise emulsions.¹⁷⁴ It was demonstrated that droplet coalescence rate was reduced in emulsions stabilised by mixture of poly(vinyl alcohol) (PVA) and CTAB compared to emulsions stabilised by PVA or CTAB alone.¹⁷⁴ It was hypothesised that this observation was due to formation of polymer-surfactant complexes that generated a rigid film at the o/w interface.¹⁷⁴

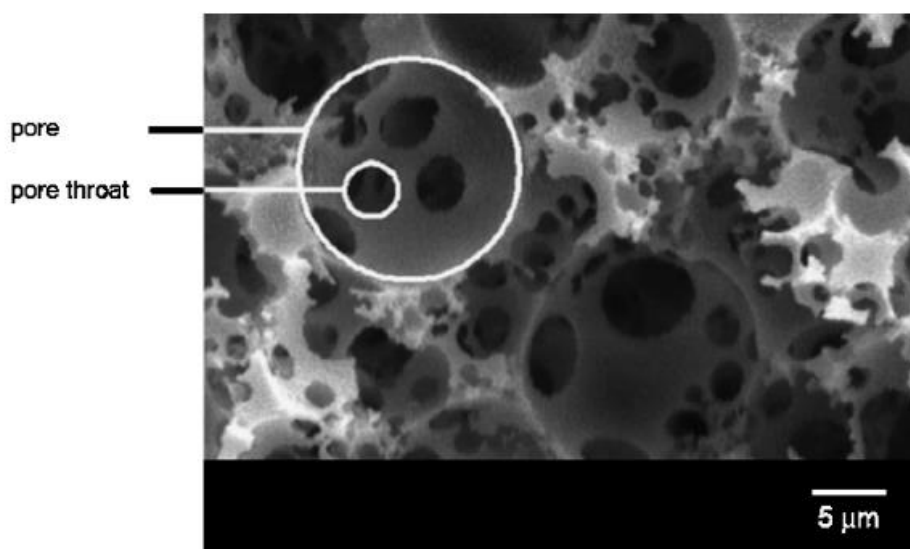


Figure 12. Typical microstructure exhibited by macroporous polymers synthesised using emulsion templating process. (reprinted from Menner, A. and Bismarck, A.,¹⁶⁹ copyright 2006, with permission of John Wiley and Sons)

Emulsion templating involves the polymerisation of the continuous emulsion phase containing monomers followed by the removal of the internal (dispersed) templating phase, which results in macroporous polymers (Figure 12) with tuneable mechanical and morphological properties.²² The mechanical properties can be adjusted by the choice of monomers and crosslinkers forming the polymer walls as well as the internal phase volume used to adjust the porosity of the resulting macroporous polymers.²² The structure/morphology of liquid emulsion template at the gel point of the polymerisation determines the morphology of resulting macroporous polymers.²² The morphology of emulsion templated porous polymers can be tailored by adjusting the internal volume phase ratio of the emulsion template to achieve the desired porosity.¹⁷⁰ The average pore size and pore size distribution can be controlled by adjusting the droplet size of the internal phase in the emulsion template.¹⁷⁵ Increased surfactant concentrations result in smaller average emulsion droplet size.¹⁷⁶ In addition, greater energy input during emulsification, such as increased mixing speed and/or time results in smaller emulsion droplets.¹⁷⁵

The liquid but viscous nature of H/MIPE templates allows for their manipulation. Moulding of H/MIPEs enables the production of porous polymer monoliths (a form of a continuous bulk porous polymer) with various shapes.¹⁷⁷ Dispersion of H/MIPEs in immiscible solvents (third phase) results in multiple emulsions, which can be polymerised yielding macroporous polymer beads.¹⁷⁷ The resulting macroporous polymers produced by polymerisation followed by template removal are called: poly(merised)HIPEs, polyMIPEs and polyLIPEs after their corresponding emulsion templates.¹⁷⁰

3 Summary of Publications: Experiments

3.1 Materials

Recrystallisation of acrylamide (AAm) ($\geq 99\%$, Sigma Aldrich) was performed twice from acetone ($\geq 99.5\%$, Donauchem). Styrene (St) ($\geq 99\%$), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, $\geq 99\%$), cetyltrimethylammonium bromide (CTAB, $\geq 98\%$), sodium azide (NaN_3 , $\geq 99.5\%$), sodium nitrate (NaNO_3 , $\geq 98\%$), deuterium oxide (D_2O , 99.9 at.% D), formamide ($\geq 99\%$), magnesium sulphate (MgSO_4 , $\geq 99.5\%$), toluene ($\geq 99.5\%$), cyclohexane ($\geq 99.5\%$), dioxane ($\geq 99.0\%$), hexane ($\geq 95\%$), 2-hydroxyethyl methacrylate (HEMA, $\geq 99\%$), N,N-methylenebisacrylamide (MBAm, $\geq 99\%$), ammonium persulfate (APS, $\geq 98\%$), N,N,N',N'-tetramethyl ethylenediamine (TEMED), were purchased from Sigma-Aldrich, and methanol ($\geq 99.8\%$) from Fisher Scientific and all used as received. Polyacrylamides (PAAm) having nominal molecular weights $M_w = 0.5$ (PAAm0.5) and $M_w = 1.0 \cdot 10^6$ g/mol (PAAm1) were kindly supplied by SNF Floerger (Andrézieux, France). Polyethylene oxide ($M_w = 24 \cdot 10^3$ g/mol, PEO-24K) and dextran ($M_w = 69 \cdot 10^3$ g/mol, Dextran-T69K) standards were purchased from Malvern, and dishwasher salt (sodium chloride, NaCl) (Tandil) from Hofer. Nitrogen ($\geq 99.999\%$, Messer) was utilised to ensure an inert atmosphere during polymer syntheses. To purify polymers, dialysis tubing (Bio Design, Thermo Fisher Scientific) with a molecular weight cut off (MWCO) of 8000 Da was utilised. All experiments, except for those in the pipe flow facility, were performed using deionised water having conductivity of $0.055 \mu\text{S/cm}$ (Water Purifier, Elga, UK).

3.2 Experimental part

3.2.1 Poly(acrylamide-co-styrene) synthesis route

I should mention that different synthesis routes were explored to synthesise hydrophobically modified PAAm-based copolymers, which either did not yield any product or the polymerisation yield was too low for the amount of polymer required for DR applications—and could not be scaled-up. These synthesis routes include RAFT polymerisation; no product was obtained regardless of the reaction system used and applied conditions. RAFT polymerisation allows for control over polymer M_w . However, when used to synthesise polymers with M_w of up to 1000 kg/mol, the amount of RAFT agent used is too low to initiate the controlled polymerisation, which was complicated by the high probability for hydrolysis of the agent that might have led to the unsuccessful polymerisation of acrylamide and styrene in water and

water/dioxane mixtures. Reactions were initiated by heat and UV light but with no success. An approach using PAAm containing weak links, temperature sensitive azo groups as a macroinitiator, reproduced from literature,¹⁴⁷ to graft styrene moieties was also utilised. Using the macroinitiator approach the following challenges were encountered: It was impossible to find a solvent or solvent mixture in which both the hydrophilic PAAm macroinitiator and hydrophobic styrene were soluble to yield a product in solution polymerisation. For this reason, interfacial polymerisation was carried out dissolving PAAm macroinitiator in water and styrene in either toluene, hexane or using pure styrene but no product was obtained. Using this approach, it was difficult to adjust viscosity of the macroinitiator reaction solution, i.e., effective (macro)monomer concentration. Having too low concentration of the PAAm macroinitiator containing a few weak azo links per backbone leads to an insufficient number of radicals forming in the reaction medium—likely to result in radical recombination over polymerisation, whereas a high concentration produces viscous solutions and thus inefficient transport of radicals through the reaction medium. Inverse toluene-in-water microemulsion polymerisation was also used to polymerise acrylamide and styrene. This reaction yielded poly(acrylamide-co-styrene) copolymers having $M_w \approx 4000$ kg/mol, however due to the low yield (<20%) of the obtained products this approach was not further explored.

Poly(acrylamide-co-styrene) P(AAm-co-St) copolymers were produced adapting a previously described method⁵⁹ via aqueous micellar copolymerisation. The micellar copolymerisation method allowed for various amounts of hydrophobic monomer to be introduced into the copolymer backbone. Styrene amounts of 37.27 mg (0.36 mmol), 74.54 mg (0.72 mmol), or 149.08 mg (1.44 mmol) were added to 50 mL aqueous solution containing either 3.50 g (9.60 mmol) or 1.48 g (4.06 mmol) dissolved CTAB, to obtain hydrophobic monomer content of 1, 2 and 4 mol.% in the copolymer. The reaction mixture was stirred overnight to allow for solubilisation of St within the aqueous reaction medium. Once 2.50 g (35.17 mmol) AAm was dissolved (~30 min), three freeze-pump-thaw cycles were performed using a Schlenk line to degas the mixture. The initiator $K_2S_2O_8$ (88.25 mg, 0.33 mmol) was dissolved in 2 mL deionised water, degassed, and slowly added to the reaction mixture at 80°C to initiate the reaction. The inert atmosphere was maintained over the course of the reaction (24 h). The polymerisation reaction was terminated by cooling in ice water and the polymer recovered via slow precipitation in methanol under mild mixing to remove majority of CTAB. P(AAm-co-St) copolymers were used with different levels of purification: 1) without further purification after being recovered from the reaction mixture (denoted as as-synthesised), 2) with further

purification comprising two additional steps of re-dissolution in water and precipitation in methanol, and 3) further purification of 2) using dialysis against ~4 L deionised water for 10 d (denoted purified). The purified copolymers level 2) were used only for DR experiments in turbulent pipe flow, while other experiments were performed using as-synthesised and/or purified copolymers.

The copolymers used for characterisation and DR assessment in **Publication I** are referred to as 1P(AAm-co-1St), 0.7P(AAm-co-1St) and 0.5P(AAm-co-2St), with the first number representing their molecular weight in 10^6 g/mol obtained by gel permeation chromatography (**Publication I**, Table 1). The molar ratio of St/AAm is denoted by the second number, which was either 1 or 2 mol%.

The copolymers used in **Publication II** and **III** are denoted as P(AAm-co-4St), with the number referring to the molar ratio 4 mol.% of St/AAm.

3.2.2 Polymer characterisation

3.2.2.1 Static light scattering

Static light scattering (SLS) was utilised to determine the weight-average molecular weight M_w and radius of gyration R_g for individual polymer molecules and polymer associations. The SLS system comprised a compact goniometer (ALV/CGS-3, Langen, Germany) equipped with a 22 mW He-Ne laser (632.8 nm). The SLS measurements were conducted at scattering angles ranging from 30 to 130° with an increase of 10 angular steps. Solvents formamide and aqueous 0.025 M MgSO₄ solution were used to prepare polymer solutions for the SLS measurements; formamide was used to prepare non-associated polymer solutions, and the aqueous 0.025 M MgSO₄ solution to initiate polymer associations by shielding residual charges in the copolymer. The data measured for a minimum five different concentrations were reduced using the Zimm or Berry method (ALV-Fit and Plot software) to determine M_w and R_g . Detailed description of the SLS experiments can be found in **Publication I**.

3.2.2.2 Rheological analysis

The viscosity averaged molecular weight M_η and hydrodynamic radii R_η were calculated from viscosities measured using a rheometer (TA Instruments Discovery HR-2) equipped with a water circulatory thermostat (Thermo Cube) to maintain a constant temperature of $25 \pm 0.1^\circ\text{C}$.

The Mark–Houwink equation with the Mark–Houwink parameters¹⁷⁸ $K = 9.33 \cdot 10^{-3} \text{ cm}^3/\text{g}$ and $\alpha = 0.75$ was used to determine M_η . The intrinsic viscosity $[\eta]$ is defined as:¹⁷⁹

$$[\eta] = \frac{1}{c_m} \left[3 \ln \eta_r + \frac{3}{2} \eta_{sp}^2 - 3 \eta_{sp} \right]^{\frac{1}{3}} \quad (5)$$

where c_m [g/mL] is the mass concentration of polymer, η_r and η_{sp} the relative and the specific viscosities, respectively. The determined $[\eta]$ was further used to calculate the R_η :

$$R_\eta = \left[\frac{3[\eta]M_\eta}{10\pi N_A} \right]^{\frac{1}{3}} \quad (6)$$

with N_A being Avogadro's number.

3.2.2.3 Drag reduction in turbulent pipe flow

The pilot-scale test flow facility Vienna Experiment for Drag Reducing Agents (ViEDRA) was utilised to perform the DR characterisation in turbulent pipe flow. The ViEDRA set-up comprises a mixing tank to prepare polymer solutions reaching 300 L, compressed air pumping the solution, and ~20 m of pipe and hose system. The test section includes six differential pressure sensors (Deltabar S, Endress+Hauser, Germany) placed along a 7.2 m long stainless-steel pipe having inner diameter of 26 mm. The Darcy-Weisbach equation was used to calculate the Fanning friction factor f from the measured pressures:

$$f = \frac{\Delta p}{l_p} \frac{d}{2 \rho U^2} \quad (7)$$

where Δp is the pressure drop along the pipe, l_p and d the pipe length and diameter, ρ the solution density and U the volume averaged velocity.

A magneto-inductive flowmeter (Sitrans F M Magflo MAG5000, Siemens, Denmark) is used to measure the flow speed. Constant flowrate, or Reynolds number $Re = \frac{\rho d U}{\eta}$, is maintained by a feedback controller regulating the pumping pressure.

The friction factor f was used to calculate DR:

$$DR(\%) = \left(\frac{f_s - f_p}{f_s} \right)_{Re=const.} \cdot 100\% \quad (8)$$

with f_s and f_p being the Fanning friction factors for pure solvent and polymer solution.

3.2.2.4 Polymer characterisation by gel permeation chromatography

M_w of the polymers was also characterised utilising gel permeation chromatography (GPC). A triple detection GPC-system (Viscotec TDA 302, Malvern Panalytic) consisting of a high-performance liquid chromatography (HPLC) pump (LC-20 ADVP, SHIMADZU DEUTSCHLAND GmbH), a degasser (CSI6150 4 channel degasser, laserchrom), a solvent reservoir, and an automatic sample injector (S5200 Sykam GmbH) was used. The detectors were calibrated using PEO ($M_w = 23651$ g/mol) and dextran ($M_w = 68991$ g/mol) standards. The eluent used was aqueous 0.1 mol/L NaNO_3 containing 0.02 wt.% NaN_3 . The flow rate of 0.7 mL/min and temperature of 30°C were maintained constant during the measurements.

3.2.3 ‘Self-removal’ of poly(acrylamide-co-styrene) from aqueous solution

3.2.3.1 Foam initiation and polymer removal in turbulent pipe flow

To test the removal of poly(acrylamide-co-styrene) copolymers from solution I used P(AAm-co-4St) dissolved in aqueous 0.1 M NaCl. These experiments were performed in the ViEDRA set-up. Foaming was initiated by pumping the polymer solution approximately 150 times through ViEDRA and the foam was extracted from the mixing tank after 3-5 pumping cycles.

3.2.3.2 Quantification of polymer removal and molecular weight M_w

GPC measurements to determine M_w or concentration of P(AAm-co-4St) were performed using copolymer solutions prepared in two different ways: P(AAm-co-4St) solutions prepared by re-dissolving P(AAm-co-4St) dry foams, and P(AAm-co-4St) solutions prepared in ViEDRA.

3.2.3.3 Characterisation of liquid polymer foam

The P(AAm-co-4St) stabilised liquid foams generated in ViEDRA were extracted and characterised in a dynamic foam analyser (DFA100, Krüss, Hamburg, Germany). The experimental procedure included filling a glass cylinder with approximately 28 mL of the copolymer solution and subsequently adding ~250 mL of liquid foam on top of the solution. Foam and total foam/liquid volume (V_F and V_T , respectively) were recorded over time to examine the foam stability. The time-dependent liquid content LC was also recorded to analyse the moisture and drainage characteristics of aqueous copolymer foams. The foam structure was characterised measuring the bubble size (mean bubble area, $\overline{MBA}$) and their statistical distribution (bubble count, BC) as a function of time.

3.2.4 P(AAm-co-St) as a macrosurfactant for production of poly(HEMA-co-MBAm)H/MIPE hydrogels

3.2.4.1 Synthesis of macroporous poly(HEMA-co-MBAm)H/MIPE hydrogels

A literature protocol^{29,180} for production of macroporous poly(HEMA-co-MBAm)H/MIPE hydrogels was adapted. Oil-in-water H/MIPE templates comprised ~60 and 70 wt.% internal cyclohexane phase. The aqueous phase was prepared by dissolving P(AAm-co-4St), the comonomers HEMA and MBAm, and initiator APS in deionised water, to which cyclohexane was added slowly over 20 min while vortexing. To produce uniform o/w H/MIPE templates vortexing was extended for further 10 min. Addition of the reducing agent TEMED initiated the polymerisation reaction at room temperature. Polymerisation continued for 1 h. The produced polyH/MIPE hydrogels were placed into a vented oven overnight at 60°C to remove the internal cyclohexane phase prior to drying in a vacuum oven for 48 h at 25°C. The H/MIPE template recipes can be found in the appended **Publication III**. In the **executive summary** of my thesis, I will only discuss macroporous poly(HEMA-co-MBAm)H/MIPE hydrogels produced from H/MIPE templates stabilised by as-synthesised P(AAm-co-4St) containing molar ratio of MBAm of 21 mol.%, since these polyH/MIPE hydrogels were chosen as representative samples for water sorption and mechanical characterisation.

3.2.4.2 Mechanical characterisation of polyH/MIPE hydrogels

A dual column universal testing frame (Instron 5969, Instron Ltd., Buckinghamshire, UK) equipped with a 1 kN load cell was utilised to conduct compression tests on poly(HEMA-co-MBAm)HIPE monoliths. PolyH/MIPE disks 10 mm in height and with diameters of 23 mm were produced for the testing by cutting the polyH/MIPE monoliths. The specimens were compressed at a speed of 1 mm/min to strain of 70% for dry samples and 50% for water swollen specimens. Cyclic compression tests were performed on water swollen hydrogels comprising loading, unloading, and reloading steps. Elastic moduli E_c and crush strengths σ_c were determined from the recorded stress-strain curves.

3.2.4.3 Water sorption of polyH/MIPE hydrogels

PolyH/MIPE hydrogels were immersed into water for up to 18 h and the mass change Δm ($= m_s - m_d$) recorded to determine the water swelling capacity Q :

$$Q = \frac{m_s - m_d}{m_d} \quad (9)$$

with m_s and m_d being the mass of a swollen sample and dry sample, respectively. Water sorption capacity ($= m_s/m_d$) was also determined to ease comparison with literature values.

3.2.5 Morphology of dry macroporous polymers

Scanning electron microscopy (SEM, JCM-6000, JEOL GmbH, Eching, Germany) was used to characterise structure of dry porous polymer. Sample preparation comprised sticking a small quantity of the foam on a carbon tape attached to a SEM sample holder. Electrical conductivity of the dry foams was achieved via gold coating (JFC-1200, JEOL GmbH, Eching, Germany).

4 Summary of Publications: Results and Discussion

4.1 Drag reduction by aqueous solutions of poly(acrylamide-co-styrene) (Publication I)

Liberatore et al.¹³⁵ demonstrated that non-associating PAAm homopolymers having $M_w = 1400$ kg/mol at $c = 0.02$ wt.% produced low DR of up to 5% while PAAm having $M_w = 2500$ kg/mol exhibited significant DR of up to 42%. Amphiphilic associating PAAm having such high M_w ($M_w \geq 1000$ kg/mol) also reduce frictional drag but the effect of aggregations on DR performance of associating hydrophobically modified copolymers with $M_w \geq 1000$ kg/mol remained as of yet unresolved.⁹¹

The weight averaged M_w , viscosity averaged molecular weight M_η , radius of gyration R_g and hydrodynamic radius R_η for individual polymer molecules and polymer associations are summarised in Table 1. Reference samples of commercial PAAm with nominal $M_w = 500$ and 1000 kg/mol were used for comparison exhibiting measured M_w of 290 ± 3 kg/mol and 1134 ± 54 kg/mol, respectively. The copolymers 1P(AAm-co-1St) and 0.7P(AAm-co-1St) generated associations in 0.025 M MgSO_4 , exhibiting two-three times greater M_w compared to M_w of single molecules; M_w of associations were 3200 ± 290 and 2360 ± 680 kg/mol, respectively. It was found that (co)polymers with increased hydrophobic monomer content and shorter molecular chains displayed more prominent aggregation (Table 1). The copolymer 0.5P(AAm-co-2St) containing the highest hydrophobe amount (~ 2 mol.%) had M_w of individual molecules of 600 ± 10 kg/mol in formamide, which in aqueous MgSO_4 associated to $M_w = 20600 \pm 4700$ kg/mol. M_η and R_η were identical in aqueous MgSO_4 and formamide indicating that hydrophobic associations were weak and the shear rate of $\dot{\gamma} \leq 200 \text{ s}^{-1}$ was sufficient to disrupt them.

Table 1. Weight averaged (M_w), viscosity averaged (M_η) molecular weight, radius of gyration R_g , viscosity averaged hydrodynamic radius R_η . The data was obtained using static light scattering, gel permeation chromatography and rheology.

Sample	M_η (kg/mol) ^a	M_w (kg/mol) ^b	M_w (kg/mol) ^c	R_g (nm)	R_η (nm)
PAAm1	1030 [#]	1134 ± 54	1000 ± 50 [#]	70 ± 3 [#]	37 [#]
	950 ^{##}		1400 ± 60 ^{##}	86 ± 2 ^{##}	35 ^{##}
1P(AAm-co-1St)	1310 [#]	1022 ± 30	1180 ± 70 [#]	84 ± 4 [#]	42 [#]
	1370 ^{##}		3200 ± 290 ^{##}	136 ± 4 ^{##}	43 ^{##}
PAAm0.5	310 [#]	290 ± 3	200 ± 10 [#]	27 ± 7 [#]	18 [#]
	190 ^{##}		880 ± 160 ^{##}	110 ± 8 ^{##}	14 ^{##}
0.7P(AAm-co-1St)	720 [#]	730 ± 40	970 ± 70 [#]	113 ± 5 [#]	30 [#]
	470 ^{##}		2360 ± 680 ^{##}	148 ± 13 ^{##}	23 ^{##}
0.5P(AAm-co-2St)	500 [#]	510 ± 30	600 ± 10 [#]	54 ± 2 [#]	24 [#]
	510 ^{##}		20600 ± 4700 ^{##}	224 ± 13 ^{##}	24 ^{##}

^{a, b, c} Weight averaged molecular weight determined using rheometer, gel permeation chromatography and static light scattering, respectively. [#] Results gained in formamide; ^{##} Results gained in aqueous 0.025 M MgSO₄.

The DR capabilities of the P(AAm-co-St) copolymers and commercial PAAm were investigated in turbulent pipe flow at $c = 0.01$ wt.% and $Re = 100\,000$. Flow distances of up to ~2.5 km were achieved by recirculation of (co)polymer solutions in the pipe flow test facility ViEDRA (Figures 13a and 14a). The obtained results for DR(%) were averaged for every cycle and plotted as solid line relative to flow distance with the shaded area in the same colour representing the measurement error. I also tested the DR(%) as a function of Re , which allowed to plot the results in Prandtl-Kármán coordinates (Figures 13b-d and 14b-c) where friction factor in turbulent pipe flow defined by the Prandtl-Kármán law is illustrated as dashed lines and the measured flow of the solvent as the solid lines. It is worth noting that DR experiments in pipe flow for salt solutions were conducted in 0.1 M NaCl instead of MgSO₄ due to the amount of salt needed in ViEDRA.

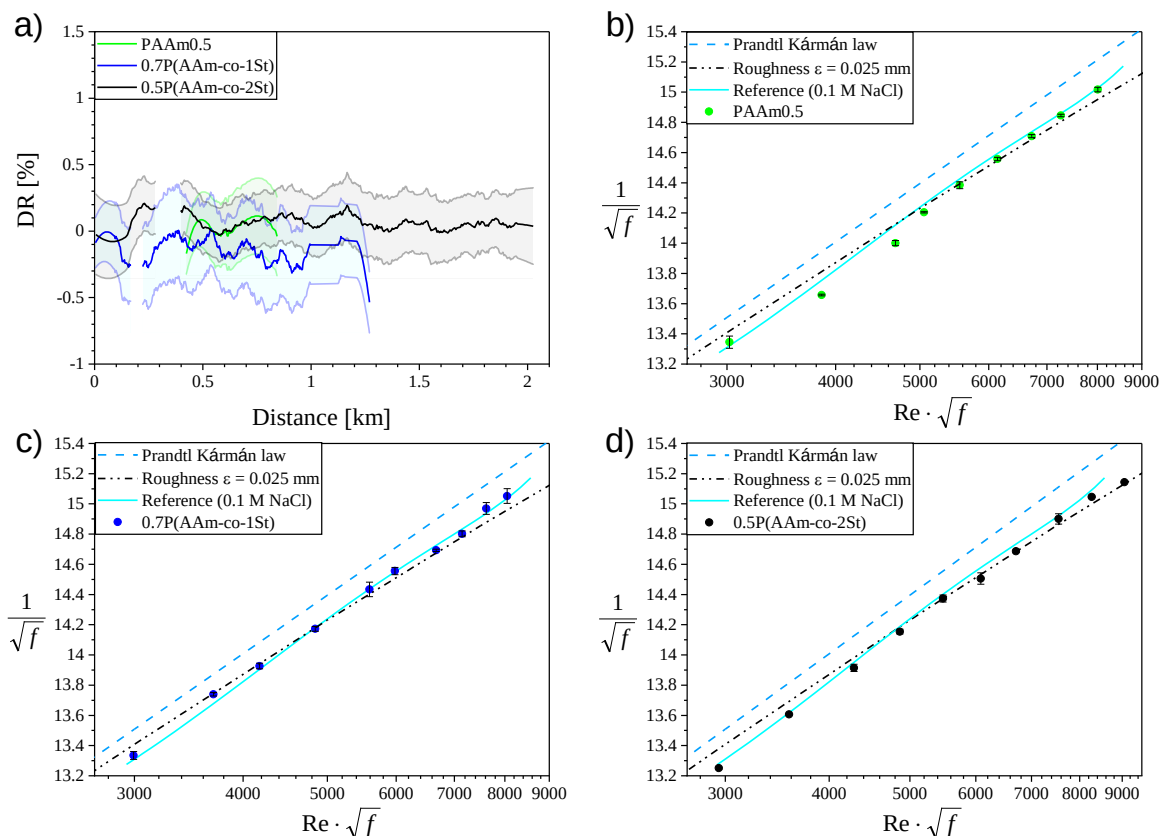


Figure 13. a) Drag reduction DR(%) effect of polymers having $M_w < 1000$ kg/mol in dependence of flow distance in ViEDRA. Constant parameters are: polymer concentration $c = 0.01$ wt.% and $Re = 100\,000$. Prandtl-Kármán graphs for: b) PAAm0.5, c) 0.7P(AAm-co-1St), and d) 0.5P(AAm-co-2St). The impact of pipe roughness is given by the dash double dot line.

For low M_w commercial homopolymer PAAm0.5 no DR(%) was observed but neither for the amphiphilic PAAm of similar molecular weight, regardless of the hydrophobic monomer amount (0.7P(AAm-co-1St) and 0.5P(AAm-co-2St)), despite forming associations in quiescent conditions (Table 1). The absence of DR of the tested polymers having $M_w < 1000$ kg/mol (as determined by GPC) was also seen in the DR(%) measurements at different Re -numbers (Figure 13b-d); the polymer solutions did not exhibit deviation from the behaviour of the pure solvent in Prandtl-Kármán coordinates.

The DR performance of polymers with $M_w \approx 1000$ kg/mol, PAAm1 and 1P(AAm-co-1St), was initially tested in pure water. In order to investigate whether the addition of salt assists the (re)formation of macromolecular aggregations resulting in improved DR, NaCl was subsequently added to the polymer solutions every ~ 0.5 km to achieve salt concentrations of 0.1, 0.5 and 1.0 M (Figure 14a).

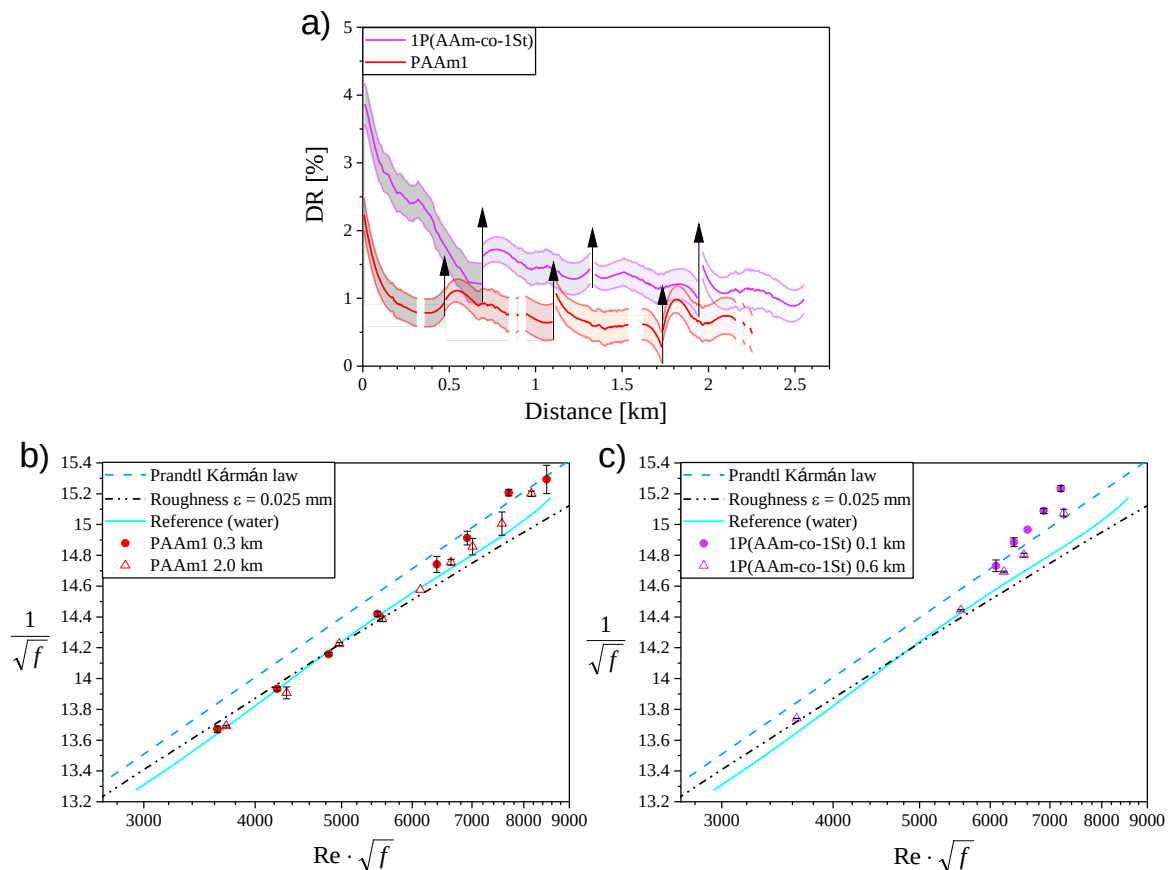


Figure 14. a) Drag reduction DR(%) effectiveness of polymers having $M_w \approx 1000$ kg/mol as function of flow distance in ViEDRA. Constant parameters are: polymer $c = 0.01$ wt.% and $Re = 100\,000$. Salt addition is represented by the upward arrows. Prandtl-Kármán plots for: b) PAAm1 after 0.3 and 2.0 km given by closed and open symbols, and c) 1P(AAm-co-1St) 0.1 and 0.6 km represented by closed and open symbols.

A notable reduction in DR was observed in water as function of flow distance. For hydrophobically modified polymer 1P(AAm-co-1St) DR decreased from 4% to approximately 1.25% and for commercial homopolymer PAAm1 the DR decreased from 2.25% to around 0.75%. This reduction in DR(%) was not related to polymer backbone degradation since the determined M_w of the polymers after travelling various distances through the pipe was unchanged. Thus, it is fair to hypothesise that the reduction in DR(%) was caused by break up of polymer associations, which inhibited the degradation of the polymer backbone. For both polymers, the addition of salt resulted in a minor increase in DR(%), suggesting a possible (re)formation of associations (Figure 14a). The observed increase for PAAm1 was characterised by a rapid decrease, whereas for 1P(AAm-co-1St), the decay in DR was comparatively slower.

My research findings demonstrate that the amphiphilic copolymer 1P(AAm-co-1St) exhibited greater DR efficiency albeit at low level compared to commercial homopolymer PAAm with a similar molecular weight (Figure 14). Despite 0.5P(AAm-co-2St) showing a considerable number of aggregations according to the SLS results (Table 1), its DR performance was found to be similar to that of the reference PAAm0.5. I observed pronounced foaming of P(AAm-co-St) solutions which increased with increasing hydrophobe content in the copolymer. The foaming led to decrease of the effective P(AAm-co-St) concentration in solution affecting their DR effectiveness. Suggested compositional heterogeneity of amphiphilic copolymers⁶⁶ could have also contributed to the association and DR behaviour of P(AAm-co-St), which is elaborated into more detail in the attached **Publication I** but also in section 2.2.1.

4.2 ‘Self-removal’ of poly(acrylamide-co-styrene) from aqueous solution (Publication II)

After observing foaming of associating amphiphilic copolymers P(AAm-co-St) during the investigation of their DR performance in turbulent pipe flows, which I briefly introduced in the previous section, I became interested in exploring the ability of P(AAm-co-St) to ‘self-remove’ from aqueous solutions after DR applications and their potential to stabilise aqueous foams. Hydraulic fracturing is an effective but water-intensive process utilised to increase the extraction of gas and oil from tight reservoirs.⁷ In high-volume hydraulic fracturing operations, polymer DRAs are utilised to decrease the energy required to pump the fracking fluid resulting in enhanced flow efficiency while fracturing the underground rock formations.⁷ Return wastewater after fracking is a significant source of environmental pollution still lacking efficient treatment,^{7,181} which is also complicated by the presence of polymer due to polymer long-term retention in water or the ground.¹⁴³

I used an aqueous ‘fracking fluid’ containing P(AAm-co-4St) as DRA to demonstrate a potential polymer ‘self-removal’ approach allowing to recover the copolymer from aqueous solutions. The ‘self-removal’ capability of P(AAm-co-4St) from a 0.1 M NaCl aqueous solution at $c = 174$ ppm was tested in our pilot-scale test flow facility ViEDRA operated at $Re = 100\,000$ relevant to intended applications. The approach includes foaming the P(AAm-co-St) using external trigger, i.e., sparging gas into fluid or a free-falling liquid. The produced foam is rich in the copolymer because of the copolymer's affinity to adsorb at the air/water interface resulting in a decrease of the polymer concentration in solution. Analysing the refractive index

(RI) response as function of the retention volume (Figure 15) enabled to calculate the concentration of the copolymer remaining in solution and to quantify the degree of polymer removal from 0.1 M NaCl solution. The observed decrease in the RI peak intensity was associated with a decrease of polymer solution concentration from the initial 174 ppm to 78 ppm. ~55% of P(AAm-co-4St) was thus removed from the solution via foaming.

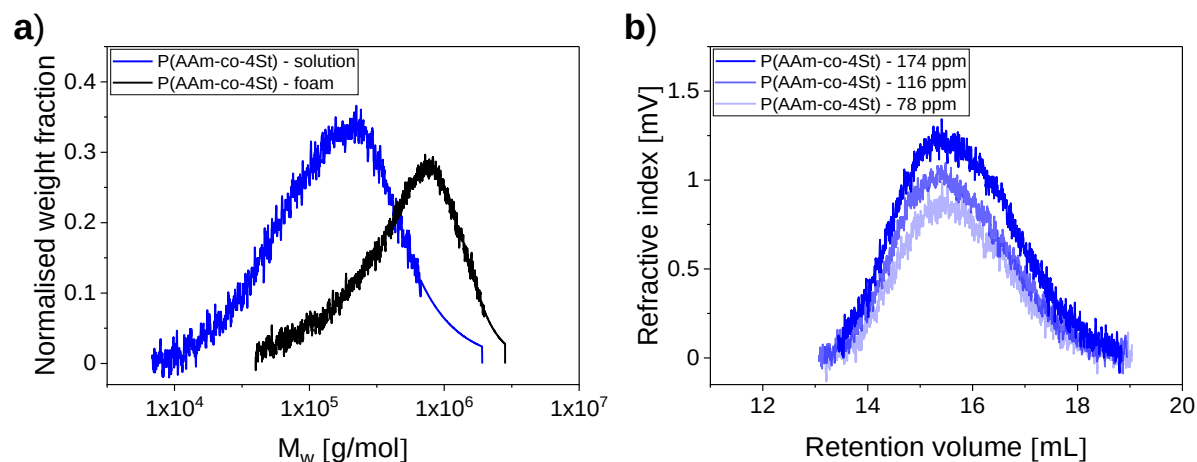


Figure 15. a) Normalised weight fraction as function of molecular weight M_w for P(AAm-co-4St) re-dissolved foam (black) and solution (blue) taken from ViEDRA. b) Recorded refractive index intensity as function of retention volume for P(AAm-co-4St) solutions taken from ViEDRA at various time intervals to follow the P(AAm-co-4St) concentration reduction, which decreased from 174 ppm, 116 ppm to 78 ppm.

The rate at which the foam collapsed over 9 h (Figure 16a-b) was followed to test the stability of liquid foams stabilised by P(AAm-co-4St). The foam was extracted from aqueous 0.1 M NaCl solution from ViEDRA having a nominal bulk solution concentration of $c = 174$ ppm. The foam volume, the liquid content, and the mean bubble area results (Figure 16) showed that P(AAm-co-4St) stabilised aqueous 0.1 M NaCl foam over 9 h with slight bubble coalescence during drying resulting in a polymer foam.

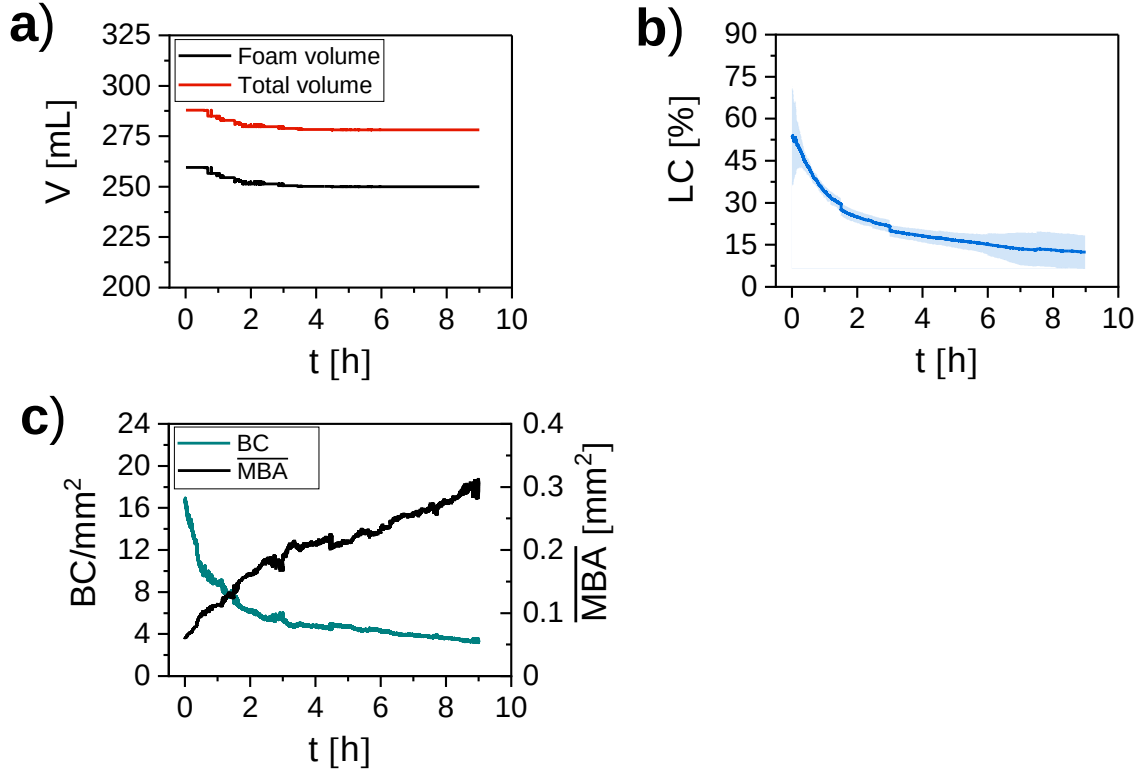


Figure 16. a) Time-dependent volume V of foam and total volume. b) Time-dependent liquid content LC with solid line illustrating average values and shaded area their standard deviation. c) Time dependent bubble count BC per mm² and mean bubble area $\overline{MBA}$. The characterised P(AAm-co-4St) foams were extracted from 0.1 M NaCl solution in ViEDRA.

I further demonstrated that the extracted aqueous P(AAm-co-4St) foam was stable resisting collapse during freeze- or air-drying. Microstructure of the freeze-dried foam experienced partially open cells, with some cells being covered by polymer films (Figure 17a-b), while the air-dried foam (Figure 17c-d) exhibited mainly closed cells.

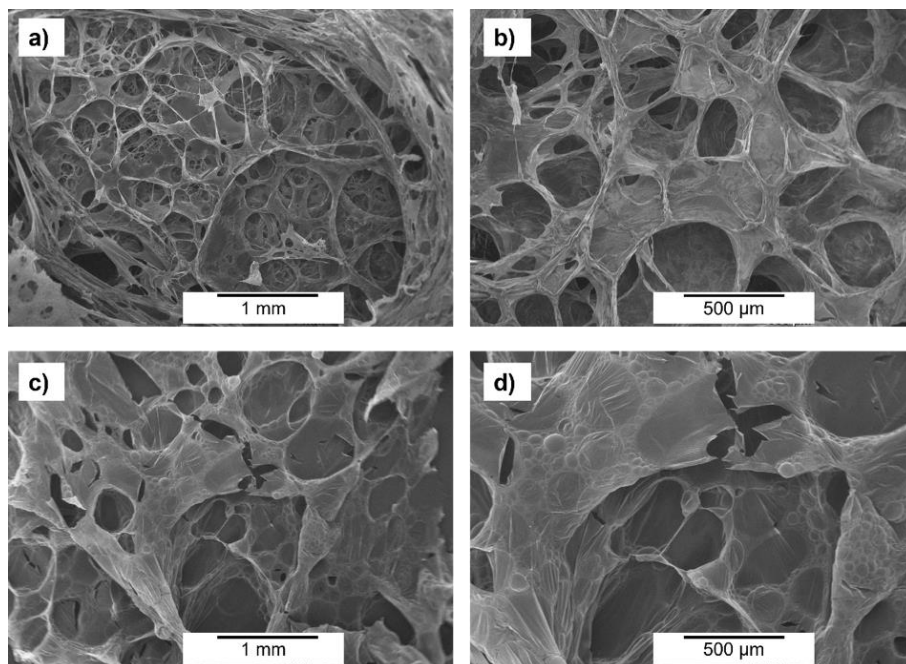


Figure 17. SEM images representing a)-b) freeze-dried and c)-d) air-dried P(AAm-co-4St) foam extracted from ViEDRA.

My results show that the approach I utilised for removing or recovering DRAs after drag reduction applications from fracking fluids by free-falling liquid into aqueous P(AAm-co-St) solutions is a convenient method. The P(AAm-co-St) copolymer extracted from the liquid foam was dried and could be redissolved in water, offering the potential for reuse in further DR applications, especially since mainly high M_w polymer fraction is enriched within the foam. Recovered polymer DRAs could be reused (if not degraded) for DR applications. Alternatively, recovered polymers could be used to stabilise foam or emulsion templates, which are useful for production of macroporous polymer materials.

4.3 P(AAm-co-St) as a macrosurfactant for production of poly(HEMA-co-MBAm)H/MIPE hydrogels (Publication III)

I investigated the suitability of amphiphilic P(AAm-co-St) as a “*macrosurfactant*” to stabilise high or medium internal phase emulsion (H/MIPE) templates to be polymerised yielding macroporous polymers, namely poly(merised)H/MIPES. Forming stable o/w H/MIPE templates involves substantial quantities of relatively costly smaller M_w surfactants.^{24,25} Retention of small-molecule surfactants in the polyH/MIPE structure leads to plasticisation negatively affecting the dimensional stability of the produced porous polymers (Figure 18).²⁷

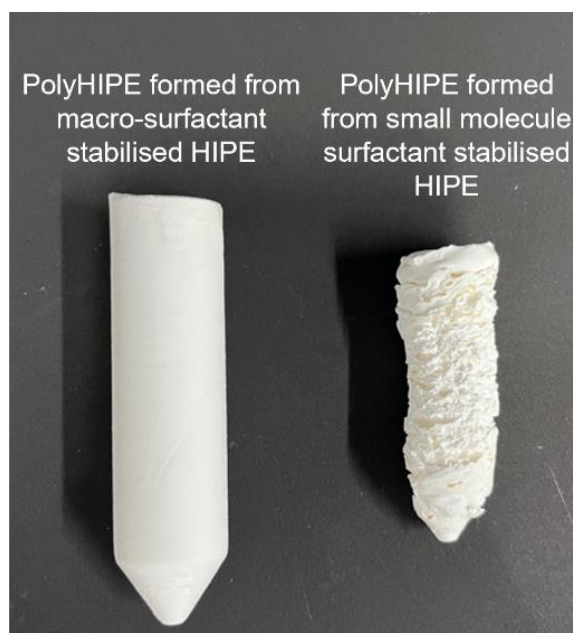


Figure 18. PolyHIPE monolith at the left was synthesised from a HIPE template stabilised by as-synthesised P(AAm-co-4St). PolyHIPE monolith at the right side was synthesised from a HIPE template formulated using a recipe from literature²⁹ stabilised by PVA at $c = 0.73$ wt.% and the small molecule surfactant Triton X-405 at $c = 6.38$ wt.%.

Amphiphilic copolymers were recognised as efficient emulsifiers and are referred to as "macrosurfactants".²¹ I demonstrated that cyclohexane-in-water H/MIPE templates containing 2-hydroxyethyl methacrylate (HEMA) and N,N-methylenebisacrylamide (MBAm) comonomers dissolved in the aqueous continuous phase can be stabilised by as little as 0.1 wt.% of as-synthesised P(AAm-co-4St) still associated with 0.01 wt.% CTAB (as determined using elemental analysis). Polymerisation of these templates yielded macroporous poly(HEMA-co-MBAm)H/MIPEs with porosities ranging between 85% and 90%. The pore structure of polyHIPEs stabilised by 0.1 wt.% of as-synthesised P(AAm-co-4St) was mainly interconnected, while increased macrosurfactant concentration in HIPE templates resulted in polyHIPEs having mainly closed pores—thin P(AAm-co-4St) polymer films partially covered the pore throats (Figure 19).

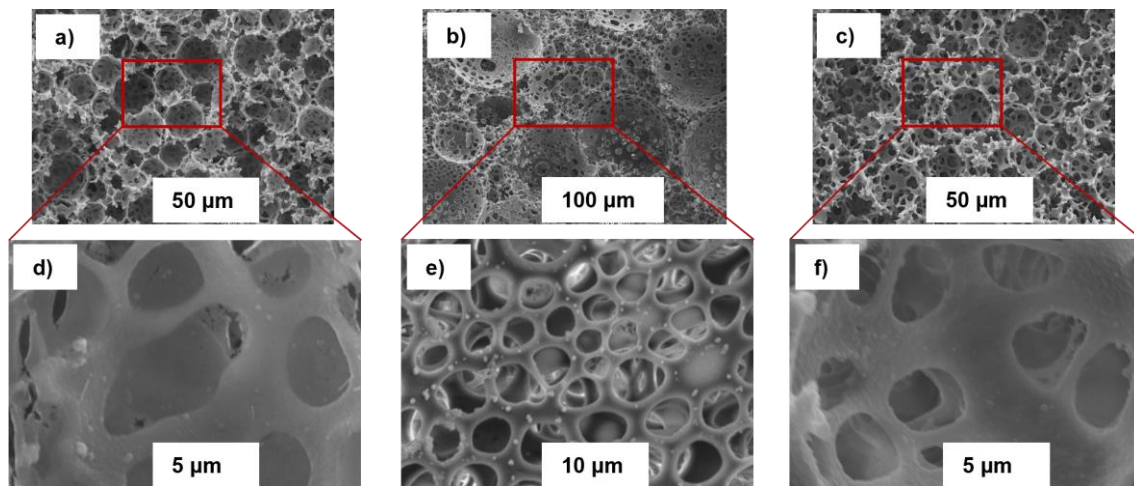


Figure 19. Typical SEM images representing polyHIPEs P8 a) and P8' b), and polyMIPEs P11 c). Typical pore throats of polyHIPEs and polyMIPEs are illustrated by micrographs d), e), and f).

Compression tests were performed on dried polyH/MIPEs to examine their mechanical properties (Figure 20). PolyHIPEs produced from templates stabilised by 0.15 wt.% P(AAm-co-St) (P8) exhibited lower elastic moduli E_c and crush strengths σ_c than polyMIPEs (P11) (Table 2), which was attributed to their lower foam density. Decreasing the P(AAm-co-St) concentration used to stabilise HIPE templates to 0.1 wt.% resulted in stiffer but more brittle polyHIPEs (P8'); P8' possessed an E_c 80% greater than P8 but the same crush strength σ_c .

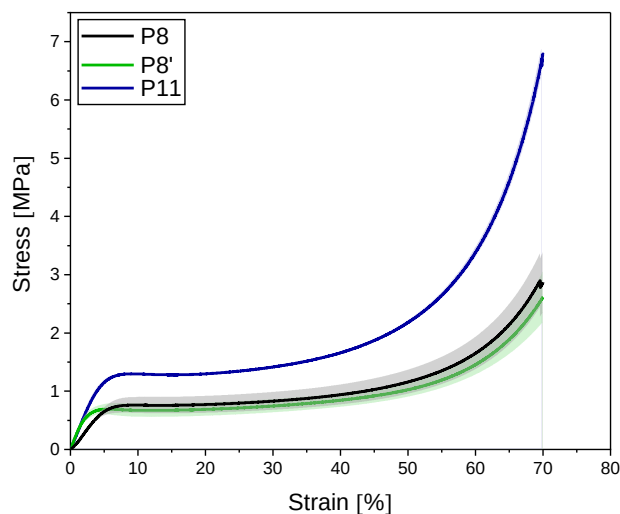


Figure 20. Stress-strain curves from compression tests determined for poly(HEMA-co-MBAm)H/MIPE hydrogels in dry state: P8, P8' and P11. Averaged values are illustrated by solid lines and their standard deviation by shaded areas.

Compared to E_c (~6 MPa) of poly(HEMA-co-MBAm)HIPEs previously reported in the literature,²⁹ E_c of my poly(HEMA-co-MBAm)HIPEs having the same foam densities within

error was over 200% higher. It is probable that the reduced amount of surfactant that I used to stabilise the emulsion templates resulted in a lower plasticising effect caused by any residual small-molecule surfactant in the polyHIPEs.

Table 2. Calculated elastic moduli E_c and crush strengths σ_c for polyHIPEs P8 and P8', and polyMIPEs P11 tested in dry and water swollen states.

Sample	E_c (MPa)	σ_c (MPa)	E_c (kPa)	σ_c (kPa)
	dry		water swollen	
P8	17.3 ± 2.0	0.77 ± 0.14	270 ± 30	22 ± 3
P8'	31.9 ± 1.5	0.70 ± 0.1	400 ± 60	33 ± 3
P11	28.9 ± 2.7	1.33 ± 0.02	440 ± 70	37 ± 7

The water sorption capacities of the dried polyH/MIPEs ranged from 6.2 ± 1.2 to 9.3 ± 1.1 (Figure 21), which are equivalent to water sorption capacities ($= m_s/m_d$) ranging between $720 \pm 120\%$ and $1020 \pm 120\%$. My poly(HEMA-co-MBAm)HIPEs reached their equilibrium water sorption capacity within 2 h, which was significantly faster compared to water sorption capacities of poly(HEMA-co-MBAm)HIPEs reported by Kulygin and Silverstein;²⁹ their polyHIPEs reached maximum water sorption capacities of up to 800% only after 45 h.

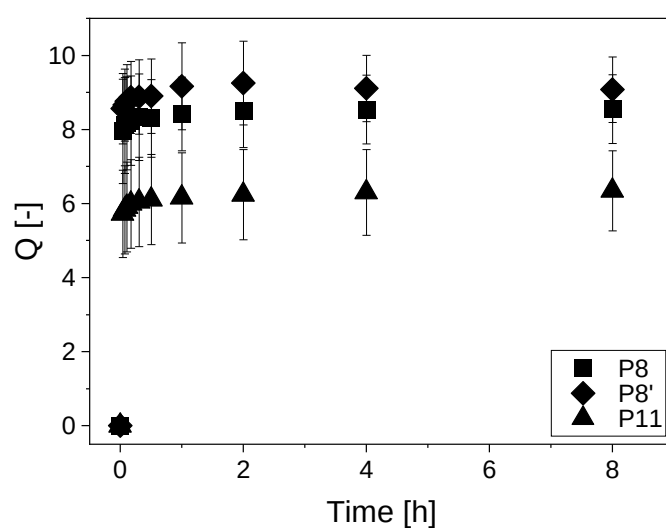


Figure 21. Time-dependent water swelling ratio (Q) for polyHIPEs P8 and P8', and polyMIPE P11.

Cyclic compression tests performed on swollen polyH/MIPEs provided E_c and σ_c values lower than E_c and σ_c obtained by compression of the corresponding polyH/MIPE samples in dry state (Table 2). When compressed, the porous polyH/MIPE hydrogels released water but resorbed 98% of the water during unloading. Upon repeated loading, the polyH/MIPE hydrogels followed the initial loading curves (Figure 22).

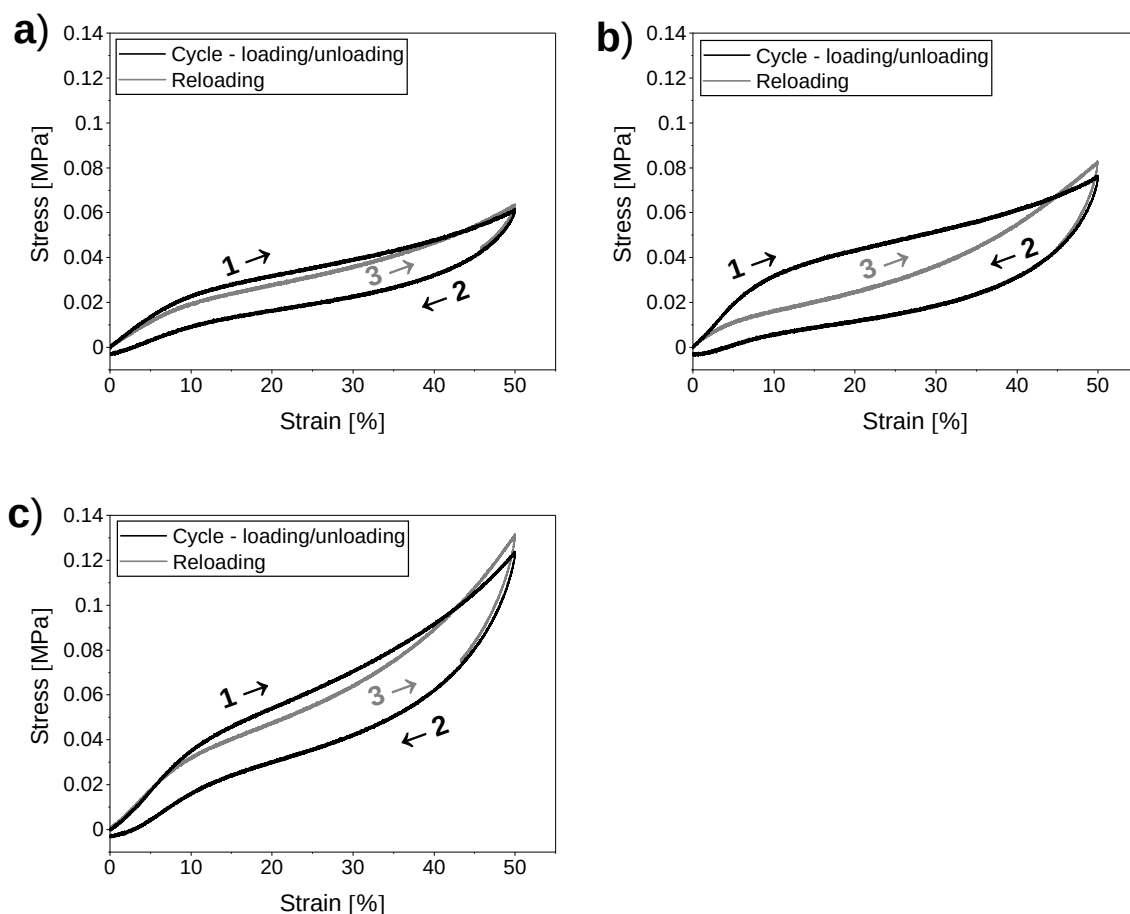


Figure 22. Stress-strain compression curves representing loading, unloading, and reloading measurement steps of swollen poly(HEMA-co-MBAm)H/MIPE hydrogels: a) P8, b) P8' and c) P11.

My results reported in **Publication III** illustrated that using as-synthesised P(AAm-co-4St) still associated with residual CTAB is a convenient approach to reduce required emulsifier amounts to produce stable o/w H/MIPE templates. These H/MIPE templates can be polymerised to yield mechanically robust, porous poly(HEMA-co-MBAm) hydrogels exhibiting great water sorption capabilities.

5 Conclusions and Future Work

5.1 Conclusions

The initial aim of my PhD thesis was to determine the DR capabilities of aqueous solutions of high M_w associations, produced by lower M_w hydrophobically modified copolymers of acrylamide, in turbulent water pipe flow. To accomplish this aim, the first objective was to identify a synthesis technique allowing to fine-tune the aggregation behaviour of copolymers. Micellar copolymerisation was reported to enable control over chemical composition and molecular weight of resulting copolymers providing the control over their association properties. Another advantage of this copolymerisation technique is scalability and simplicity. Thus, I selected micellar copolymerisation to synthesise poly(acrylamide-co-styrene) copolymers and varied acrylamide/styrene molar ratios and M_w . P(AAm-co-St) copolymers with molecular weights $M_w \approx 1000$ and < 1000 kg/mol were produced to assess contribution of hydrophobic associations on DR effect of these copolymers. P(AAm-co-St) formed associations in aqueous 0.025 MgSO₄ solution, which scaled with increasing hydrophobic moiety content and shorter individual polymer molecules. The P(AAm-co-St) copolymer, having $M_w \approx 1000$ kg/mol and lower hydrophobe content, produced increased DR effect (by factor of ~ 2) at a low level compared to reference homopolymer PAAm of similar M_w . P(AAm-co-St), containing higher hydrophobe amount and $M_w < 1000$ kg/mol, did not produce any DR although it exhibited pronounced associating behaviour. These results were explained by considerable foaming of aqueous P(AAm-co-St) solutions, which lowered effective concentration of the copolymers in solution negatively affecting their DR effectiveness. Proposed compositional heterogeneity of copolymers synthesised using micellar copolymerisation is another possible effect to low/no DR performance of P(AAm-co-St).

The foaming of P(AAm-co-St) aqueous solutions during DR experiments in turbulent pipe flows, motivated me to investigate the ability of P(AAm-co-St) copolymers to ‘self-remove’ after DR applications. I used aqueous P(AAm-co-St) 0.1 M NaCl solutions as model DR (fracking) fluids and demonstrated that foaming of such solutions in turbulent pipe flows resulted in the copolymer removal by up to 55%. The copolymer higher M_w fractions enriched in the foam phase. The produced self-standing liquid foams were stable and resisted collapse during freeze- and air-drying resulting in macroporous P(AAm-co-St).

The amphiphilic nature of P(AAm-co-St) effectively reducing air/water surface tensions pointed to their potential to act as macromolecular surfactant, or “macrosurfactant”, for preparation of stable o/w H/MIPE templates to produce superporous hydrogels. P(AAm-co-St), still associated with a low amount of small molecule surfactant (CTAB), enabled the formation of stable cyclohexane-in-HEMA/MBAm dissolved in water H/MIPE templates already at concentrations as low as 0.1 wt.%. These H/MIPE templates were successfully polymerised to yield macroporous poly(HEMA-co-MBAm)H/MIPE hydrogels with porosities reaching 90%. The porous structure of poly(HEMA-co-MBAm)H/MIPE hydrogels was either fully or partially interconnected. Increased P(AAm-co-St) concentration (0.15 wt.%) in the HIPE templates reduced the pore interconnectivity due to formation of polymer films initially adsorbed at the o/w interface stabilising the emulsions, that remained covering the pore throats. These films only partially ruptured. Decreasing the P(AAm-co-St) concentration (0.1 wt.%) in the HIPE templates yielded porous hydrogels exhibiting fully interconnected pores and elastic moduli higher than those for partially open polyHIPEs. Poly(HEMA-co-MBAm)HIPEs I synthesised exhibited much better mechanical properties ($E_c = 32$ MPa) and water uptake values compared to poly(HEMA-co-MBAm)HIPEs found in literature. My polyH/MIPE hydrogels when swollen in water also displayed appealing mechanical behaviour when exposed to cyclic compression.

I demonstrated that P(AAm-co-St) copolymers having $M_w \approx 1000$ kg/mol improve DR in turbulent pipe flows at low DR level compared to the commercial homopolymer PAAm having similar M_w . These copolymers ‘self-remove’ from aqueous solutions by simple method, i.e., sparging gas into solutions, and provide a potential to be reused for further applications. P(AAm-co-St) is also an efficient emulsifier at concentrations significantly lower compared to conventional surfactants.

5.2 Future work

The research findings described in my thesis present a step further in developing effective DR agents for long-term DR applications. It was shown that amphiphilic copolymers with $M_w \approx 1000$ kg/mol of individual polymer molecules exhibited higher DR effect compared to commercial unmodified analogues. Hydrophobically modified copolymers having $M_w \geq 1000$ kg/mol are known to reduce frictional drag. At such high M_w corresponding homopolymers also produce DR and the contribution of hydrophobic associations was unanswered. I aimed at

tackling this research question by producing also amphiphilic copolymers having $M_w < 1000$ kg/mol forming higher M_w associations via hydrophobic interactions. The encountered foaming of amphiphilic copolymer solutions led to reduced concentration of the copolymers in solution and, thus, I was not able to assess the contribution of hydrophobically-driven macromolecular associations on DR performance of amphiphilic copolymers. Rheological investigations suggested that the formed high M_w associations are susceptible to degradation already at low shear rates indicating low ‘bond’ strength. These observations allow for future developments of copolymers forming stronger and larger associations to resist high shear, which ideally are not surface active to avoid adsorption at any interfaces. A first step towards improvements of hydrophobically-driven associations is to identify a polymerisation technique enabling adjustment of copolymer microstructure (without compositional heterogeneity) and M_w . Polymerisation technique should also comprise simple steps and be scalable, due to large amounts of polymer DRAs needed for DR applications. The precise copolymer microstructure needs to be determined to answer the question whether the hydrophobic comonomer is distributed in blocks or smaller units along the hydrophilic polymer backbone.

The observed foaming led to unravelling new possible advanced features of amphiphilic copolymers—to ‘self-remove’ from aqueous solutions after DR applications. I showed that the copolymer ‘self-removal’ can be achieved via a simple, chemical saving approach comprising sparging the gas into solutions. The tested copolymers, previously characterised as DRAs, did not exhibit any/considerable DR effectiveness which partially could be due to reduced polymer concentration in the solution. A compromise between ‘self-removal’ and DR effectiveness is still required. Improved copolymers should provide DR at least 2130 m down a well during hydraulic fracturing which was intended application area for my amphiphilic polymer DRAs. Due to the fact that removed liquid polymer foams yielded dry macroporous polymer foams and were easily re-dissolved in water, it is worth investigating the usefulness of removed polymer DRAs for other applications, such as templating methods to produce macroporous materials.

One of the key insights of my thesis was the production of stable o/w H/MIPE templates using amphiphilic copolymers as macrosurfactants enabling the use of considerably lower emulsifier amounts compared to conventional surfactants. Polymerisation of H/MIPE templates stabilised with macrosurfactants resulted in macroporous hydrogels with better mechanical properties than those previously reported in literature. Further progress in mechanical properties can still be made since polyHIPEs produced from templates stabilised with lower macrosurfactant

amount were strong but brittle. However, increasing the amount of macrosurfactant in HIPE templates resulted in partially closed pores, which might be undesirable for certain applications, such as tissue engineering. The effect of macrosurfactant in the whole process but also on the performance affecting the application of the final product needs to be assessed. Further questions to be answered are: Does the macrosurfactant have to be removed from the final products and if yes, how can it be removed? Potential applications of the superporous polyM/HIPE hydrogels will have to be explored, such as the use as microreactors or for tissue engineering.

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7 Publications

Aqueous Solutions of Associating Poly(acrylamide-co-styrene): A Path to Improve Drag Reduction?

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Cite This: *Macromolecules* 2022, 55, 10479–10490



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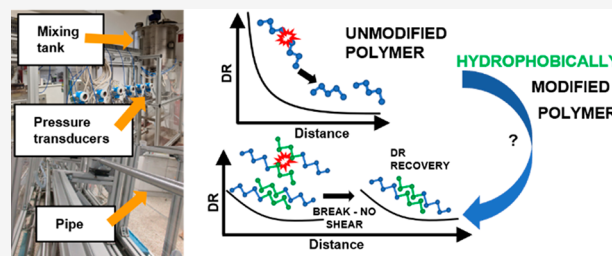


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ABSTRACT: Hydrophobically modified associating polymers could be effective drag-reducing agents containing weak “links” which after degradation can reform, protecting the polymer backbone from fast scission. Previous studies using hydrophobically modified polymers in drag reduction applications used polymers with $M_w \geq 1000$ kg/mol. Homopolymers of this high M_w already show significant drag reduction (DR), and the contribution of macromolecular associations on DR remained unclear. We synthesized associating poly(acrylamide-co-styrene) copolymers with $M_w \leq 1000$ kg/mol and various hydrophobic moiety content. Their DR effectiveness in turbulent flow was studied using a pilot-scale pipe flow facility and a rotating “disc” apparatus. We show that hydrophobically modified copolymers with $M_w \approx 1000$ kg/mol increase DR in pipe flow by a factor of ~ 2 compared to the unmodified polyacrylamide of similar M_w albeit at low DR level. Moreover, we discuss challenges encountered when using hydrophobically modified polymers synthesized via micellar polymerization.



INTRODUCTION

Fully developed turbulence in pipe flows produces frictional drag resulting in dissipation of the input energy driving the flow. Fluid friction can be significantly reduced by the addition of minute amounts of polymers (10–100 wppm) causing an increase in flow rate for a given pressure gradient.¹ This phenomenon, referred to as polymer drag reduction (DR), implies that the pressure drop for dilute polymer solutions passing through a pipe will be notably lower than for the pure solvent at the same flow rate. For this reason, polymer-induced drag reduction is of immense interest for industrial applications, such as efficient pipeline transport of fluids,² hydraulic fracturing and drilling operations,^{3,4} sewers,⁵ fire-fighting,⁶ irrigation systems,⁷ and drift control during spraying in agriculture.⁸

Virk⁹ showed that the molecular weight of flexible polymers is the essential property determining the effectiveness of a polymer drag-reducing agent. It was shown that the shear wall stress in pipe flow is inversely proportional to the molecular weight of the polymer drag-reducing agent.^{9,10} Besides molecular weight, other parameters such as polymer chain flexibility, concentration, molecular structure, and polymer conformation in solution affect drag reduction.^{11–14} For water poly(ethylene oxide) (PEO) and polyacrylamide (PAAm) are most effective, and PAAm is the most commercially used polymeric drag reducer.^{9,15–20} Unfortunately, drag-reducing polymers lose effectiveness due to mechanical degradation caused by high shear in turbulent flow.²¹ The mechanism of

drag reduction is closely related to polymer degradation.^{22,23} Horn and Merrill²⁴ studied the degradation behavior of linear polymers and unveiled that high-molecular-weight polymers are more sensitive to degradation compared with lower molecular weight ones. They observed that macromolecules are greatly stretched before they break, causing backbone scission near the chain midpoint, producing a narrower molecular weight distribution. Similar findings were reported by others.^{25–27} But broader distributions of breaking points are also possible.²⁸ On the other hand, aggregates might be more effective drag reducers than individual polymer molecules since they form structures of higher molecular weight.⁴ Cox et al.²⁹ reported that aggregates of molecules may be important for polymer DR effectiveness since shear is expected to break aggregates rather than the polymer backbone. Aggregations can reform and therefore promote long-term DR. Such polymer associations do occur in aqueous solutions of hydrophobically modified water-soluble polymers, which form micellar structures^{30–36} or a “temporary three-dimensional network in aqueous solutions”,³⁰ which affect the viscosity at various shear rates, offering the potential to be useful drag-reducing agents in

Received: June 11, 2022

Revised: November 11, 2022

Published: November 30, 2022

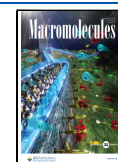


Table 1. Weight Averaged (M_w) and Viscosity Averaged (M_η) Molecular Weight, Polydispersity Index $\mathcal{D}$, Molecular Dimensions in Solution, Namely, Radius of Gyration R_g , Hydrodynamic Radius R_H , Viscosity Averaged Hydrodynamic Radius R_η , Polymer Volume Fraction in Solution ϕ , and 2(Osmotic) Viral Coefficient A_2 ^a

sample	M_η (kg/mol) ^b	M_w (kg/mol) ^c	$\mathcal{D}$	M_w (kg/mol) ^d	R_g (nm)	$A_2 \times 10^{-7}$ (mol dm ³ /g ²)	R_η (nm)	R_H (nm)	ϕ (%) ^e
PAAm1	1030 ^f 950 ^g	1134 ± 54	2.0 ± 0.1	1000 ± 50 ^f 1400 ± 60 ^g	70 ± 3 ^f 86 ± 2 ^g	5.9 ± 0.1 ^f 3.0 ± 0.7 ^g	37 ^f 35 ^g	31 ± 1 ^f 68 ± 2 ^g	1.2 ^f 1.2 ^g
1P(AAm-co-1St)	1310 ^f 1370 ^g	1022 ± 30	1.4 ± 0.0	1180 ± 70 ^f 3200 ± 290 ^g	84 ± 4 ^f 136 ± 4 ^g	3.9 ± 0.8 ^f 4.3 ± 0.4 ^g	42 ^f 43 ^g	24 ± 1 ^f 118 ± 1 ^g	1.5 ^f 1.5 ^g
PAAm0.5	310 ^f 190 ^g	290 ± 3	2.1 ± 0.0	200 ± 10 ^f 880 ± 160 ^g	27 ± 7 ^f 110 ± 8 ^g	6.8 ± 0.4 ^f 5.3 ± 1.3 ^g	18 ^f 14 ^g	16 ± 1 ^f 37 ± 1 ^g	0.5 ^f 0.3 ^g
0.7P(AAm-co-1St)	720 ^f 470 ^g	730 ± 40	1.5 ± 0.1	970 ± 70 ^f 2360 ± 680 ^g	113 ± 5 ^f 148 ± 13 ^g	1.7 ± 0.3 ^f 4.9 ± 0.8 ^g	30 ^f 23 ^g	28 ± 1 ^f 110 ± 1 ^g	0.9 ^f 0.7 ^g
0.5P(AAm-co-2St)	500 ^f 510 ^g	510 ± 30	1.4 ± 0.0	600 ± 10 ^f 20600 ± 4700 ^g	54 ± 2 ^f 224 ± 13 ^g	3.4 ± 0.2 ^f 2.5 ± 0.2 ^g	24 ^f 24 ^g	20 ± 2 ^f 131 ± 1 ^g	0.7 ^f 0.7 ^g

^aThe quantities were extracted from static and dynamic light scattering, gel permeation chromatography, and rheology. ^{b–d}Weight-averaged molecular weight obtained using rheometer, gel permeation chromatography, and static light scattering, respectively. ^eCalculated for a polymer concentration of 0.01 wt %. ^fData obtained in formamide. ^gData obtained in aqueous 0.025 M MgSO₄.

fully developed turbulent pipe flow.^{37–41} We wish to test the hypothesis that high-molecular-weight associations formed by lower molecular weight hydrophobically modified water-soluble polymers can act as efficient drag-reducing agents. Thus far, studies on drag reduction using associating polymers focused only on polymers with molecular weights $M_w \geq 1000$ kg/mol, showing them to be good drag-reducing agents. But already McCormick et al.⁴¹ pointed to the necessity to test associating polymers with lower individual molecular weights at which nonassociating homopolymers do not display drag reduction. This will allow to gain a better understanding of the effect of hydrophobic high-molecular-weight associations on drag reduction.

Investigations of turbulent drag reduction are commonly performed either using various rotating “disc” apparatus^{25,42–45} or in pipe flow setups.^{2,24} However, the flow pattern in both experimental setups is different. To gain comprehensive insights into polymer-induced drag reduction, an appropriate combination of measuring techniques is of utmost importance. We set out to test the influence of the association behavior of hydrophobically modified polymers on drag reduction performance at application-relevant conditions using a pilot-scale flow facility. We use a pressure-driven horizontal pipe flow device to simulate long pipelines and thus ensure real-time drag reduction measurements. In addition, we use a double-gap geometry to compare polymer DR behavior in a rotating “disc” apparatus to that in a horizontal pipe. We synthesized poly(acrylamide-co-styrene) with molecular weights at which pure PAAm does not produce significant drag reduction and varied the hydrophobe content in the polymer, since associative properties are more pronounced with increasing content of hydrophobic moieties³⁰ and incorporation of aromatic groups.⁴⁰ We present the effect of hydrophobe content in the polymer main chain on the association, rheological, and drag reduction behavior.

EXPERIMENTAL SECTION

Materials. Acrylamide (AAm) ($\geq 99\%$, Sigma-Aldrich) was recrystallized twice from acetone ($\geq 99.5\%$, Donauchem). Styrene (St) ($\geq 99\%$), potassium persulfate (K₂S₂O₈, $\geq 99\%$), hexadecyltrimethylammonium bromide (CTAB, $\geq 98\%$), sodium azide (NaN₃, $\geq 99.5\%$), sodium nitrate (NaNO₃, $\geq 98\%$), deuterium oxide (D₂O, 99.9 atom % D), formamide ($\geq 99\%$), and magnesium sulfate (MgSO₄, $\geq 99.5\%$) were purchased from Sigma-Aldrich and

used without further purification. Methanol ($\geq 99.8\%$, Fisher Scientific) and potassium chloride (KCl, 99.5%, BDH, VWR) were used as received. Polyacrylamides with nominal molecular weights $M_w = 0.5$ (PAAm0.5) and $M_w = 1.0 \times 10^6$ g/mol (PAAm1) were kindly provided by SNF Floerger (Andrézieux, France). Poly(ethylene oxide) ($M_w = 24 \times 10^3$ g/mol, PEO-24K) and dextran ($M_w = 69 \times 10^3$ g/mol, Dextran-T69K) standards were purchased from Malvern. Dishwasher salt (sodium chloride, NaCl) (Tandil) was bought from Hofer. Nitrogen ($\geq 99.999\%$, Messer) was used to provide an inert atmosphere during synthesis. The dialysis tubing (Bio Design, Thermo Fisher Scientific) used for purification of polymers had a molecular weight cutoff (MWCO) of 8000 Da. Deionized water (conductivity of 0.055 μ S/cm, Water Purifier, Elga, UK) was used for all experiments, except for the flow facility.

Synthesis of Poly(acrylamide-co-styrene). Poly(acrylamide-co-styrene), P(AAm-co-St), copolymers were synthesized via micellar polymerization adapting a previously reported method³⁶ to vary the hydrophobe content in the polymer chain. PAAm, without hydrophobe incorporated, was also synthesized as a reference for the structure analysis using NMR. Either 3.50 g (9.60 mmol) or 1.48 g (4.06 mmol) of CTAB was dissolved in 50 mL of deionized water in a round-bottom flask under magnetic stirring followed by addition of 37.27 mg (0.36 mmol) or 74.54 mg (0.72 mmol) of styrene for 1 mol % or 2 mol % hydrophobe content in the copolymer. The mixture was stirred overnight to enable micellization. Afterward, 2.50 g (35.17 mmol) of AAm was dissolved in the reaction mixture for ~ 30 min. The mixture was degassed by three freeze–pump–thaw cycles using a Schlenk line. The initiator solution was prepared by dissolving K₂S₂O₈ (88.25 mg, 0.33 mmol) in 2 mL of deionized water. This solution was degassed by nitrogen injection. The reaction mixture was heated to 80 °C, and the initiator solution injected using a degassed syringe. This mixture was continuously purged with nitrogen. After 24 h the reaction was stopped by cooling in ice water. The polymer was precipitated by dropwise addition into methanol under gentle stirring. The white precipitate was stirred in methanol overnight, and the solid removed by filtration, redissolved in deionized water, and again precipitated in methanol. This purification process was repeated twice. To purify the polymer further, it was dissolved in water and then dialyzed against ~ 4 L of deionized water for 10 d. The polymer was recovered by freeze-drying.

The polymerization yield (Y) was determined as follows:

$$Y(\%) = \frac{W_p}{W_M} \times 100 \quad (1)$$

where W_p is the weight (g) of the purified polymer and W_M that of the monomers. The yields for all the synthesized polymers after dialysis ranged between 85% and 95%.

The copolymers are denoted as 1P(AAm-co-1St), 0.7P(AAm-co-1St), and 0.5P(AAm-co-2St); the first number denotes their molecular weight in 10^6 g/mol as determined by gel permeation chromatography (see Table 1) and the second the molar ratio of St/AAm, which was either 1 or 2 mol %.

Characterization of Poly(acrylamide-co-styrene). ^1H NMR spectra were acquired in D_2O using a 600 MHz NMR (Bruker BioSpin, Rheinstetten, Germany) and processed using TopSpin 4.0.9. The amount of incorporated styrene in P(AAm-co-St) was calculated as follows:

$$\text{St(mol \%)} = \frac{2I_{7.3 \text{ ppm}}}{3I_{1.5-1.8 \text{ ppm}} + 2I_{7.3 \text{ ppm}}} \times 100 \quad (2)$$

where $I_{7.3 \text{ ppm}}$ represents an integral of a triplet corresponding to protons of phenyl groups ($-\text{C}_6\text{H}_5$) and $I_{1.5-1.8 \text{ ppm}}$ an integral of protons corresponding to methylene ($-\text{CH}_2-$) groups present in the polymer backbone.

Dynamic and Static Light Scattering. Dynamic (DLS) and static light scattering (SLS) were performed using a compact goniometer system (ALV/CGS-3, Langen, Germany) equipped with a 22 mW helium–neon laser (632.8 nm). Samples for light scattering measurements were prepared as follows: the polymer was dissolved in formamide to obtain nonassociated polymer solutions as well as in an aqueous solution of 0.025 M MgSO_4 to allow for polymer associations to form by screening any residual charges. Stock solutions were first shaken at 200 rpm using an orbital shaker (PSU-10i, Biosan) for 48 h. Then they were heated for an additional 48 h at 50 °C accompanied by mechanical mixing at 100 rpm using a magnetic stirrer (RCT basic, IKA) equipped with a temperature sensor (PT 1000.60). The stock solutions were diluted to concentrations ranging from 0.005 to 0.06 wt % for those prepared in aqueous MgSO_4 solutions, while those prepared in formamide from 0.01 to 0.2 wt %. Prior to DLS and SLS measurements, all the solutions were filtered through 0.45 μm filters (CHROMAFIL Xtra PVDF-45/25) to remove dust particles present. To eliminate any impurities, the filters were always first rinsed with solvent followed by flushing the filters with ~ 2 mL of a sample solution to prevent polymer retention by the filters.

The molecular weights of single polymer molecules and macromolecular associations were determined via SLS. The SLS measurements were carried out at scattering angles (30–130°) in 10 angular steps. The refractive index increment (dn/dc) was determined using a differential refractometer (Brookhaven BI-DNDC). A minimum of five concentrations was used to determine the apparent weight-average molecular weight M_w , radius of gyration R_g , and second virial coefficient A_2 using either the Zimm or Berry data reduction method, processed by ALV-Fit and Plot software. Data points at low angles that were considerably deviating from linearity were excluded in the analysis.

DLS measurements were performed at a goniometer angle of 90° to determine the hydrodynamic radii (R_H) of polymer molecules/aggregates. The measured correlation function was transformed into the translational diffusion coefficient D and converted into R_H using the Stokes–Einstein relation:

$$R_H = \frac{k_B T}{6\pi\eta D} \quad (3)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η the viscosity of the solvent.

Rheological Characterization. The rheological measurements were carried out using a rheometer (TA Instruments Discovery HR-2) at 25 ± 0.1 °C. The temperature was controlled using a water circulatory thermostat (Thermo Cube). Linear viscoelasticity and dynamic experiments were performed. The rheometer was also used as a rotary “disk” apparatus to assess DR capabilities of polymer solutions on a small scale. Stock solutions were prepared at concentrations of approximately 8 wt % polymer in water. MgSO_4 was added to the dilute solutions to a concentration of 0.025 M. Experiments with polymer concentrations ranging from 0.0001 to 0.9

wt % were performed in a double-gap cylindrical geometry ($d_1 = 30.20$ mm, $d_2 = 32.03$ mm, $d_3 = 34.99$ mm, $d_4 = 37.00$ mm, and rotor height $L = 55.00$ mm), while for polymer solutions with concentrations from 2 to 8 wt % a cone–plate geometry ($d = 40.00$ mm, cone angle 1°) was used. Sample volume in the double-gap geometry was 12 mL, and 0.3 mL in cone–plate geometry. Viscosity measurements were performed at a constant shear rate of 10 s^{-1} for 90 s. The runs were repeated four times and values averaged. The shear rate dependence of viscosity was acquired in a shear rate-controlled mode. The shear rate was increased in steps, and when equilibrium was reached, data were taken for 10 s. Three shear rate intervals were chosen for these experiments depending on solution viscosity (concentration): $1\text{--}120 \text{ s}^{-1}$, $1\text{--}140 \text{ s}^{-1}$, or $1\text{--}1000 \text{ s}^{-1}$. The limit of the linear viscoelastic region was determined prior to the dynamic measurements using a strain-controlled amplitude sweep. The dynamic measurements were conducted at a frequency of $1\text{--}200 \text{ rad/s}^{-1}$. All measurements were performed at a constant strain of 0.1 that led to a linear response.

The viscosity averaged molecular weight M_η was determined from the measured viscosities at dilute concentrations using the Mark–Houwink equation. We used the Mark–Houwink parameters $K = 9.33 \times 10^{-3} \text{ cm}^3/\text{g}$ and $\alpha = 0.75$ determined in 0.1 M NaCl solution,⁴⁶ as its ionic strength is equivalent to that of 0.025 M MgSO_4 . The intrinsic viscosity $[\eta]$ was determined from measured viscosities as follows:⁴⁷

$$[\eta] = \frac{1}{c_m} \left[3 \ln \eta_r + \frac{3}{2} \eta_{sp}^2 - 3\eta_{sp} \right]^{1/3} \quad (4)$$

where c_m is the polymer mass concentration in g/mL and η_r the relative and η_{sp} the specific viscosity. The viscosity averaged hydrodynamic radii R_η were calculated from $[\eta]$

$$R_\eta = \left[\frac{3[\eta]M_\eta}{10\pi N_A} \right]^{1/3} \quad (5)$$

where N_A is Avogadro's number.

Errors for M_η , R_η , and φ calculated from viscosities data were lower than 0.001% and thus are not presented in Table 1.

DR characterization in Taylor flow on a small characteristic length scale was performed in the rheometer equipped with the double-gap geometry using the method described by Nakken et al.⁴⁴ and Pereira et al.¹⁸ The double-gap measuring cell has a large contact area and, therefore, allows for good reproducibility.¹⁸ The onset of Taylor flow is visible by an abrupt change of the slope of the function $\eta = f(\dot{\gamma})$ where $\dot{\gamma}$ is the shear rate. Taylor flow onset was detected by increasing the shear rate in steps from 100 to 3000 s^{-1} , enabling equilibrium at each step. The critical shear rate $\dot{\gamma}_c$ at Taylor flow onset was determined by a piecewise linear fit to $\eta = f(\dot{\gamma})$ in the region around $\dot{\gamma}_c$. $\dot{\gamma}_c$ was then converted to the critical angular velocity ω_c :¹⁸

$$\dot{\gamma}_c = K\omega_c = K \frac{2\pi}{60} n \quad (6)$$

where n is the speed of rotation and K a geometrical factor: $K = \frac{2R_4^2}{R_4^2 - R_3^2} \approx \frac{2R_2^2}{R_2^2 - R_1^2}$, where R_i are the radii of the geometry. The apparent viscosity at the Taylor flow onset was calculated as follows:⁴⁴

$$\left(\frac{\rho\omega_c}{\eta} \right)^2 = \frac{\pi^4(\delta + 1)}{2(\delta - 1)^3 r_3^4} \times \frac{1 - 0.652(\delta - 1)}{0.00056 + 0.0571[1 - 0.652(\delta - 1)]^2} \quad (7)$$

where ρ is the solution density, η the apparent viscosity at onset, and δ the ratio of the distance between rotor and stator $\delta = R_4/R_3 = R_2/R_1$.

DR is defined as

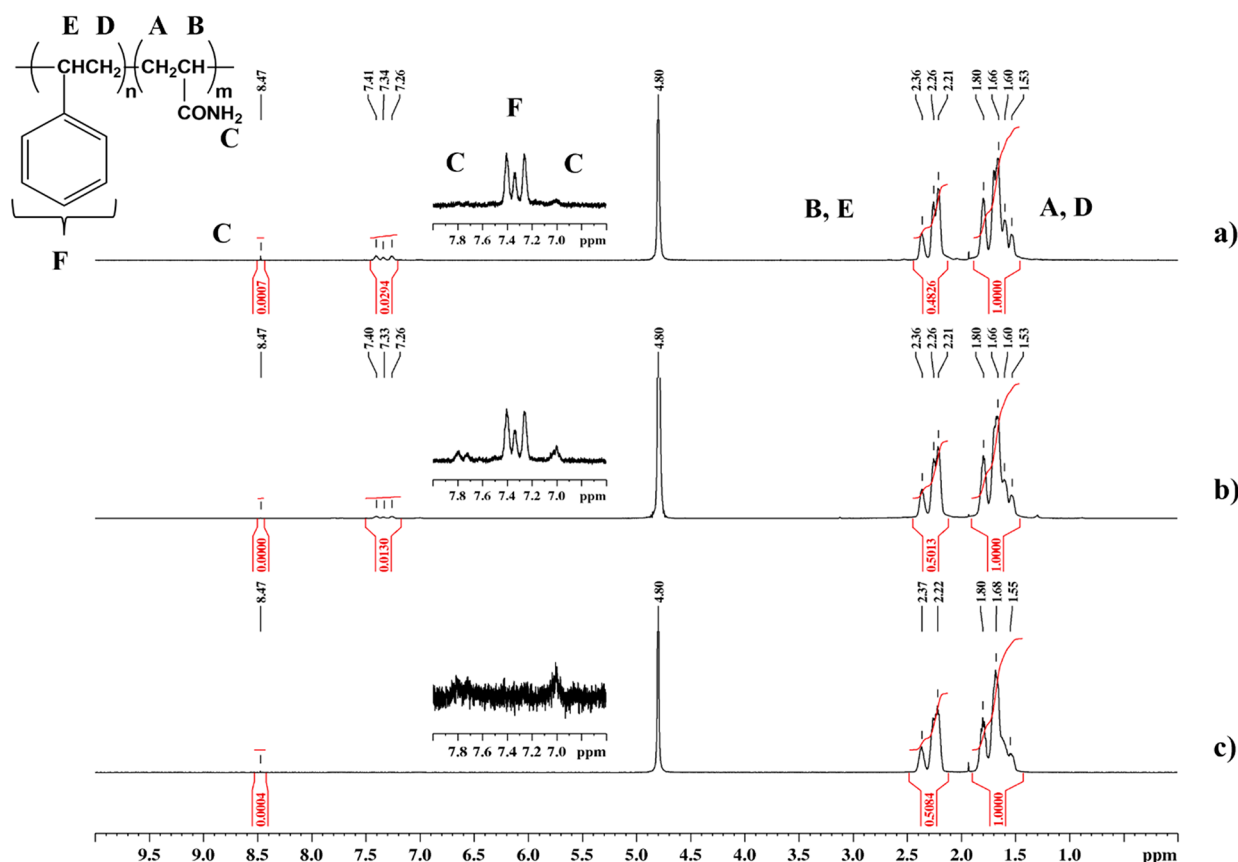


Figure 1. ^1H NMR spectra recorded in D_2O for (a) 0.5P(AAm-co-2St), (b) 0.7P(AAm-co-1St), and (c) PAAm homopolymer.

$$\text{DR}(\%) = \left(\frac{f_s - f_p}{f_s} \right)_{Re=\text{const.}} \times 100\% \quad (8)$$

where f_s and f_p are the Fanning friction factors of pure solvent and polymer solution. f is calculated as follows:¹⁸

$$f = \frac{2\tau}{\rho u^2} = \frac{2\tau}{\rho(\omega \bar{R})^2} \quad (9)$$

where τ is the shear stress, u the linear velocity, and $\bar{R}$ the mean radius: $\bar{R} = \frac{R_2 + R_3}{2}$.

τ was determined from the measured torque exerted on the rotor T :

$$\tau = \frac{T(1 + \delta^2)}{4\pi L(\delta^2 R_3^2 + R_2^2)} \quad (10)$$

The Reynolds number Re for the flow in the double-gap geometry is defined as¹⁸

$$Re = \frac{\rho \bar{h} u}{\eta} = \frac{\rho(\bar{h})(\omega \bar{R})}{\eta} \quad (11)$$

where $\omega \bar{R}$ is the characteristic velocity and $\bar{h}$ the average gap width calculated as follows: $\bar{h} = \frac{1}{2}((R_2 - R_1) + (R_4 - R_3))$.

Vienna Experiment for Drag-Reducing Agents. The characterization of the DR capability in turbulent pipe flow was performed in our pilot-scale flow facility called Vienna Experiment for Drag Reducing Agents (ViEDRA). Large volumes (up to 300 L) of polymer solutions were prepared in a mixing tank. Compressed air was used to drive the solution through a system of pipes and hoses of a total length of ~ 20 m per cycle. This includes a 7.2 m long stainless-steel pipe with an inner diameter of 26 mm representing the test section. Along this test section six differential pressure sensors are located

(Deltabar S, Endress+Hauser, Germany). The measured pressures allow for calculation of the fanning friction factor f using the Darcy–Weisbach relation:

$$f = \frac{\Delta p}{l} \frac{d}{2\rho U^2} \quad (12)$$

where Δp is the pressure drop along the test section, l the length of the test section, d the pipe diameter, ρ the solution density, and U the volume averaged velocity.

The flow rate is measured using a magneto-inductive flowmeter (Sitrans F M Magflo MAG5000, Siemens, Denmark). A feedback controller adjusts the driving pressure and allows for experiments at constant flow rate and thus with constant $Re = \frac{\rho d U}{\eta}$.

Each polymer solution was cycled multiple times through ViEDRA in order to investigate the degradation of the DR agents. Details on the flow device will be published elsewhere.

Gel Permeation Chromatography. M_w and polydispersity D of the polymers were determined using a triple detection GPC system (Viscotec TDA 302, Malvern Panalytic) equipped with a solvent reservoir, a degasser (CSI6150 4 channel degasser, laserchrom), a high-performance liquid chromatography (HPLC) pump (LC-20 ADV, Shimadzu Deutschland GmbH), and an automatic sample injector (S5200 Sykam GmbH). The polymer molecules were separated according to their hydrodynamic volumes using a guard column (A-Guard, Viscotek, Malvern) and two analytical columns (A4000 with an exclusion limit of 1×10^6 g/mol and A6000 M with an exclusion limit of 20×10^6 g/mol). The postcolumn filter had a pore size of 0.2 μm (Nylon Membrane Filters, Whatman). A PEO standard ($M_w = 23\,651$ g/mol) in combination with a validation standard of dextran ($M_w = 68\,991$ g/mol) was used to calibrate the detectors. The temperature was kept constant at 30 $^\circ\text{C}$. The aqueous eluent contained 0.1 mol/L NaNO_3 and 0.02 wt % NaN_3 . The flow rate during the measurements was kept constant at 0.7 mL/min. Prior

to the measurements, the polymer samples were filtered through a $0.45\ \mu\text{m}$ filter. The chromatograms were analyzed using the OmniSEC 5.02 software.

RESULTS AND DISCUSSION

^1H NMR spectra (Figure 1) of hydrophobically modified and pure PAAm exhibited strong signals at ~ 1.53 – 1.80 and 2.21 – 2.37 ppm corresponding to methylene ($-\text{CH}_2-$) and methine ($>\text{CH}-$) protons present in the polymer backbone, while the weak signals at ~ 7.0 , 7.8 , and 8.47 ppm were assigned to amide groups ($-\text{CONH}_2$). The signal at 4.80 ppm corresponds to solvent D_2O (or HOD). Copolymers additionally exhibited a weak triplet in the range 7.26 – 7.41 ppm corresponding to the protons of phenyl groups ($-\text{C}_6\text{H}_5$), which is stronger for $0.5\text{P}(\text{AAm-co-2St})$, which contained ~ 2 (actual amount 1.92) mol % St (Figure 1a) in its backbone when compared to $0.7\text{P}(\text{AAm-co-1St})$, containing 0.86 mol % St (Figure 1b). It is noteworthy that the amounts of St incorporated in $\text{P}(\text{AAm-co-St})$ were in good agreement with the amounts of St added to the reaction mixture. The ^1H NMR spectra of $0.7\text{P}(\text{AAm-co-1St})$ and $1\text{P}(\text{AAm-co-1St})$ are identical (see SI, Figure S1), and the St content in $1\text{P}(\text{AAm-co-1St})$ was found to be 0.92 mol %. Elemental analysis confirmed that the polymers comprised C, H, N, and O (Table S1). Additionally, bromine (Br) from CTAB was detected, which remained in the sample after purification. The Br amount was found to be <0.01 wt %, indicating that most CTAB was successfully removed during polymer purification.

Molecular Dimensions. The molecular weight, molecular dimensions in solution, and second virial coefficient A_2 are summarized in Table 1. Using SLS we determined M_w , R_g , and A_2 . M_w was also obtained using GPC. In addition, we calculated M_η and R_η from measured viscosities. Two commercial PAAm with nominal molecular weights 500 and 1000 kg/mol, similar to those synthesized, were utilized as control samples; their M_w obtained using GPC were 290 ± 3 and 1134 ± 54 kg/mol, respectively. Macromolecular associations, which formed in 0.025 M MgSO_4 of $1\text{P}(\text{AAm-co-1St})$ and $0.7\text{P}(\text{AAm-co-1St})$, had M_w 's of 3200 ± 290 and 2360 ± 680 kg/mol, respectively, which is approximately two or three times higher than the M_w of individual molecules as determined by GPC and SLS in formamide. $0.5\text{P}(\text{AAm-co-2St})$, having a M_w of single chains of 600 ± 10 kg/mol in formamide (Figure S2), formed macromolecular associations in aqueous MgSO_4 solution (Figure S3) with a M_w of $20\,600 \pm 4700$ kg/mol. It is worth noting that the polymer molecular weights determined by different measurements were in quite good agreement.

The hydrophobically modified polymers synthesized as well as the commercial control PAAm can be classified into two groups with similar molecular weights ($M_w \approx 1000$ kg/mol and $M_w < 1000$ kg/mol). It is important to point out that these two groups were selected on the basis of M_w determined by GPC measurements. The reason for selecting GPC M_w data is that we tracked M_w of polymers during DR measurements in ViEDRA using GPC. In all cases the values of A_2 were positive. Thus, all polymers were dissolved in "good" solvents in the dilute range having a polymer volume fraction in solution $\phi < 0.20$ ⁴⁸ for subsequent drag reduction measurements. From SLS it is obvious that all polymers tend to associate in aqueous 0.025 M MgSO_4 solution (see Table 1). This is more pronounced for polymers containing hydrophobic blocks and for shorter individual chains. R_H from DLS (Figure S4)

support these observations. The molecular weight derived from viscosity M_η is not affected when changing from formamide to aqueous MgSO_4 . R_η remains approximately constant. Possibly the shear rate of $\dot{\gamma} \leq 200\ \text{s}^{-1}$ is already sufficiently high to break up hydrophobic associations.

Rheological Properties. The viscoelastic behavior of the polymers was characterized by measuring the concentration dependence of zero-shear viscosity η_0 , the shear rate dependence of apparent viscosity η , and frequency dependencies of the storage G' and loss G'' moduli. The polymer dynamics is greatly influenced by configurational interactions that restrict movement of polymer chains.⁴⁹ These configurational restrictions are not prominent in dilute solutions, but the dynamic polymer properties are controlled by translation and rotation of the chains.⁴⁹ Due to low polymer c in dilute solutions, their viscosity is governed by the solvent viscosity and only the weak polymer contribution depends on c . At high polymer c for which $\eta_0 \gg \eta_{\text{solvent}}$, the η_0 increases steeply as described by the power law $\eta_0 \sim c^\alpha$ with $\alpha = 3.75$.⁴⁹ This steep increase in viscosity is caused by polymer molecular entanglements⁴⁹ affecting the polymer diffusion. We can distinguish dilute and semidilute entangled regimes based on $\eta_0 = f(c)$.³³ The transition between these two concentration regimes is defined as a semidilute unentangled regime.³³ The semidilute unentangled regime sets in at the first abrupt change in slope of $\eta_0 = f(c)$ denoting the overlap of polymer chains, with c^* being the overlap concentration. The second change in slope represents entanglement of polymer chains with the corresponding concentration being the entanglement concentration c_e , and the semidilute entangled regime comes into play. Viscosity of polymer solutions in the entangled state will depend on polymer chain length referring to the molecular weight via the relation $\eta_0 \sim M^\alpha$ with $\alpha = 3$.⁴⁹

Regalado et al.³³ related c^* of unmodified polymers to the concentration where hydrophobically modified copolymers start to aggregate. Thus, we compared the concentration dependence of η_0 of $0.7\text{P}(\text{AAm-co-1St})$ and $0.5\text{P}(\text{AAm-co-2St})$ to that of PAAm0.5 (Figure 2). The two copolymers having different hydrophobe amounts exhibited similar c^* obeying the relation $c^* \propto M^{-0.8}$, which agrees with the observations made by Regalado et al.³³ c^* was scaling with molecular weight of

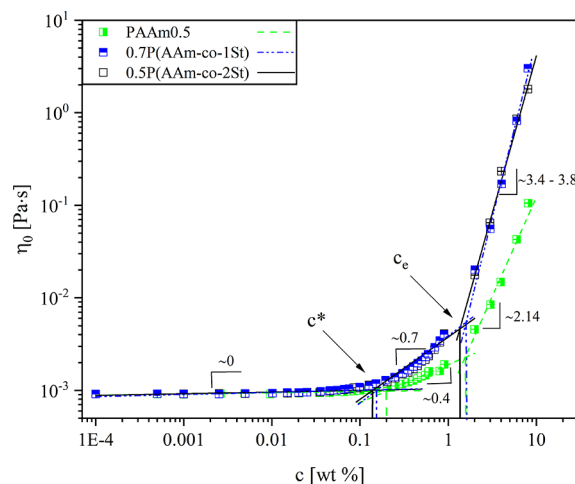


Figure 2. Influence of the hydrophobe amount on concentration c dependence of the zero-shear viscosity η_0 determined in aqueous 0.025 M MgSO_4 for polymers with $M_w < 1000$ kg/mol.

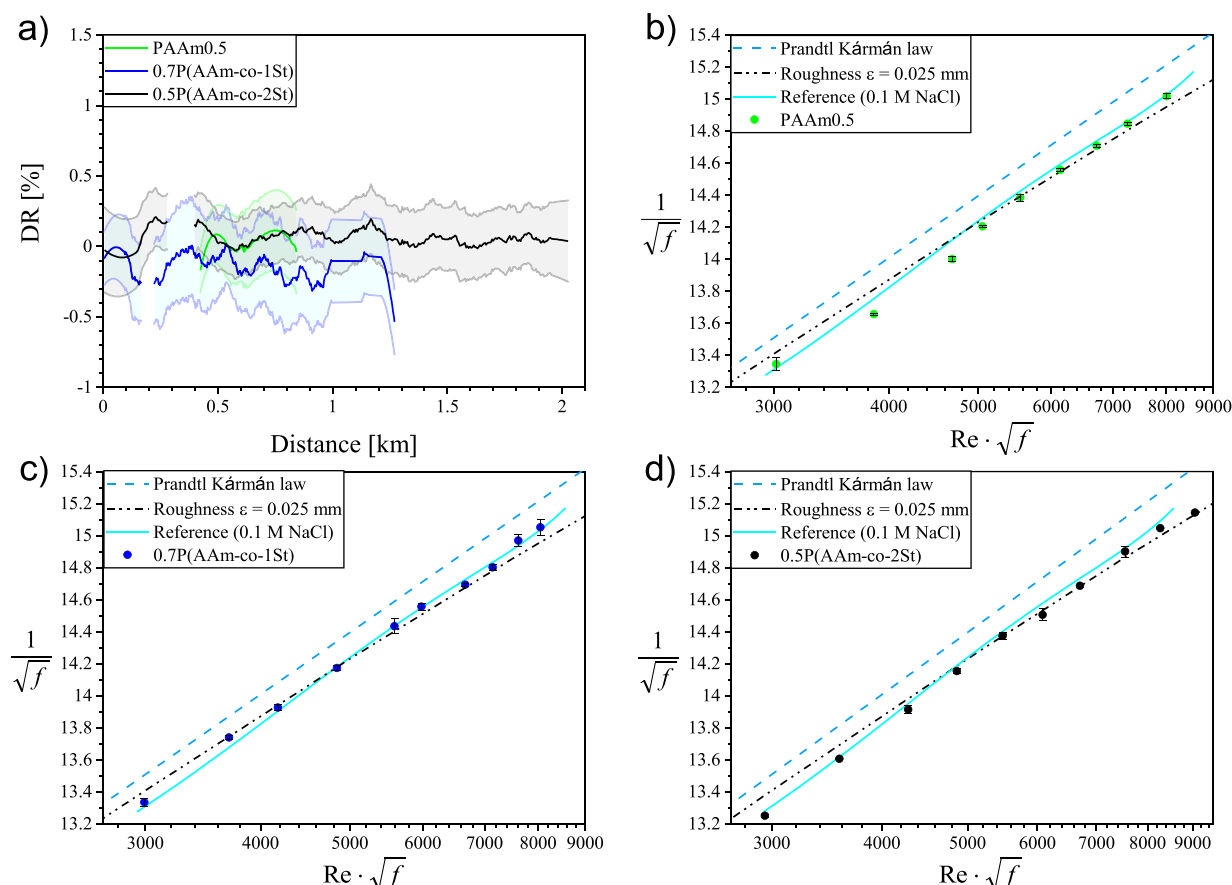


Figure 3. (a) Drag reduction DR(%) performance of polymers with $M_w < 1000$ kg/mol as a function of traveled distance through ViEDRA at constant polymer concentration $c = 0.01$ wt % and $Re = 100\,000$. Prandtl–Kármán plots for (b) PAAm0.5, (c) 0.7P(AAm-co-1St), and (d) 0.5P(AAm-co-2St). The dash double dot line represents the influence of pipe surface roughness.

polymer molecules, and for PAAm0.5 c^* shifted to higher values compared to the copolymers. For all polymers c_e was found to be similar and the ratio of c_e/c^* was in the range of 5–10, which agrees with the literature.³³ At $c > c_e$ the copolymers followed the power law ($\eta_0 \sim c^{3.75}$) displaying slopes close to theoretical values (Table S2). PAAm0.5 had a slope of 2.14 ± 0.19 , indicating that polymer chains are too short for entanglements to govern its viscoelastic behavior. This observation agrees with the exponent range⁵⁰ established for systems consisting of short chains that are marginally affected by entanglements $2.5 \geq \alpha \geq 1$.

In experiments on shear rate dependence of η in the semidilute entangled concentration regime (Figure S6) we observed shear thinning for 0.7P(AAm-co-1St) and 0.5P(AAm-co-2St) at $c \geq 4$ wt %, while no shear thinning was observed for PAAm0.5 in the tested concentration range. η of 0.7P(AAm-co-1St) and 0.5P(AAm-co-2St) in the semidilute entangled region were in approximately the same range, except for $c = 8$ wt %, where 0.7P(AAm-co-1St) had a η about ~ 2 higher than 0.5P(AAm-co-2St). Our observations are broadly in line with those reported by Martínez Narváez et al.⁵¹ for hydrophobically modified hydroxyethyl cellulose. G' and G'' (Figure S7) for 0.5P(AAm-co-2St) were approximately in the same range as for 0.7P(AAm-co-1St). The frequency dependences of G' and G'' (Figure S7) for PAAm0.5 indicated that the crossover point of G' and G'' —different from 0.7P(AAm-co-1St) and 0.5P(AAm-co-2St)—was not reached in the examined c and ω range. G' and G'' are one magnitude of

order lower than for other polymers tested. Overall, the dynamic properties of the investigated polymers scaled with M_w of the polymers.

PAAm1 already followed the power law $\ln \eta = \alpha \ln c$ (Table S2) in accordance with the behavior of the modified polymers 0.7P(AAm-co-1St) and 0.5P(AAm-co-2St) (Figures S6a and S7a). Therefore, we did not perform the rheological analysis of the 1P(AAm-co-1St) in the semidilute entangled regime (Figure S5).

Drag Reduction Behavior. We assessed the DR performance of the hydrophobically modified PAAm in pipe flow and compared it with commercial PAAm of similar molecular weight. We performed these experiments at a constant polymer concentration of 0.01 wt % and constant $Re = 100\,000$. $c = 0.01$ wt % was chosen for two reasons: first, the SLS analysis showed the formation of associations in the c range between 0.005 and 0.06 wt %, and second the concentration of polymeric DR agents used in industrial applications ranges from 0.001 to 0.01 wt %.¹³ The polymer solutions were recirculated through ViEDRA to reach flow distances of up to ~ 2.5 km (Figures 3a and 4a). Shown are the mean DR(%) of each cycle over travel distance (solid line) and associated variance as the shaded area in the same color. We also analyzed the dependence of DR(%) on Re . The results are shown as Prandtl–Kármán plots (Figures 3b–d and 4b,c). In all these graphs, the dashed lines represent the friction factor in turbulent pipe flow as described by the Prandtl–Kármán law, and the solid lines the measured flow behavior of the pure

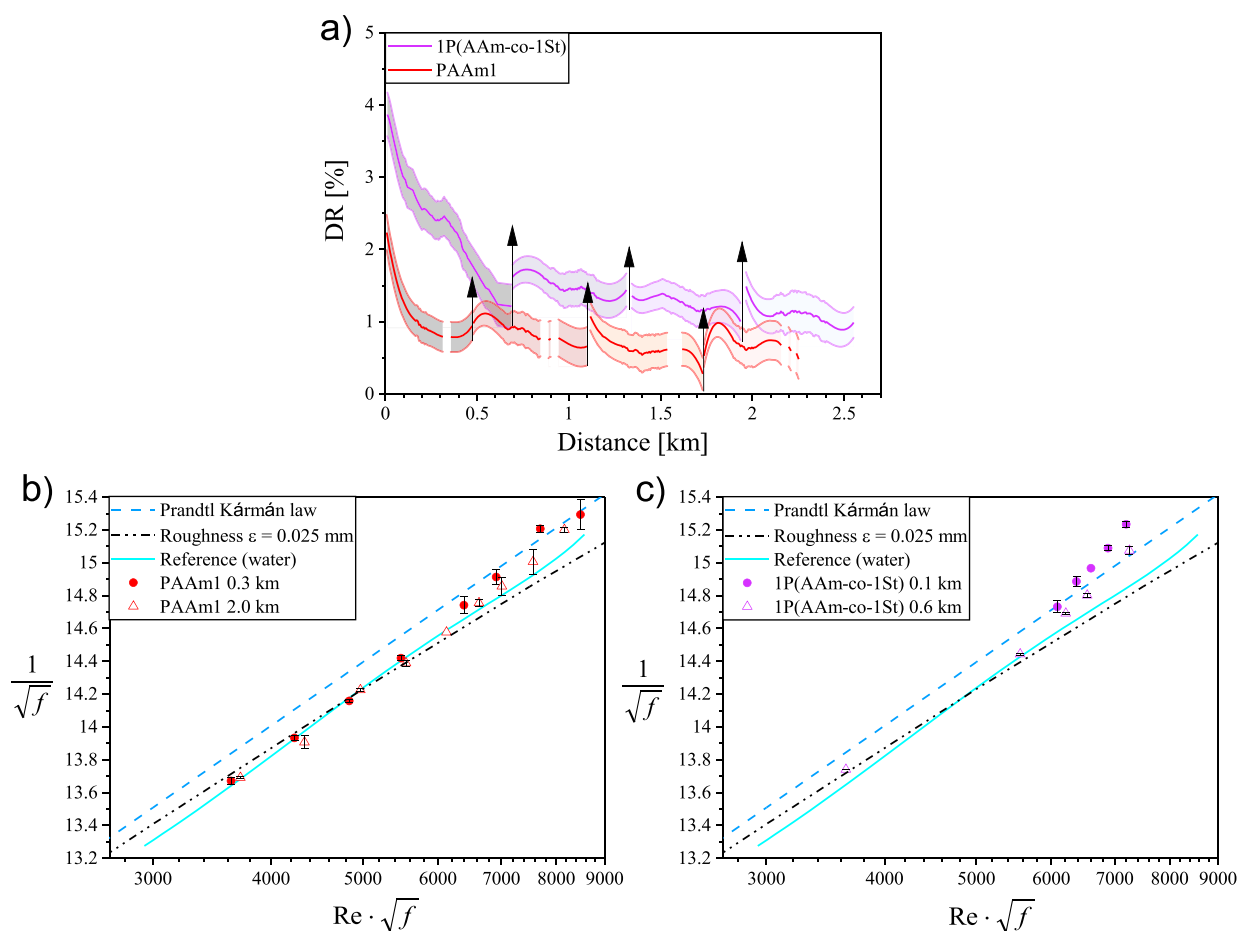


Figure 4. (a) Drag reduction DR(%) of polymers $M_w \approx 1000$ kg/mol as a function of distance traveled through the test section at constant polymer $c = 0.01$ wt % and $Re = 100\,000$. The arrows pointing upward represent points of salt addition. Prandtl–Kármán plots for (b) PAAm1 after 0.3 and 2.0 km represented by closed and open symbols and (c) 1P(AAm-co-1St) 0.1 and 0.6 km illustrated by closed and open symbols.

solvent. The deviation between the actual behavior of pure solvent and the Prandtl–Kármán law is assigned to pipe roughness, which is also considered and presented in Figures 3b–d and 4b,c.

DR effectiveness is known to increase with increasing polymer molecular weight.^{4,52} An increase in molecular weight results in an increased hydrodynamic volume (for simplicity $\propto R_g^3$) of polymer coils in solution but is also dependent on polymer structures and solvent quality. Therefore, “ultralong” ($M_w \geq 1000$ kg/mol) nonassociating polymers are able, already at small elongation rates, to absorb energy by stretching, causing the fluid body to oppose elongation, which results in reduced drag.⁵³ The importance of elastic effects for DR was discussed by Metzner and Graham Park⁵⁴ and Kalashnikov.⁵⁵ Nonassociating PAAm homopolymers with $M_w = 1400$ kg/mol at $c = 0.02$ wt % exhibited a DR maximum of 5%, while considerable DR capabilities of up to 42% were achieved for polyacrylamide with $M_w = 2500$ kg/mol.⁵⁷ McCormick et al.⁴¹ reported that higher M_w ($M_w \geq 1000$ kg/mol) hydrophobically modified associating PAAm produce DR. Consequently, in their study the contribution of associations on DR efficiency by associating copolymers with $M_w \geq 1000$ kg/mol was not clear.⁴¹ In addition, Wei et al.⁵³ suggested that associating di-end-functionalized polymers, able to mimic “ultralong” polymers, must possess strongly associating functionalities at both chain ends to enable pairwise end-association. These associating polymers manifest expanded

conformation in quiescent conditions that enables their elongation under flow.⁵³ To test the hypothesis that high-molecular-weight associations formed by lower molecular weight hydrophobically modified water-soluble polymers act as efficient drag-reducing agents, we compared the DR efficiencies of such polymers with pure PAAm having molecular weights of $M_w \leq 1000$ kg/mol, which do not show DR without association (Figure 3a). These experiments were performed in 0.1 M NaCl (rather than $MgSO_4$ because of the amount of salt required in ViEDRA) for all three polymers. As expected, PAAm0.5 did not provide any DR(%), but also no DR(%) was seen for the hydrophobically modified PAAm of similar molecular weight independent of hydrophobe content (0.7P(AAm-co-1St) and 0.5P(AAm-co-2St)), which both did form aggregates in quiescent conditions (see Table 1). At no or very low DR(%), where $f_s \approx f_p$, the relative error in calculated DR(%) increased, causing fluctuations that lead to negative DR values (Figure 3a). The friction factor for pure solvent (0.1 M NaCl solution) and polymer solutions tested at various Re -numbers followed the Prandtl–Kármán law showing that the tested polymers possessed indeed no DR (Figure 3b–d).

The DR efficiency of PAAm1 and 1P(AAm-co-1St) both having M_w slightly above 1000 kg/mol were initially determined in water to which later NaCl was added after every ~ 0.5 km to reach concentrations of 0.1, 0.5, and 1.0 M (Figure 4a) to test if salt addition does promote (re)formation

of polymer associations and result in enhanced DR. In water we observed a significant decrease in DR as a function of flow distance: DR dropped from 4% to $\sim 1.25\%$ for 1P(AAm-co-1St) and from 2.25% to $\sim 0.75\%$ for pure PAAm1. We probed M_w of the polymers after passing through the pipe for different distances during the experiment using gel permeation chromatography (GPC) (Figure S8) and found that this decrease in DR(%) was not associated with polymer degradation. The DR(%) decrease might be due to aggregate destruction,⁵⁶ which prevented backbone cleavage. Salt addition caused a slight increase in DR, which could indicate aggregate (re)formation for both polymers (Figure 4a). For PAAm1 this increase was followed by a fast decay, while for 1P(AAm-co-1St) the decay was slower.

When comparing flow distance dependence of DR(%) in the salt solution with constant salt c and in the salt solution with varying salt c , it is apparent that the salt addition had an effect already on reference PAAm promoting association formation, which resulted in higher DR(%) (Figure 5).

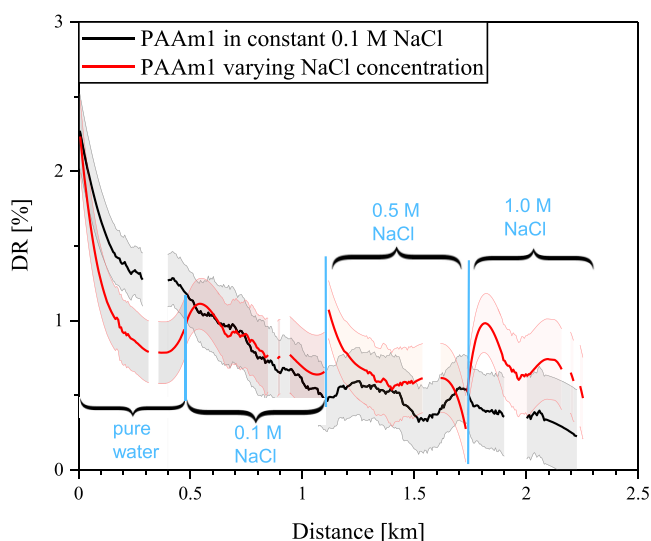


Figure 5. Salt influence on DR performance of reference PAAm1. Black line is for DR of PAAm1 in aqueous NaCl at constant $c = 0.1$ M and red line for DR in varying NaCl concentration.

In addition, to test possible recovery of macromolecular associations for both PAAm1 and 1P(AAm-co-1St), during the experiments we allowed the polymer solutions to rest in quiescent conditions either overnight or for up to 2 days. No DR(%) increase was observed after storage at quiescent conditions. Even if the aggregates reformed during storage, it seems they are not sufficiently stable to provide improved long-term DR. Incorporating Poiseuille's law and maximum drag reduction asymptote (MDR) established by Virk⁹ into the Prandtl–Kármán plots (Figure S9) indicates that the most pronounced DR(%) achieved by 1P(AAm-co-1St) was only 4%, which is in the very low DR(%) range. Hence, the use of 1P(AAm-co-1St) provided an improvement in initial DR, reaching 4% compared with the DR of PAAm1 (2.25%), indicating that the DR performance of the modified PAAm improved by a factor of ~ 2 compared to unmodified PAAm at low DR(%). Furthermore, when plotting the Re dependence of DR(%) in a Prandtl–Kármán plot, a more pronounced friction reduction was observed for 1P(AAm-co-1St) than for PAAm1. The modified polymer shows the same DR(%) at 0.6 km as

commercial PAAm at a shorter distance of 0.3 km (Figure 4b,c). It is also visible that DR(%) increases with Re .

The presented results indicated that hydrophobically modified polymer 1P(AAm-co-1St) showed higher DR capabilities at a low level compared to pure PAAm of approximately the same molecular weight (Figure 4). Even though 0.5P(AAm-co-2St) exhibited a high number of associations as indicated by SLS results (Table 1), its DR capabilities were in the range of reference PAAm0.5. On one hand, this result is affected by foam formation, which is more in-depth discussed below, and on the other hand, hydrophobically modified copolymers synthesized using micellar polymerization are assumed to consist of hydrophobe moieties distributed in small blocks.⁵⁸ However, Lacik et al.⁵⁸ argue that these copolymers suffer from compositional heterogeneity at high hydrophobe incorporation and comonomer conversion because hydrophobic monomers are being consumed and incorporated as small blocks at the early stage of the reaction, resulting in later reaction stages in homopolymer formation. This compositional heterogeneity greatly aggravates the copolymer performance as viscosity modifiers, causing no significant difference when compared with the homopolymer.⁵⁶ Wei et al.⁵³ discussed that polymers having associating functionalities distributed along their backbone form flower-like, collapsed, and rigid “supramolecules”, which do not provide the benefits of di-end-functionalized polymers for DR. The compositional heterogeneity contributes to an important aspect, which is the stability of associations in shear. Considering R_H and R_η (Table 1) it is likely that already low shear rates ($\dot{\gamma} \leq 200 \text{ s}^{-1}$) are sufficient to destroy the aggregates. Therefore, the question is will polymers forming stronger associations in water (but with association strength lower than C–O bonds) produce more effective associations resulting in improved DR(%) and reduced chain scission? Wei et al.⁵³ used statistical mechanics to design polymers capable of self-assembling into “megaspupramolecules” with $M_w \geq 5000$ kg/mol at $c \leq 0.3$ wt % useful for mist control and DR in low-polarity fluids, such as liquid fuels. Theoretical estimations suggested that an optimum concentration of “megaspupramolecules” of $c > 0.005$ wt % formed from long end-functionalized telechelic polymers ($M_w = 400\text{--}1000$ kg/mol) when present at concentrations of 0.14 wt %.⁵³ However, the fraction of “megaspupramolecules” is rather small compared to the total polymer amount. The telechelic end-functionalities provided an end-association strength between 16 and 18 $k_B T$.⁵³ These telechelic polymers were reported to be effective in drag reduction and mist control at $c = 0.1$ wt %, retaining their properties after 5 passes through a pump, in contrast to “ultralong” ($M_w = 4200$ kg/mol) nonassociating polymers at $c = 0.02$ wt %.⁵³ Short backbone di-end-functionalized polymers ($M_w < 400$ kg/mol) resulted in small ring micelle formation and do not influence rheological properties of the solution, while very long backbones ($M_w > 1000$ kg/mol) are prone to fast degradation under strong flows.⁵³ The association strength has to be $\gg 1 k_B T$ for associations to form, but also $\ll 150 k_B T$ (average strength of covalent bonds) to provide reversible secondary bonds acting as a “physical fuse” protecting the backbone from degradation in turbulent flows.⁵³

The overlap concentration, which Regalado et al.³³ predict to be the critical aggregation concentration for hydrophobically modified PAAm, is slightly higher than 0.1 wt % (Figure 2). To test the DR capabilities at higher concentrations of (hydrophobically modified) polymers, we used a rotating “disc”

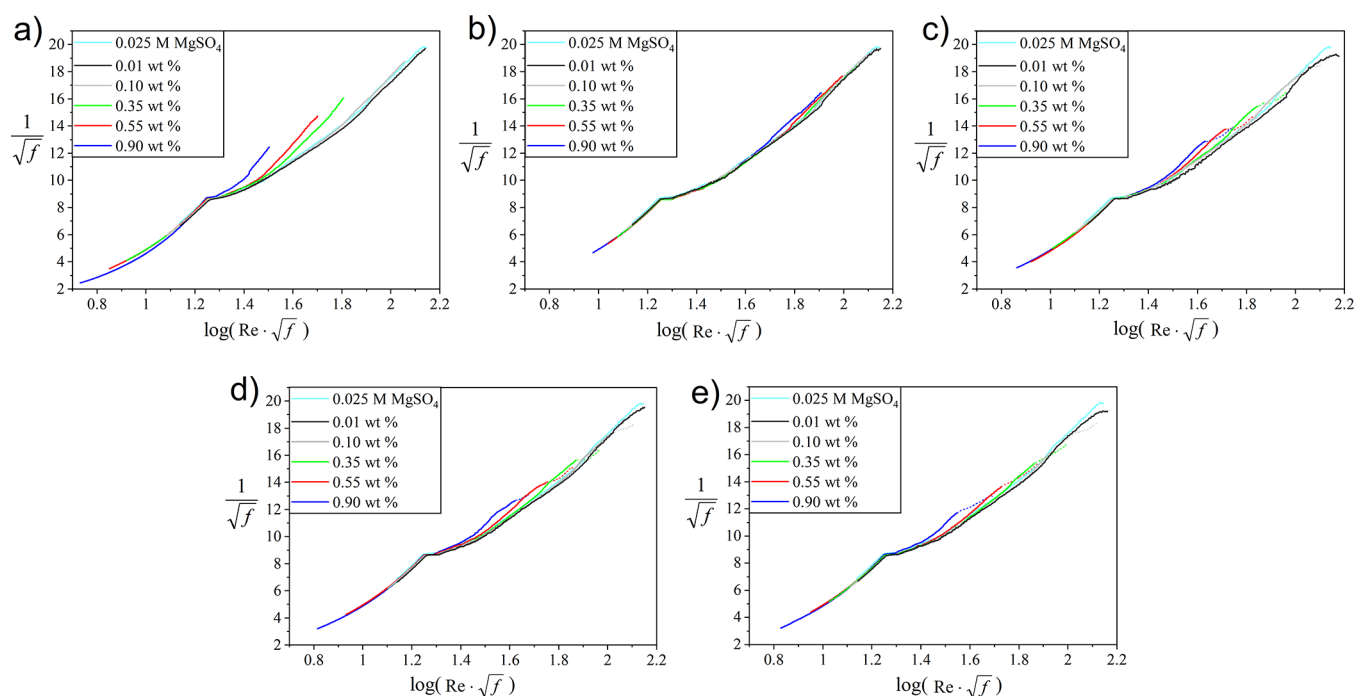


Figure 6. Prandtl–Kármán plots of the data obtained in a double-gap geometry at polymer $c = 0.01, 0.1, 0.35, 0.55$, and 0.90 wt % in aqueous 0.025 M MgSO_4 for (a) PAAm1, (b) PAAm0.5, (c) 1P(AAm-co-1St), (d) 0.7P(AAm-co-1St), and (e) 0.5P(AAm-co-2St).

apparatus (i.e., a rheometer) requiring lower solution volumes and thus less polymer. DR in Taylor–Couette flow differs from DR in turbulent pipe flow. Without polymer additive the instabilities in pipe flow and Taylor–Couette flow are inertia driven.⁵⁵ Polymer addition introduces locally viscoelastic behavior which causes DR.⁵⁵ In the presence of polymers Taylor–Couette flow in rotational geometry can be driven by elastic instabilities only.^{59–61} In pipe flow at a given flow rate, inertia-driven instabilities of a pure solvent are replaced by elasto-inertial instabilities in polymer solutions, resulting in drag reduction.^{62,63} In both inertia-elastic-driven turbulent viscoelastic pipe flow and elastically driven viscoelastic Taylor–Couette flow a cyclic drive⁶⁴—velocity fluctuations generate stress fluctuations in polymer chains which produce velocity fluctuations when the elastic stress is released—is established. Polymer extension is induced by inertia in turbulent pipe flow, while elastic instabilities in rotational geometry are related to curved streamlines.⁶⁴ Even though polymer molecules in Taylor–Couette flow might interact differently with the flow compared to turbulent pipe flow, it was shown that assessment of DR capabilities of polymeric drag-reducing agents is possible using a rotating “disk” apparatus,^{18,44,45,45} which might be attributed to the similarity in polymer–flow interaction. We performed these experiments in aqueous 0.025 M MgSO_4 solution at concentrations up to 0.9 wt %. The DR results are presented as Prandtl–Kármán plots (Figure 6a–e). All tested polymers produced no DR at a concentration of 0.01 wt %. Also at 0.1 wt % no DR was observed. However, at concentrations of $0.35, 0.55$, and 0.9 wt % the polymers displayed some DR capabilities (Table S3). While commercial PAAm having an M_w of 1000 kg/mol is more effective in reducing DR than the hydrophobically modified PAAm (1P(AAm-co-1St)), it must be noted that the hydrophobically modified PAAm started to foam during the experiments (Figure S10). Foaming started at a lower $\dot{\gamma}$ threshold before the maximum DR was observed and increases

with c . Foam formation resulted in an increased fluid volume in the test geometry, thus producing increased drag (see dotted lines in Figure 6c–e). Moreover, during foaming the effective polymer concentration in solution decreases significantly, which also affects its DR capabilities. Therefore, we were not able to quantify the real DR efficiencies of P(AAm-co-St) in the rotating “disc” apparatus.

The formation of very stable foams for hydrophobically modified PAAm was also encountered during the pipe flow experiments (Figure S11). The foam formation lowered the effective polymer concentration, thus resulting in lower DR. We air-dried the foam of 0.5P(AAm-co-2St) and obtained a solid polymer foam (Figure S11c). The foam volume as well as stability and density increased considerably for the copolymer with a higher hydrophobe content (0.5P(AAm-co-2St)) compared to the copolymer with a lower hydrophobe amount (1P(AAm-co-1St)) (Figure S11b and a, respectively). The reason for foam formation is still not fully understood, but a possible explanation is that the foam formed due to residual CTAB (present after purification) still being associated with the polymer. Assuming the concentration of CTAB in the copolymer sample to be 0.01 wt %, as shown by the elemental analysis results (Table S1), the total CTAB concentration in 300 L of polymer solution containing 30 g of polymer is 2.74×10^{-8} M, very much lower than the critical micelle concentration of CTAB (0.9×10^{-3} M), and thus insufficient to produce stable foams.⁶⁵ However, CTAB copolymer complexes could act as polymeric surfactant due to their amphiphilic nature.

CONCLUSION

Hydrophobically modified P(AAm-co-St) with different hydrophobe molar ratios and two M_w were synthesized using micellar copolymerization. The association properties of hydrophobically modified PAAm as well as unmodified reference PAAm in aqueous 0.025 M MgSO_4 were determined

using SLS and DLS. Their rheological and DR properties were compared to pure PAAm of similar M_w . Our results provide evidence that hydrophobically modified copolymers produced using micellar polymerization with $M_w \approx 1000$ kg/mol provided higher DR by a factor of ~ 2 compared to the unmodified PAAm of similar M_w albeit at low DR level. DR increased with salt concentration, which promoted association formation. However, DR capabilities of copolymers with $M_w < 1000$ kg/mol were not improved in turbulent pipe flow compared to reference PAAm. Foam formation of modified polymers contributed to lowering the effective polymer c , resulting in decreased DR performance of the polymers. Even though associating polymers of lower M_w form high M_w associations, they seem to be easily destroyed already at low shear rates. In general, comparing R_η and R_g/R_H the associations seem to be very sensitive to shear. In addition, DR measurements in the rotating “disc” apparatus showed no DR effect for polymer $c < 0.1$ wt %, while the DR effect in a horizontal pipe flow was observed already at $c = 0.01$ wt %. This observation highlights the essentiality of a combination of measuring techniques to adequately assess polymer-induced DR.

The concept of hydrophobically driven associations in aqueous solutions of modified PAAm improving long-term DR has to be still advanced to polymers forming more robust, higher association strength and larger associations to withstand higher shear rates.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.2c01219>.

Elemental analysis experimental procedure and results; supporting results such as ^1H NMR spectrum, SLS and DLS graphs, additional rheological characterization, GPC spectra, DR graphs from ViEDRA measurements, photographs of foam formation (PDF)

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Author Contributions

All authors contributed to the conceptualization of the work, E.M. performed most synthetic and characterization work and analyzed the data; L.B. and E.M. performed ViEDRA experiments and analyzed the data; J.S. performed the rheological characterization. E.M. and A.B. wrote the manuscript and designed the figures. H.W.M. and A.B. supervised the work. All authors contributed to manuscript review and editing.

Funding

E.M. gratefully acknowledges financial support by the Institute of Materials Chemistry of University of Vienna (grant number 371300), and L.B. and A.B. acknowledge the support of Doctoral College Advanced Functional Materials (DCAFM) funded by the Austrian Science Fund (FWF, grant number: DOC 85 doc.funds). Open Access is funded by the Austrian Science Fund (FWF).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the financial support from the Faculty of Chemistry, University of Vienna (Austria). E.M. acknowledges Mag. Johannes Theiner for technical assistance with elemental analysis and Prof. Dominik Eder, Dr. Niuscha Lasemi, and Dr. Davide Ret for providing resources and technical support with SLS and DLS measurements.

■ SYMBOLS

A_2 , second virial coefficient ($\times 10^{-7}$ mol dm³/g²); c , concentration (wt %); c_e , entanglement concentration (wt %); c_m , mass concentration (g/mL); c^* , overlap concentration (wt %); d , diameter (mm); D , translational diffusion coefficient (m²/s); dn/dc , refractive index increment (mL/g); DR, drag reduction (%); G'' , loss modulus (Pa); G' , storage modulus (Pa); K , Mark–Houwink parameter (mL/g); k_B , Boltzmann constant (m² kg/s² K); l , length (m); L , rotor height (mm); M_η , viscosity averaged molecular weight (kg/mol); M_w , weight-average molecular weight (kg/mol); n , speed of rotation (s⁻¹); N_A , Avogadro's number (mol⁻¹); Δp , pressure drop (Pa); R_g , radius of gyration (nm); R_H , hydrodynamic radius (nm); R_i , radii of the double-gap geometry (mm); R_η , viscosity averaged hydrodynamic radius (nm); $\bar{R}$, mean radius (mm); St , amount of incorporated styrene in P(AAm-co-St) (mol %); T , absolute temperature (K); u , linear velocity (m/s); U , volume averaged velocity (m/s); W_M , weight of the monomers (g); W_p , weight of the purified polymer (g); Y , polymerization yield (%)

■ GREEK LETTERS

α , Mark–Houwink parameter; $\dot{\gamma}$, shear rate (s⁻¹); $\dot{\gamma}_c$, critical shear rate at Taylor flow onset (s⁻¹); δ , ratio of the distance between rotor and stator of the double-gap geometry; η , apparent viscosity (Pa·s); η_{sp} , specific viscosity; η_r , relative viscosity; $[\eta]$, intrinsic viscosity (mL/g); η_0 , zero-shear viscosity (Pa·s); ρ , solution density (kg/m³); τ , shear stress

(Pa); ϕ , polymer volume fraction in solution (%); ω , frequency ($\text{rad}\cdot\text{s}^{-1}$); ω_c , critical angular velocity at Taylor flow onset ($\text{rad}\cdot\text{s}^{-1}$)

DIMENSIONLESS GROUPS

$\bar{D}$, polydispersity; f , Fanning friction factor; f_p , Fanning friction factor of polymer solution; f_s , Fanning friction factor of pure solvent; $\bar{h}$, average gap width; $I_{7.3 \text{ ppm}}$, integral corresponding to protons of phenyl groups ($-\text{C}_6\text{H}_5$); $I_{1.5-1.8 \text{ ppm}}$, integral corresponding to protons of methylene groups ($-\text{CH}_2-$); K , geometrical factor; Re , Reynolds number

ACRONYMS

AAM, acrylamide; Br, bromine; CTAB, hexadecyltrimethylammonium bromide; DLS, dynamic light scattering; GPC, gel permeation chromatography; HPLC, high-performance liquid chromatography; MWCO, molecular weight cutoff; NMR, nuclear magnetic resonance; PAAM, polyacrylamide; P(AAM-co-St), poly(acrylamide-co-styrene); PEO, poly(ethylene oxide); SLS, static light scattering; St, styrene; ViEDRA, Vienna Experiment for Drag Reducing Agents

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Supporting Information

Aqueous solutions of associating poly(acrylamide-co-styrene) - a path to improve drag reduction?

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EXPERIMENTAL SECTION

Elemental analysis. Elemental micro-analysis was performed at the faculty's Microanalysis Services department. Simultaneous determination of C, H, N and S was done by an automatic Elemental Analyser EA 3000 (Eurovector) using sample amounts between 1.0 and 1.5 mg. The instrument's operating procedure consists of a flash combustion combined with a Dumas-N-reduction and an on-line Gas Chromatography (GC) separation of the gaseous products N₂, CO₂, H₂O and SO₂. As a carrier gas high purity helium is used. A high temperature pyrolysis system HT 1500 (Hekatech) that operates at 1480 °C was used for oxygen determination using similar sample amounts. Solid carbon acts as a reducing agent and high purity helium is used as a carrier gas. The analytical species detected is carbon monoxide. The instrument software CALLIDUS was used for data collection in both methods. Mineralisation of up to 5.0 mg of each sample in an AQF 100 (Mitsubishi) was performed to determine the halogene amount. Milli-Q-water was utilised as an absorbent for gaseous products. Using a 7100 CE (Agilent) and a conductivity detector (TraceDec) membrane filtration and capillary ion electrophoresis were employed to prepare and characterise the resulting solution. All instrument-data were evaluated using laboratory developed software (SCADA 5.99). A typical uncertainty for the results of main constituents is below 0.3 wt.%. The limit of quantification (LOQ) is 0.05 wt.% for N and 0.02 wt.% for S. Halogenes can be detected down to 0.01 wt.%.

SUPPLEMENTARY FIGURES AND TABLES

Table S1. Elemental composition of P(AAm-co-St) and the homopolymer obtained using CHNS-O analysis

Sample	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	Br (wt.%)
Homopolymer	46.49 ± 0.01	7.23 ± 0.06	17.65 ± 0.05	< 0.02	26.67 ± 0.63	< 0.01
1P(AAm-co-1St)	46.55 ± 0.05	7.55 ± 0.05	17.62 ± 0.03	< 0.02	26.14 ± 0.30	< 0.01
0.7P(AAm-co-1St)	48.20 ± 0.88	7.35 ± 0.01	18.09 ± 0.32	< 0.02	25.26 ± 0.62	< 0.01
0.5P(AAm-co-2St)	46.42 ± 0.10	7.52 ± 0.09	17.21 ± 0.06	< 0.02	26.18 ± 0.02	< 0.01

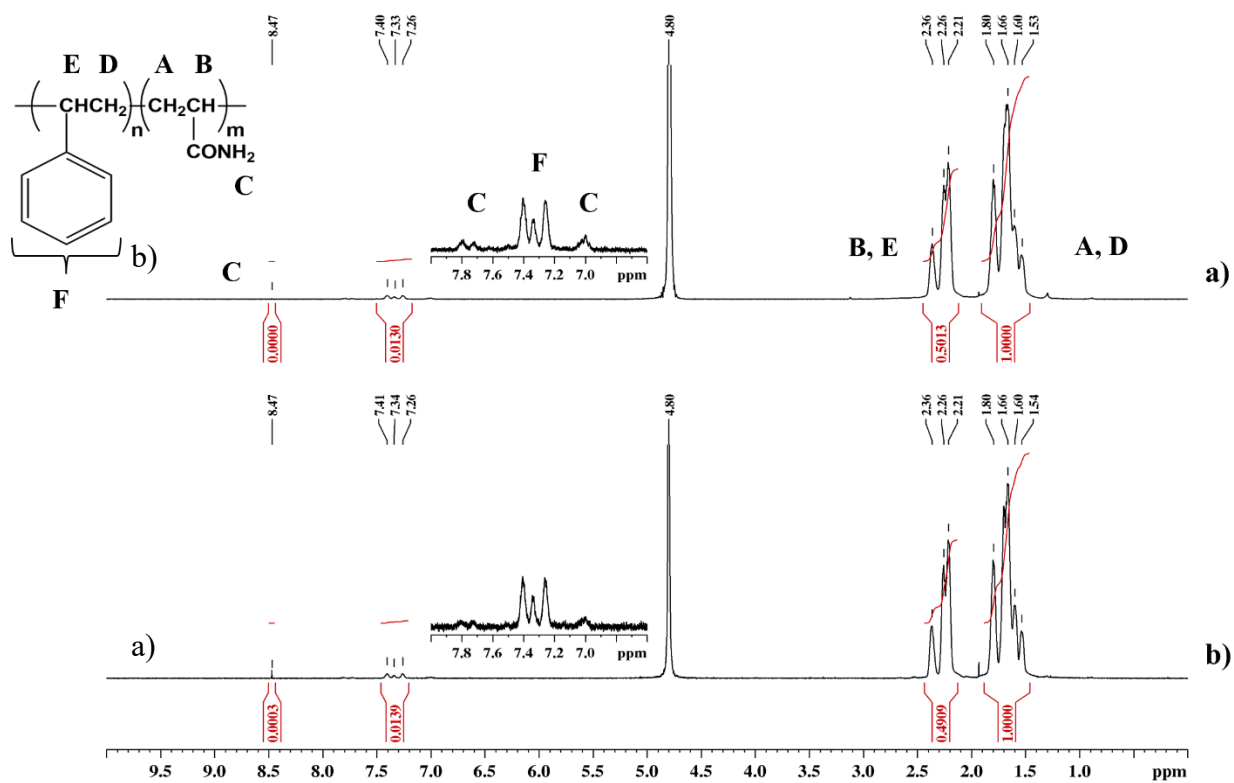


Figure S1. ¹H NMR spectrum of a) 0.7P(AAm-co-1St) and b) 1P(AAm-co-1St) acquired in D₂O

Light scattering

When analysing the SLS data the Zimm data reduction method provided negative intercept and consequently negative M_w for the 0.5P(AAm-co-2St) in aqueous $MgSO_4$. In fact, a reciprocal value for high M_w samples is very low and a little amount of signal noise can generate a negative extrapolated intercept.¹ We applied Berry's approach² which provides less curvature in the angular dependence for larger molecules. This way, linear extrapolation in the square-root of scattered light intensity $((Kc/R\theta)^{1/2})$ against angles and concentrations $q^2 + kc$ with k being a scaling factor yields a more reliable approximation. In order to ensure the consistency of the data, for all polymers acquired in aqueous $MgSO_4$ the data were processed by the same method (Figure S3). However, for the polymers analysed in formamide the Zimm method was applied since $1/M_w$ is sufficiently large (Figure S2).

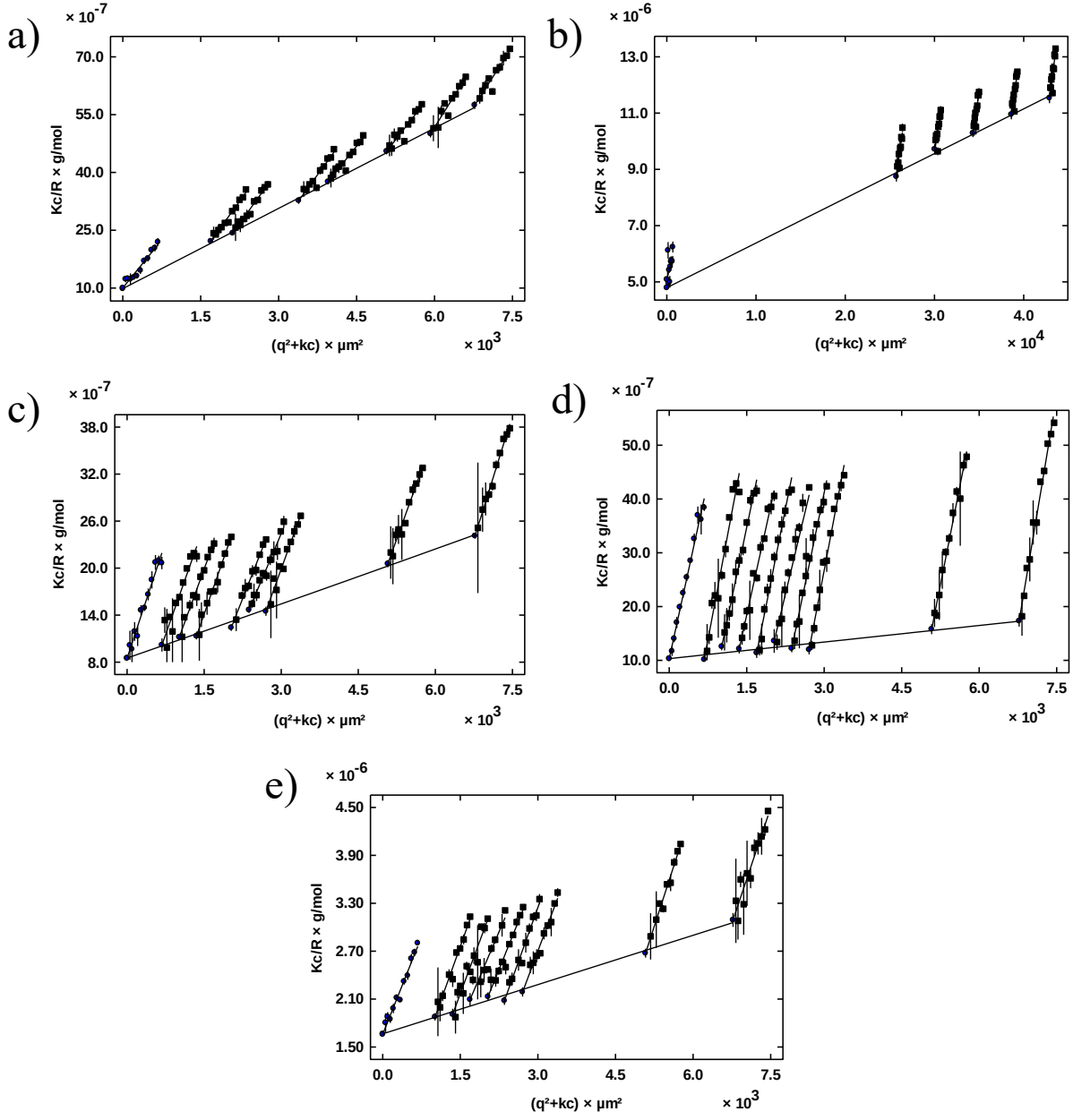


Figure S2. Static light scattering SLS data obtained in formamide and analysed using Zimm method for:

a) PAAm1 b) PAAm0.5 c) 1P(AAm-co-1St), d) 0.7P(AAm-co-1St), and e) 0.5P(AAm-co-2St).

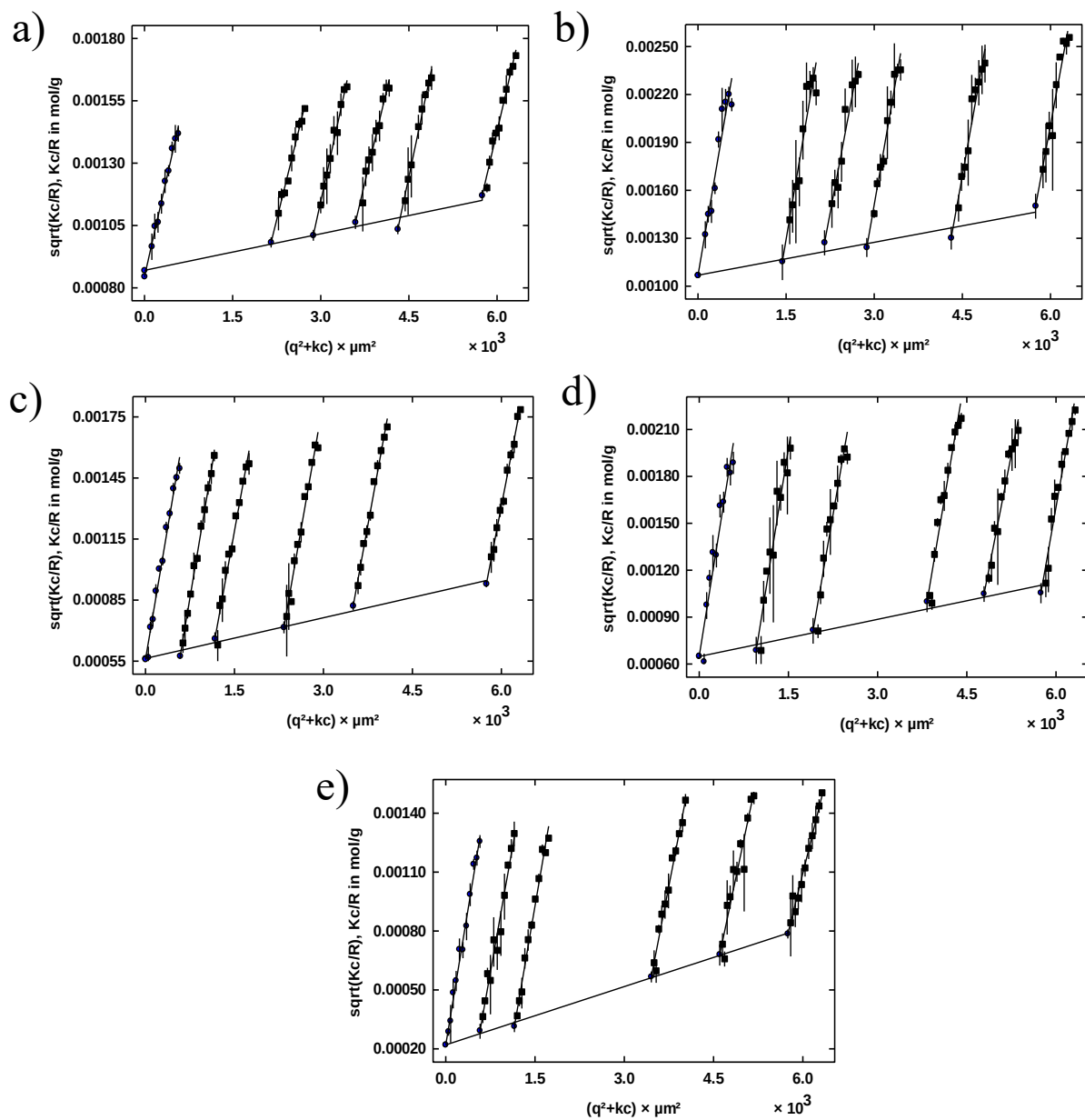


Figure S3. Static light scattering SLS data obtained in aqueous 0.025 M MgSO_4 and analysed using Berry method for: a) PAAm1 b) PAAm0.5 c) 1P(AAm-co-1St), d) 0.7P(AAm-co-1St), and e) 0.5P(AAm-co-2St).

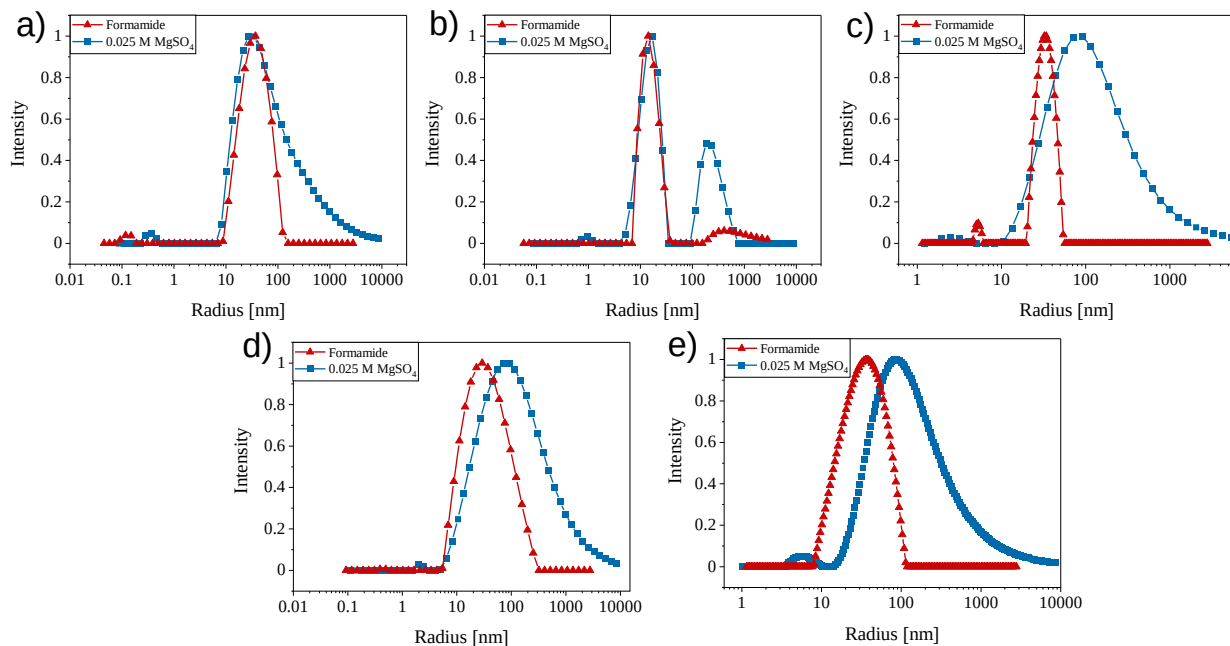


Figure S4. Dynamic light scattering DLS data obtained in formamide (red triangles) and aqueous 0.025 M MgSO_4 (blue squares) for: a) PAAm1 b) PAAm0.5 c) 1P(AAm-co-1St), d) 0.7P(AAm-co-1St) and e) 0.5P(AAm-co-2St).

Zero shear viscosity

Table S2. Slopes of fit $\ln(\eta_0) = \alpha \ln(c)$ for all polymers in three concentration regimes: dilute, semi-dilute unentangled and semi-dilute entangled regimes.

Sample	Dilute regime	Semi-dilute regime	
		unentangled	entangled
PAAm1	0.0343 ± 0.0069	1.0125 ± 0.1097	3.4549 ± 0.1111
1P(AAm-co-1St)	0.0727 ± 0.0122	0.9503 ± 0.0734	-
PAAm0.5	0.0132 ± 0.0021	0.4087 ± 0.0346	2.1416 ± 0.1927
0.7P(AAm-co-1St)	0.0231 ± 0.0037	0.7253 ± 0.0467	3.8178 ± 0.2364
0.5P(AAm-co-2St)	0.0181 ± 0.0035	0.6723 ± 0.0519	3.3978 ± 0.1029

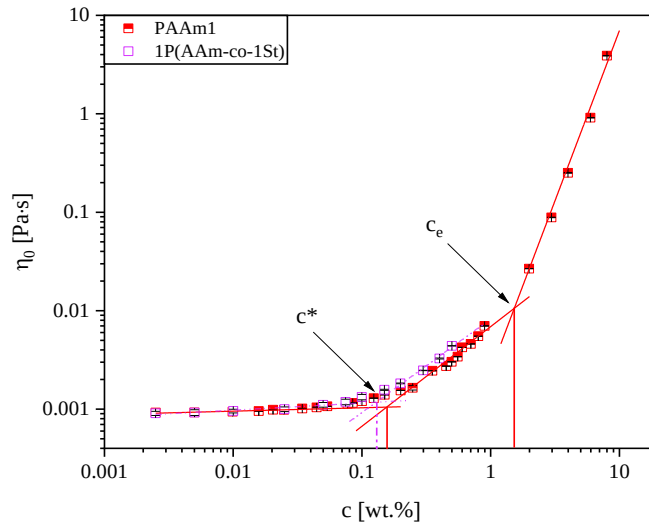


Figure S5. Concentration c dependence of the zero-shear viscosity η_0 determined in aqueous 0.025 M MgSO_4 for polymers with $M_w \approx 1000$ kg/mol.

Rheological characterisation in rheometer

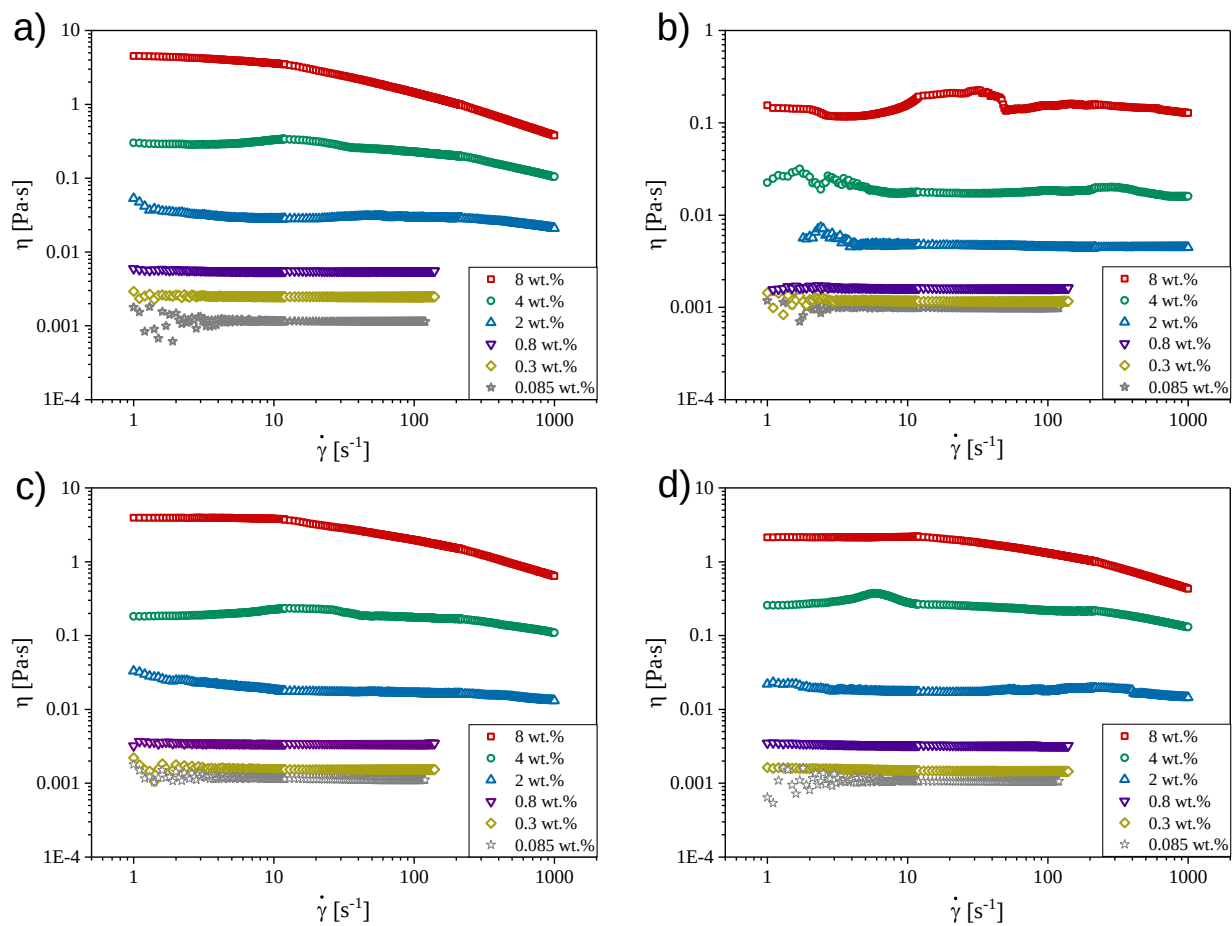


Figure S6. Shear rate $\dot{\gamma}$ dependence of viscosity η for: a) PAAm1, b) PAAm0.5, c) 0.7P(AAm-co-1St) and d) 0.5P(AAm-co-2St) obtained in aqueous 0.025 M $MgSO_4$ at different polymer concentrations.

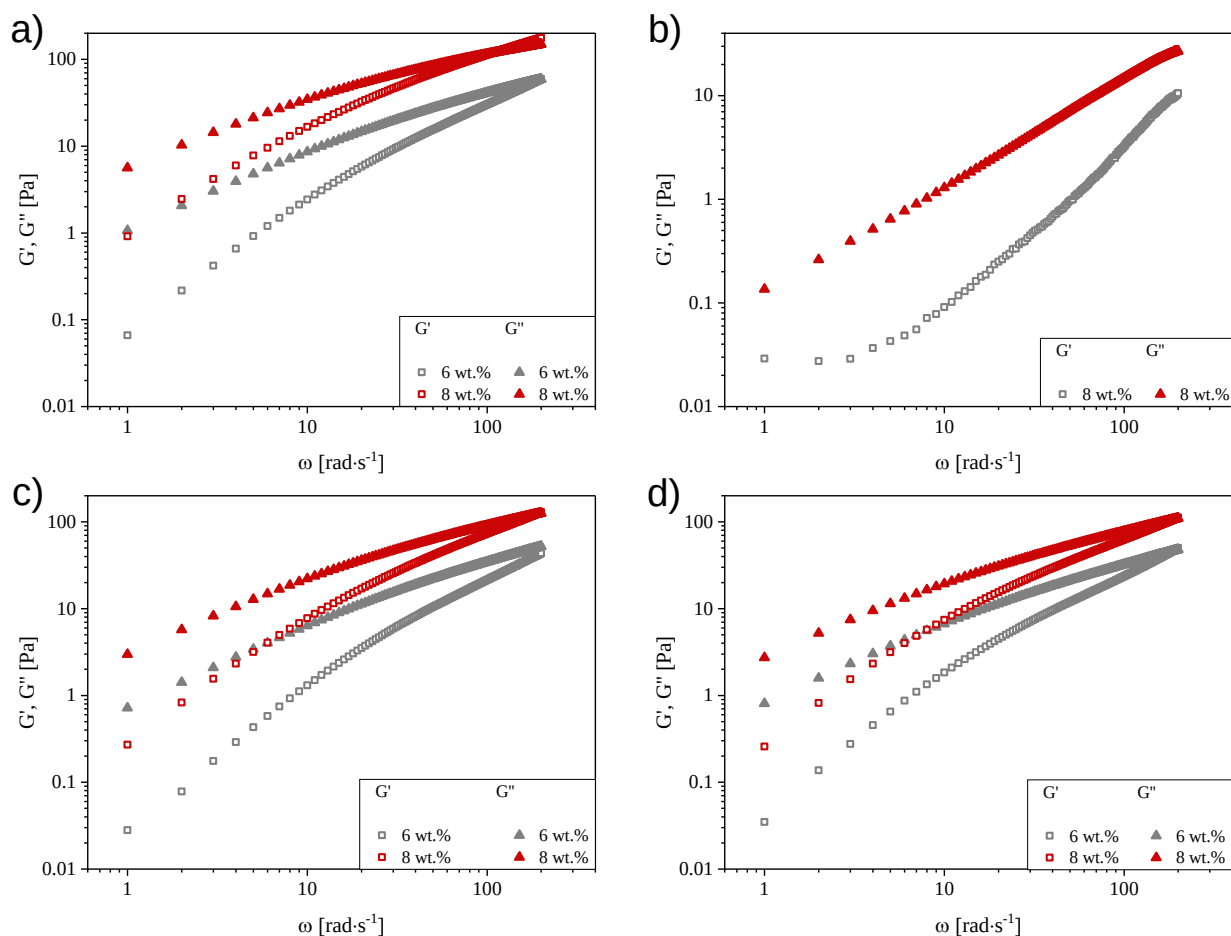


Figure S7. Frequency ω dependences of the storage (G') and loss (G'') moduli for: a) PAAm1, b) PAAm0.5, c) 0.7P(AAm-co-1St) and d) 0.5P(AAm-co-2St) obtained in aqueous 0.025 M MgSO_4 at polymer concentrations 6 and 8 wt.%.

Hydrophobically modified polymers aggregating into micellar structures at quiescent conditions undergo thermal fluctuations corresponding to approximately $1 k_B T$.³ The association network structure of end-functionalised telechelic polymers consists of “loops” formed by both polymer end groups being in a micelle, “dangling” chains having one of the ends without aggregation, and “bridging” chains that link two micelles.³ In quiescent conditions the likelihood of hydrophobes associating into micelles is proportional to the probability of their detachment, while the attraction is significantly prominent when exposed to extensional deformation induced by increased

probability of the encounter of two hydrophobic ends.³ Thus, telechelic polymers exhibit the steady shear viscosity profile that constitutes of a constant viscosity at low shear rates, shear thickening at intermediate shear rates, and pronounced shear thinning at high shear rates.³ At low shear rates, thermal fluctuations govern the association processes.³ The rates of aggregate formation and elongation-induced breakage rise nonlinearly as shear rates are enhanced.³ This phenomenon first leads to increased number of “bridging” chains due to collision of hydrophobe ends (shear thickening), and later to lowered number of “bridging” chains caused by extensional deformation (shear thinning).³ These shear and extensional deformation modes are in good agreement with the observations made by Sharma et al.⁴ for multisticker associative polymers. Owing to concentration dependence of association processes, in dilute solutions very little number of “bridging” chains exists in the micelle network.³ Martínez Narváez et al.⁵ also examined the shear and extensional rheology response for associating hydrophobically modified hydroxyethyl cellulose ($M_w = 300$ kg/mol) and compared it to the unmodified hydroxyethyl cellulose ($M_w = 720$ kg/mol). The specific viscosity of the aqueous solutions of hydrophobically modified polymer was approximately the same as the one for the solutions of two times higher M_w of unmodified polymer.⁵ Furthermore, a slight shear thickening in unentangled semidilute solutions of hydrophobically modified hydroxyethyl cellulose was observed, followed by more pronounced shear thinning when compared to the unmodified homopolymer.⁵ These superior rheological properties of associative hydrophobically modified polymers are due to combination of associations and clustering.⁵ The increased zero shear viscosity and relaxation time are caused by association–disassociation time and polymer chain–micelle dynamics.⁵

DR in turbulent pipe flow

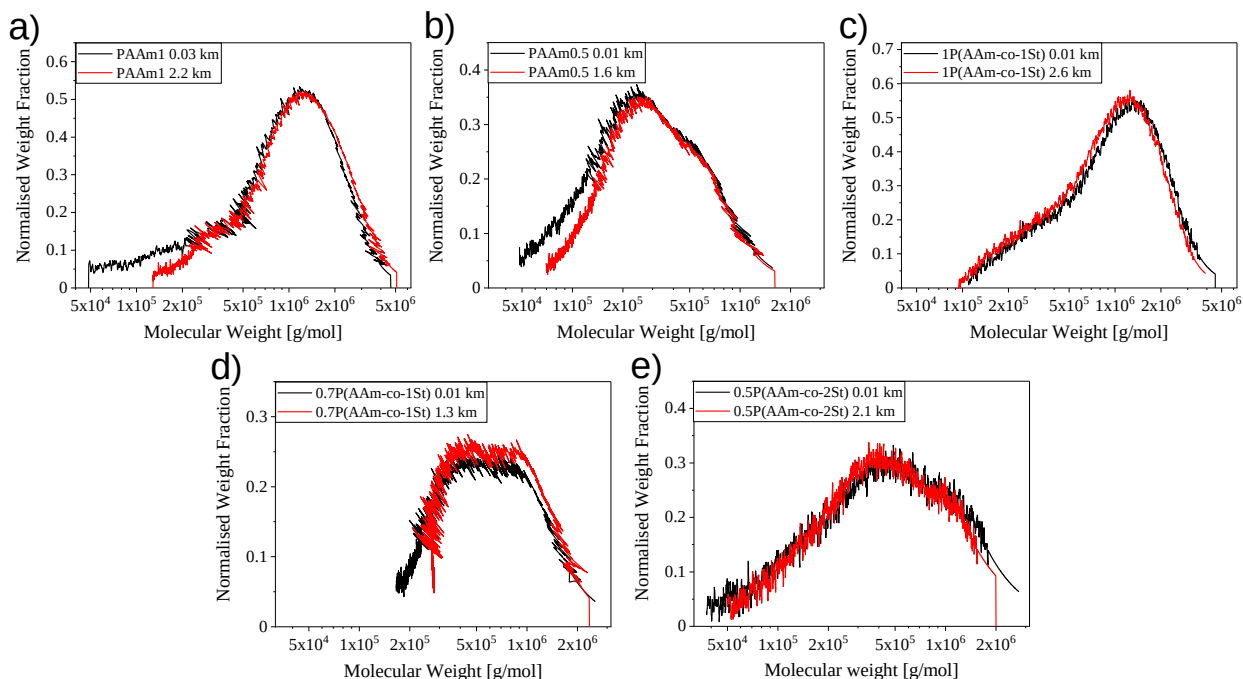


Figure S8. Molecular weight M_w distributions of the tested polymers after they travelled certain distances in ViEDRA: a) PAAm1, b) PAAm.05, c) 1P(AAm-co-1St), d) 0.7P(AAm-co-1St) and e) 0.5P(AAm-co-2St).

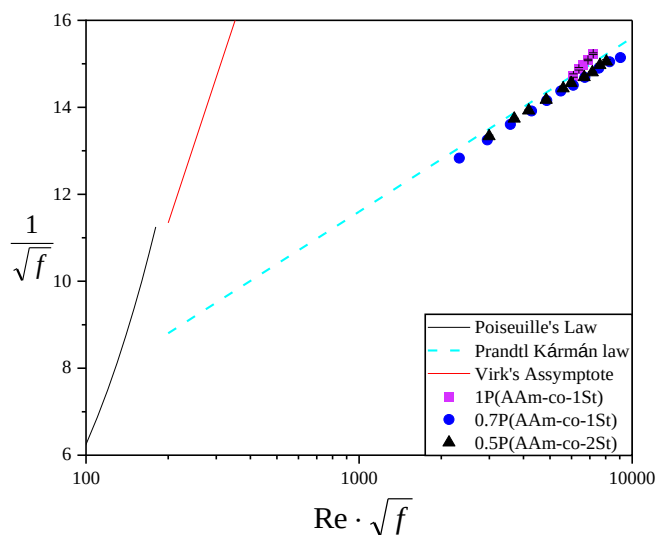


Figure S9. Prandtl-Kármán plot for hydrophobically modified polymers compared to Virk's asymptote representing maximum DR achieved and Poiseuille's law representing laminar flow.

DR experiments in rheometer

Drag reduction determined from the rheometer measurements at polymer $c > 0.1$ wt.%. Shown is the maximum DR that was achieved at the given experimental conditions and, in the case of hydrophobically modified polymers before excessive foaming started. These DR values were obtained at different Reynolds numbers Re . Re values for tested polymers were following: PAAm1 reached $Re_{c=0.35 \text{ wt.\%}} = 980$, $Re_{c=0.55 \text{ wt.\%}} = 700$, and $Re_{c=0.9 \text{ wt.\%}} = 370$; 1P(AAm-co-1St) $Re_{c=0.35 \text{ wt.\%}} = 1000$, $Re_{c=0.55 \text{ wt.\%}} = 680$, $Re_{c=0.9 \text{ wt.\%}} = 520$; PAAm0.5 $Re_{c=0.35 \text{ wt.\%}} = 2000$, $Re_{c=0.55 \text{ wt.\%}} = 1700$, $Re_{c=0.9 \text{ wt.\%}} = 1300$; 0.7P(AAm-co-1St) $Re_{c=0.35 \text{ wt.\%}} = 1100$, $Re_{c=0.55 \text{ wt.\%}} = 690$, $Re_{c=0.9 \text{ wt.\%}} = 390$; 0.5P(AAm-co-2St) $Re_{c=0.35 \text{ wt.\%}} = 1100$, $Re_{c=0.55 \text{ wt.\%}} = 700$, $Re_{c=0.9 \text{ wt.\%}} = 400$. Beyond these Re excessive foaming or splashing occurred falsifying the measurement.

Table S3. Maximum drag reduction DR values obtained for tested polymers in the rheometer

Parameter	PAAm1	1P(AAm-co-1St)	PAAm0.5	0.7P(AAm-co-1St)	0.5P(AAm-co-2St)
$DR_{c=0.35 \text{ wt.\%}} (\%)$	17	7	0	5	4
Re	980	1000	2000	1100	1100
$DR_{c=0.55 \text{ wt.\%}} (\%)$	18	9	2	7	5
Re	700	680	1700	690	700
$DR_{c=0.9 \text{ wt.\%}} (\%)$	22	10	5	10	9
Re	370	520	1300	390	400



Figure S10. Foam formation for hydrophobically modified polymers during DR experiments in the rheometer.

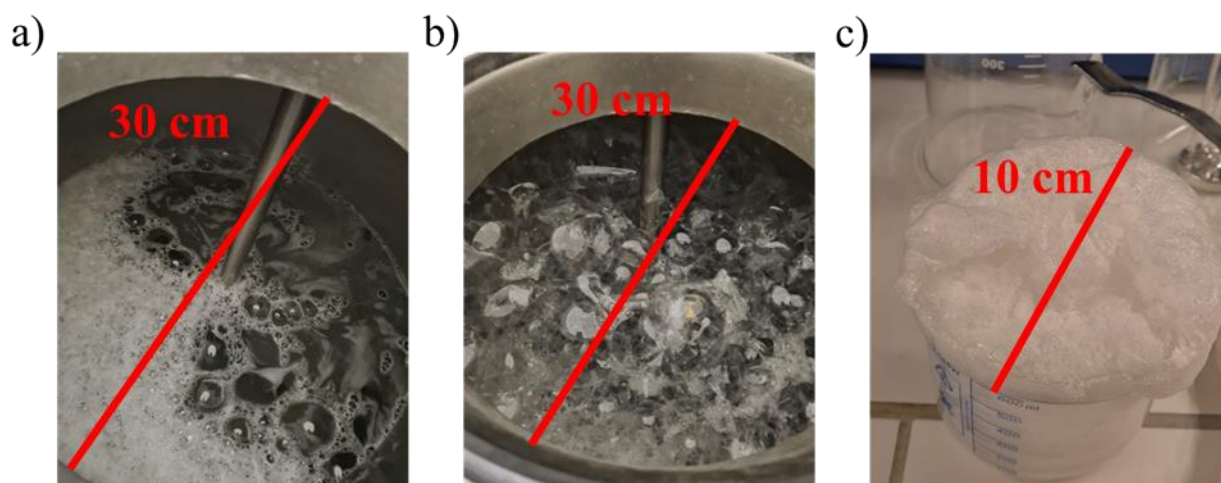


Figure S11. Foam obtained during DR experiments for hydrophobically modified polymers in ViEDRA:
a) foam of 1P(AAm-co-1St) in mixing tank, b) foam of 0.5P(AAm-co-2St) in mixing tank, c) foam of 0.5P(AAm-co-2St) taken from the mixing tank and air dried

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Publication II

Micellar Aggregation of Poly(Acrylamide-co-Styrene): Towards ‘Self-Removing’ Polymers from Solution

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KEYWORDS

Hydraulic fracturing fluid, polymer friction reducers removal, polymer-stabilised foams, self-removing hydrophobically modified copolymers

ABSTRACT

Polymer drag reducing agents (DRAs) are used in hydraulic fracturing processes to reduce frictional drag developed in fully turbulent pipe-flows. The drag reduction lowers energy consumption required to pump fluids. Removal and/or recovery of DRAs from the fracking fluids remains challenging causing environmental issues. We used model aqueous hydraulic fracturing fluids containing poly(acrylamide-co-styrene) P(AAm-co-St) as DRA and demonstrate an approach to ‘self-remove’/recover the P(AAm-co-St) copolymers by up to 55%. This approach involves foaming of the P(AAm-co-St) solutions by sparging gas into fluid (at application relevant conditions) resulting in copolymer enrichment in foam phase and subsequent removal from solution. Our observations suggest a simple method to remove or recover DRAs after drag reduction applications from fracking fluids. Liquid foams containing the P(AAm-co-St) copolymer were dried and redissolved in water offering the potential to be

reused for further drag reduction applications or, in case of waste, explored for other applications as macroporous materials.

INTRODUCTION

During the investigation of the drag reduction behaviour of associating poly(acrylamide-co-styrene) (P(AAm-co-St)) in turbulent pipe-flows¹ we observed foaming of parts of the aqueous solution and subsequent reduction of the effective P(AAm-co-St) concentration in solution. This observation inspired us to investigate the capability of P(AAm-co-St) to ‘self-remove’ from water after drag reduction applications and to stabilise aqueous foams.

Drag reduction (DR) is a key part for hydraulic fracturing. Fracturing operations are efficient but water intensive techniques used to enhance the extraction of fossil hydrocarbons from tight reservoirs,² which makes use of drag reducing agents (DRAs) added to fracturing fluids enhancing the fluid flow performance by reducing the frictional drag developed in the turbulent pipe-flow.^{2, 3, 4, 5, 6} A beneficial consequence of this effect, known as drag reduction,⁷ is that the driving pressure for a fluid containing polymer DRAs will be considerably lower compared to the pure solvent at the same flow rate. Polyacrylamide (PAAm) derivatives effectively reduce frictional drag (up to 80%) in turbulent water pipe-flows and are widely used in the oil and gas industry.³ Hydraulic fracturing processes require enormous amounts of water (millions of litres) per well to be pumped into the bedrock formations to create fractures and enable efficient oil extraction.⁸ Although the amount of PAAm DRAs used is typically around 160 ppm,⁹ the increase in fracturing operations will in turn require more polymer additives. Considering an increasing energy demand caused by population and economic growth: forecasted to grow from 275.4 million barrels of oil equivalent per day (mboe/d) in 2020 to 352 mboe/d by 2045,¹⁰ increasing of the crude oil will require a significant increase in hydraulic fracturing operations. Wastewater produced by hydraulic fracturing operations has harmful environmental impacts,^{11, 12, 13} which is worsened by the inherent stability of polymers and their presence in water or the

ground for years.¹⁴ Efforts have been made to create degradable water-soluble PAAM containing labile temperature-sensitive azo moieties in the polymer backbone.¹⁵ PAAM containing weak links provided approximately the same level of drag reduction as a pure PAAM but were able to degrade into smaller molecular weight fractions when subjected to temperatures $> 86^{\circ}\text{C}$ (the degradation temperature of azo functional groups).¹⁵ Bhambri et al.⁴ considered this irreversible degradation of DRAs to be cost ineffective and showed that thermo-responsive poly(N-isopropylacrylamide) exhibiting a lower critical solution temperature (LCST) of 32°C can be reversibly precipitated from a solution and act as an on-demand DRA offering ‘on-off’ control. However, ir/reversible coagulation approaches, also including electrocoagulation^{16, 17} and various membrane separation processes,^{18, 19, 20} used to treat the return fluids of hydraulic fracturing operations, are energy-intensive processes. Biodegradable polymers were designed as a substitution to conventional polymers for diverse applications.¹⁴ These polymers degrade into natural compounds such as CO_2 , CH_4 , water, and biomass by microbial/enzymatic action.¹⁴ Guar gum, a plant polysaccharide, is the most effective water-soluble biopolymer used as DRA in oil recovery applications.²¹ However, guar gum but also other biopolymers, suffer from fast biodegradation in water losing their drag reducing capabilities.²¹

Recently, we¹ synthesised hydrophobically modified PAAMs by copolymerisation of acrylamide and styrene resulting in copolymers containing different acrylamide/styrene ratios and tested their DR capabilities in turbulent pipe flow. The observed foaming of P(AAm-co-St) solutions may lead to ‘self-removing’ polymers for DR applications. The beauty of the self-removal of copolymers is that only a simple external trigger, namely sparging the fluid, is required, while energy intensive procedure, such as change in temperature, or material consuming procedure, such as change of pH or addition of chemicals, is not needed to degrade/precipitate the polymers. The subtracted polymeric foam could be potentially reused or the foaming itself be of interest for templating applications,²² which are worth further

investigation. Here, we show that P(AAm-co-St) copolymers could be removed from water during DR experiments in the turbulent pipe-flow and investigated the molecular weight of polymer molecules that moved from solution to the foam phase. We also studied the stability of the produced P(AAm-co-St) foams.

EXPERIMENTAL SECTION

Materials. Acetone ($\geq 99.5\%$), used to purify acrylamide (AAm $\geq 99\%$, Sigma Aldrich) was purchased from Donauchem. Styrene (St) ($\geq 99\%$), $K_2S_2O_8$ ($\geq 99\%$), cetyltrimethylammonium bromide (CTAB, $\geq 98\%$), sodium azide (NaN_3 , $\geq 99.5\%$), sodium nitrate ($NaNO_3$, $\geq 98\%$) were purchased from Sigma-Aldrich and used without further purification. Methanol ($\geq 99.8\%$) was purchased from Fisher Scientific and used as received, polyethylene oxide ($M_w = 24 \cdot 10^3$ g/mol, PEO-24K) and dextran ($M_w = 69 \cdot 10^3$ g/mol, Dextran-T69K) standards from Malvern and dishwasher salt (sodium chloride, NaCl) (Tandil) from Hofer. An inert atmosphere during copolymer synthesis was achieved using nitrogen ($\geq 99.999\%$, Messer).

Preparation of poly(acrylamide-co-styrene). Aqueous micellar copolymerisation was used to synthesise poly(acrylamide-co-styrene) P(AAm-co-St) copolymers as previously described.¹ Briefly, CTAB 3.50 g (9.60 mmol) was dissolved in 50 mL deionised water by agitation. Afterwards, in order to produce copolymers containing 2 or 4 mol% of St moieties, 74.54 mg (0.72 mmol) or 149.08 mg (1.44 mmol) of St was added to the aqueous CTAB solution, respectively. The reaction was initiated by addition of 2 mL of aqueous $K_2S_2O_8$ (88.25 mg, 0.33 mmol) solution at 80°C after dissolution of 2.50 g (35.17 mmol) AAm in the reaction mixture. Methanol was used to recover the copolymers after 24 h of reaction time and to remove most CTAB. The copolymers were not further purified and are referred to as as-synthesised P(AAm-co-St). The copolymers with different molar ratio of St/AAm are denoted as P(AAm-co-2St) and P(AAm-co-4St); the numbers stand for the molar ratio of St/AAm. Homopolymer PAAm

was prepared likewise but without St addition and was recovered and purified using the same procedure.

Surface tension. The Wilhelmy-plate method (K100, Krüss GmbH, Germany) was used to measure surface tension of the air/water interface $\gamma_{a/w}$ at 20°C for the following aqueous solutions: purified P(AAm-co-4St) with and without added CTAB, as-synthesised P(AAm-co-4St), and CTAB alone. Solution concentrations were varied from 10 to 10 000 ppm. Solutions were prepared using deionised water which was also utilised as reference.

Foam preparation and polymer removal from aqueous solutions. PAAm, used as control, or P(AAm-co-St) (co)polymers were dissolved in aqueous 0.1 M NaCl by shaking overnight at 200 rpm using an orbital shaker (PSU-10i, Biosan). Polymer solutions with concentrations ranging from 100 to 3000 ppm were prepared. These polymer solutions were used to determine the influence of the hydrophobe content on ability of (co)polymer to foam aqueous solutions. The (co)polymer screening to foam aqueous solutions was performed by handshaking the solutions for 10 min.

We used a pilot-scale flow facility, the Vienna Experiment for Drag Reducing Agents (ViEDRA), to determine the amount of the copolymer, which can be removed from aqueous 0.1 M NaCl solutions. More details on the ViEDRA setup can be found in our previous studies.^{1,}

²³ Briefly, the ViEDRA mixing tank was used to prepare 220 L P(AAm-co-4St) solution in 0.1 M NaCl. The solution was forced through a 7.2 m long stainless-steel pipe (test section) and hoses (for the backflow) using compressed air. The total distance a polymer solution was travelling is approximately 20 m per pumping cycle. Constant Reynolds number Re and flowrate were achieved by regulating the driving pressure using a feedback controller. The polymer solution was pumped ~150 times through ViEDRA to initiate foaming in the mixing tank. The foam was collected after every 3-5 pumping cycles.

Molecular weight M_w , polydispersity $\mathcal{D}$ and (co)polymer concentration were investigated using a triple detection gel permeation chromatography (GPC) system (Viscotec TDA 302,

Malvern Panalytic). The GPC system comprises a high-performance liquid chromatography (HPLC) pump (LC-20 ADVP, SHIMADZU DEUTSCHLAND GmbH), a degasser (CSI6150 4 channel degasser, laserchrom), a reservoir for solvent, and an automatic sample injector (S5200 Sykam GmbH). Three columns and a post-column filter (Nylon Membrane Filters, Whatman) having a pore size of 0.2 μm , were used for separation of polymer molecules: a guard column (A-Guard, Viscotek, Malvern) for separation based on hydrodynamic volumes of the polymer molecules and two analytical columns (A4000 exhibiting an exclusion limit of 1000 kg/mol, and A6000M with an exclusion limit of 20 000 kg/mol). Detectors were calibrated using a PEO standard ($M_w = 23651$ g/mol) and a validation dextran standard ($M_w = 68991$ g/mol). The eluent was prepared dissolving NaNO_3 ($c = 0.1$ mol/L) and NaN_3 ($c = 0.02$ wt.%) in water. The measurements were performed at constant temperature 30°C and constant flow rate 0.7 mL/min. OmniSEC 5.02 software was used to process the data. The aqueous solutions containing P(AAm-co-St) copolymers characterised using the GPC were either directly taken from the ViEDRA mixing tank or prepared by re-dissolving the (co)polymers extracted from the liquid foams by freeze drying.

Liquid foam structure and stability. Liquid foams produced in ViEDRA for P(AAm-co-4St) were characterised using a dynamic foam analyser (DFA100, Krüss, Hamburg, Germany). The glass cylinder was first filled with ~ 28 mL of polymer solution followed by filling approximately 250 ml of liquid foam, which rested on top of the liquid solution. Foam stability was analysed by measuring the time-dependent foam and total foam/liquid volume (V_F and V_T , respectively). The moisture and drainage behaviour of foam was determined measuring liquid content LC . The time dependent foam structure i.e., the bubble size (mean bubble area, $\overline{MBA}$) and their statistical distribution (bubble count, BC), was determined.

Dry foam (micro)structure. The morphology of dry foams was analysed using scanning electron microscopy (SEM, JCM-6000, JEOL GmbH, Eching, Germany). Foam samples were

prepared by placing a small fraction of liquid foam on a carbon tape fixed to a SEM sample holder followed by freeze- and air-drying. Once dried, the foam samples were gold coated (JFC-1200, JEOL GmbH, Eching, Germany) to provide electrical conductivity.

RESULTS AND DISCUSSION

Foaming capabilities of PAAm and P(AAm-co-St) were investigated by handshaking aqueous 0.1 M NaCl solutions of these (co)polymers at various concentrations. Increasing the (co)polymer concentration from 100 to 3000 ppm resulted in pronounced foaming of aqueous 0.1 M NaCl solutions of P(AAm-co-St) (Figure 1). PAAm homopolymer solutions could hardly be foamed because of the favourable homopolymer retention in the aqueous phase. An increased hydrophobic styrene moiety content in the (co)polymer (0, 2 and 4 mol.%) resulted in an increased foam volume, indicating that the hydrophobic styrene moiety assisted the formation of the liquid foam. It is worth mentioning that we¹ previously assessed the drag reducing capabilities of P(AAm-co-St) in cyclic operation and found that P(AAm-co-St) with $M_w \approx 1000$ kg/mol exhibited a factor of ~ 2 greater DR as compared to unmodified PAAm of similar M_w albeit at a very low DR level.

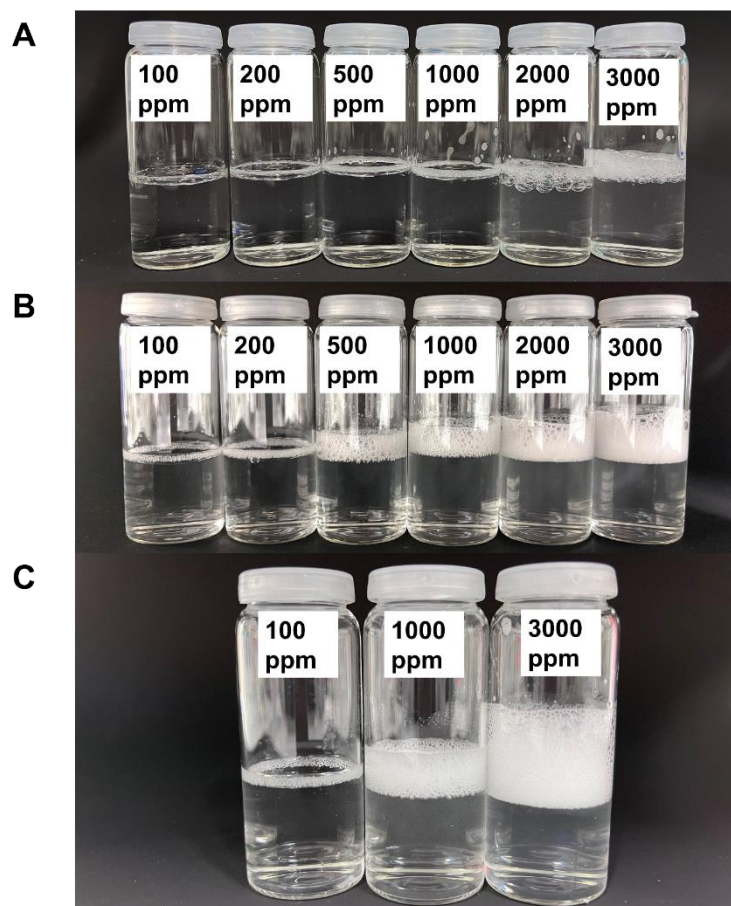


Figure 1. Shaking by hand 0.1 M NaCl aqueous solution of: a) PAAm homopolymer, b) P(AAm-co-2St), and c) P(AAm-co-4St) to produce liquid foams.

Surface tension measurements of the air/water interface $\gamma_{a/w}$ were carried out for aqueous solutions of purified P(AAm-co-4St) without and with added CTAB, as-synthesised P(AAm-co-4St), and solely CTAB in dependence of polymer concentration (Figure 2). Varied copolymer and CTAB concentration from 10 to 10 000 ppm lead to decrease of $\gamma_{a/w}$ 67 ± 0.02 mN/m; the surface tension of air/water interface ranged from $\gamma_{a/w} = 66 \pm 0.34$ mN/m to $\gamma_{a/w} = 32 \pm 0.51$ mN/m for as-synthesised P(AAm-co-4St), $\gamma_{a/w} = 72 \pm 0.1$ mN/m to $\gamma_{a/w} = 63 \pm 0.6$ mN/m for purified P(AAm-co-4St), and $\gamma_{a/w} = 50 \pm 2$ mN/m to $\gamma_{a/w} = 33 \pm 0.1$ mN/m for CTAB. A mixture containing 1000 ppm of purified P(AAm-co-4St) and various CTAB concentrations (100, 500, 1000 and 10 000 ppm) exhibited surface tension values ranging from $\gamma_{a/w} = 45 \pm 1$ to $\gamma_{a/w} = 33 \pm 0.1$ mN/m.

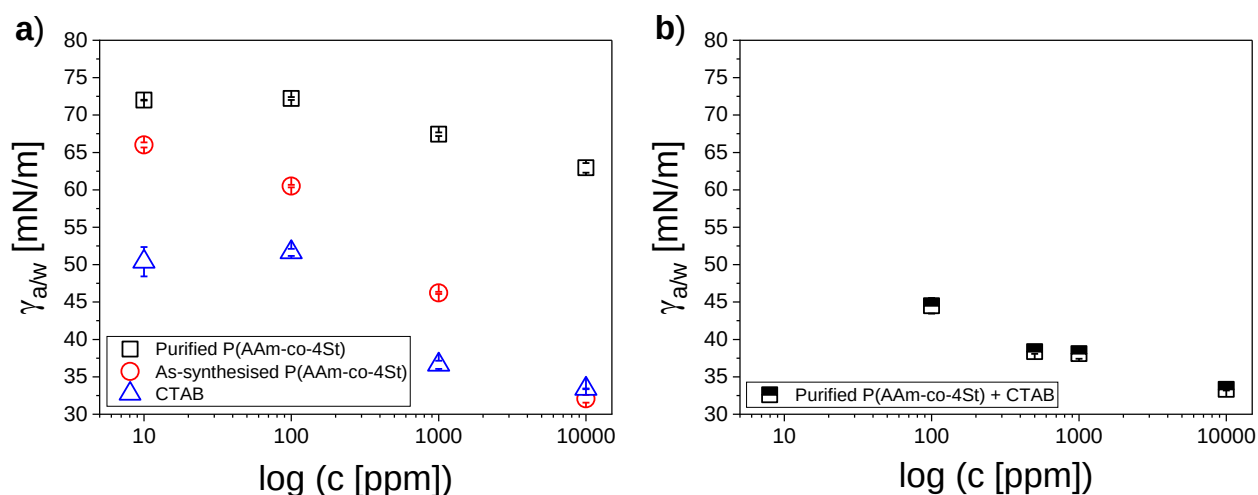


Figure 2. Surface tension $\gamma_{a/w}$ of aqueous solutions: a) purified P(AAm-co-4St), as-synthesised P(AAm-co-4St), CTAB, and b) purified P(AAm-co-4St) with added CTAB as a function of concentration. P(AAm-co-4St) concentration was kept constant at $c = 1000$ ppm for aqueous solutions of purified P(AAm-co-4St) with added CTAB, while CTAB concentration was varied as follows: 100, 500, 1000 and 10000 ppm.

Elemental analysis showed²⁴ that the copolymer still contained 0.01 wt.% (100 ppm) residual CTAB associated with the as-synthesised copolymers. This residual CTAB amount associated with the as-synthesised copolymer translates to CTAB concentration $c = 2.74 \times 10^{-11}$ M in a 10 mL P(AAm-co-4St) solution (volume of the solutions in Figure 1) with $c = 3000$ ppm. Critical micelle concentration of CTAB reported in the literature ranges from 0.82–0.98 mM.²⁵ Thus, the low concentration of residual CTAB associated with the as-synthesised copolymers in polymer solutions is insufficient for CTAB solely to stabilise aqueous foams.^{25, 26, 27} Residual CTAB associated with the copolymer is likely forming polymer/CTAB complexes at the air/water interface,^{28, 29, 30} which can also be hypothesised considering the $\gamma_{a/w}$ results for purified and as-synthesised P(AAm-co-4St). Such synergistic effects between poly(acrylamido methylpropane sulfonate) sodium salt/CTAB and pectin/CTAB at the air/water interface was reported by Fauser et al.²⁸ and Ropers et al.²⁹

Polymer removal. We tested the ‘self-removal’ of P(AAm-co-4St) at $c = 174$ ppm in a 0.1 M NaCl solution in our pilot-scale test flow facility ViEDRA at $Re = 100\,000$. When 220 L of aqueous 0.1 M NaCl solution containing the copolymer was cyclically pumped through ViEDRA, we observed over-flooding of liquid foam on top of the 300 L mixing tank (Figure S1). The extent of polymer removal from aqueous 0.1 M NaCl solution was determined using the refractive index (RI) response as a function of the retention volume (Figure 3b) from which we calculated the copolymer concentration. The recorded RI peak intensity decreased with copolymer concentration in the solution (Figure 3b). The copolymer concentration in solution decreased from initial 174 ppm to 78 ppm indicating that $55 \pm 2\%$ of P(AAm-co-4St) was removed from solution by foaming. The average M_w of P(AAm-co-4St) that adsorbed at the air/water interface–stabilising the foam–was 342 ± 23 kg/mol, while the copolymer molecules remaining in solution had an M_w of 269 ± 4 kg/mol (Figure 3a). The M_w distribution of P(AAm-co-4St) molecules in foam was slightly narrower compared to those in the solution, indicating that high M_w polymer molecules tend to enrich in the foam phase. Since we¹ previously showed that higher M_w (co)polymers are more effective DRAs in turbulent pipe-flows compared with the lower M_w ones, our ‘self-removing’ approach for DRAs which favours collection of high M_w polymer fractions in the foam phase is suitable for recovering DRAs.

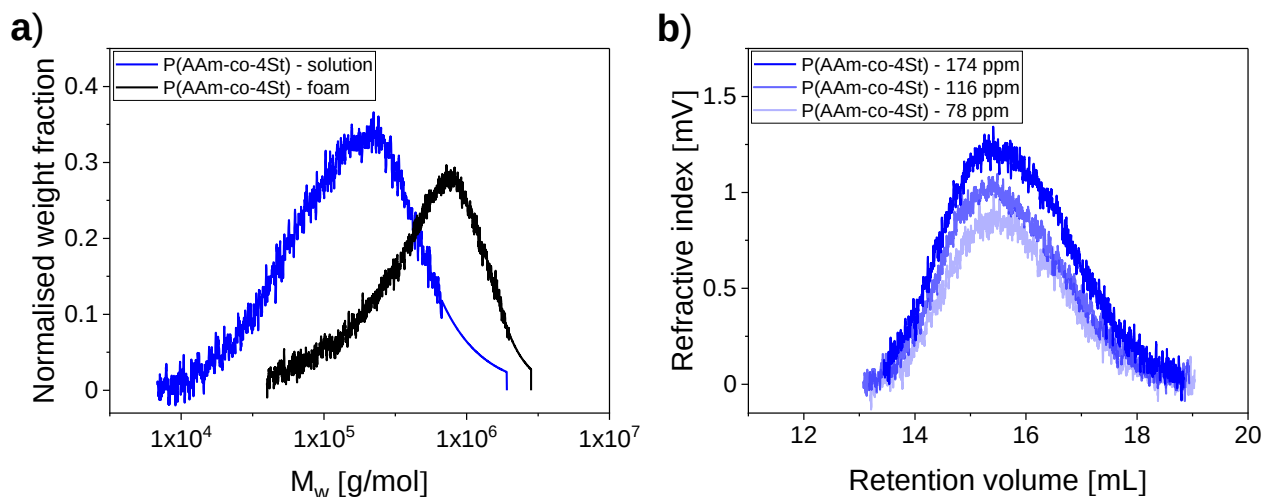


Figure 3. a) Normalised weight fraction as a function of molecular weight M_w for P(AAm-co-4St) solution extracted from foam (black) and solution (blue) remaining in ViEDRA. b) Refractive index response as a function of retention volume for P(AAm-co-4St) solutions sampled from ViEDRA at different times to monitor the P(AAm-co-4St) concentration, which dropped from 174 ppm, 116 ppm to 78 ppm.

Aqueous foam properties. The stability of liquid foams stabilised by P(AAm-co-4St) extracted from ViEDRA (Figure S2) was determined by investigating the rate of foam collapse over 9 h (Figure 4a-b). The foam comprised aqueous 0.1 M NaCl continuous phase and air as dispersed phase stabilised by as-synthesised P(AAm-co-4St) with a nominal bulk solution concentration of $c = 174$ ppm. The foam volume decreased only slightly from 288 mL reaching 280 mL over 2 h to remain constant. The liquid content of the foam decreased within 2 h by drainage from 54% to 25%, afterwards decreased slower reaching 12% after 9 h. Correspondingly, the mean bubble area only increased from 0.1 to 0.3 mm² (Figure 4c), indicating some insignificant bubble coalescence. This slight change of the mean bubble area may be caused by increase of the copolymer concentration and liquid phase viscosity associated with the liquid drainage, preventing pronounced bubble coalescence. The foam slowly dried into a polymer foam.

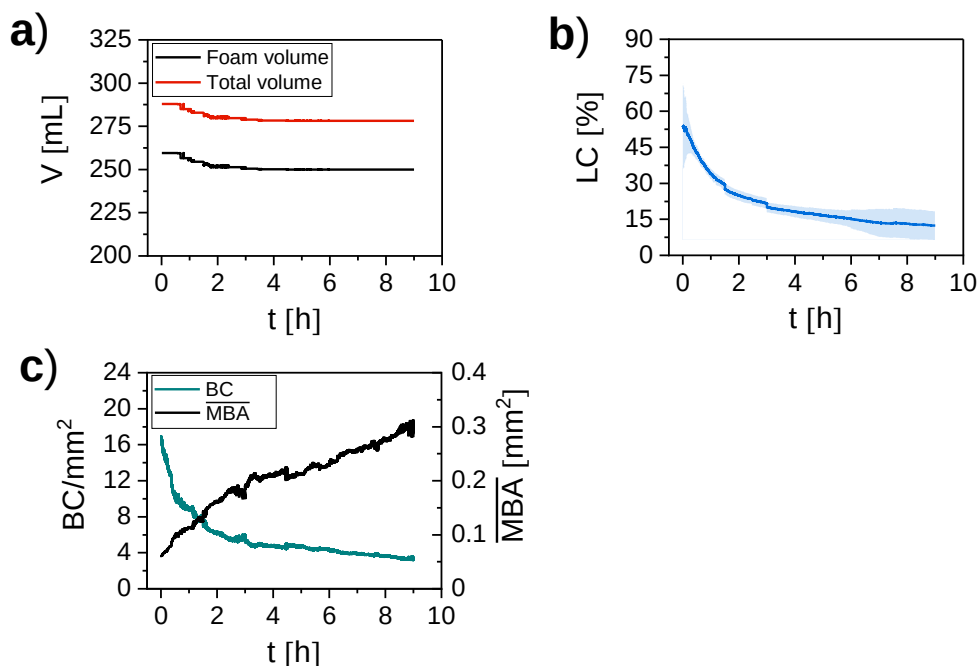


Figure 4. a) Volume V of foam and total volume as a function of time. b) Foam drainage expressed as liquid content LC over time (solid line represents mean values and shaded area their standard deviation). c) Bubble count BC per mm^2 and mean bubble area $\overline{MBA}$ over time. The P(AAm-co-4St) foam sample was extracted from 0.1 M NaCl solution in ViEDRA.

Solid foam. The extracted aqueous (0.1 M NaCl) foam stabilised by as-synthesised P(AAm-co-4St) was free-standing (Figure S2), thus we also explored whether the foam would resist collapse during freeze- or air-drying. The freeze-dried foam was partially open-celled with some cells still covered by polymer films (Figure 5a-b). The freeze-dried foam retained the volume and the shape of the container (a beaker) it was dried in (Figure S3). On the contrary, the air-dried foam (Figure 5c-d) was predominately closed-celled containing intact foam bubbles covered by a thin polymer film. Dried P(AAm-co-4St) foams can easily be redissolved in water, enabling the recovery and reuse of such polymers, for instance as drag reducing agent.

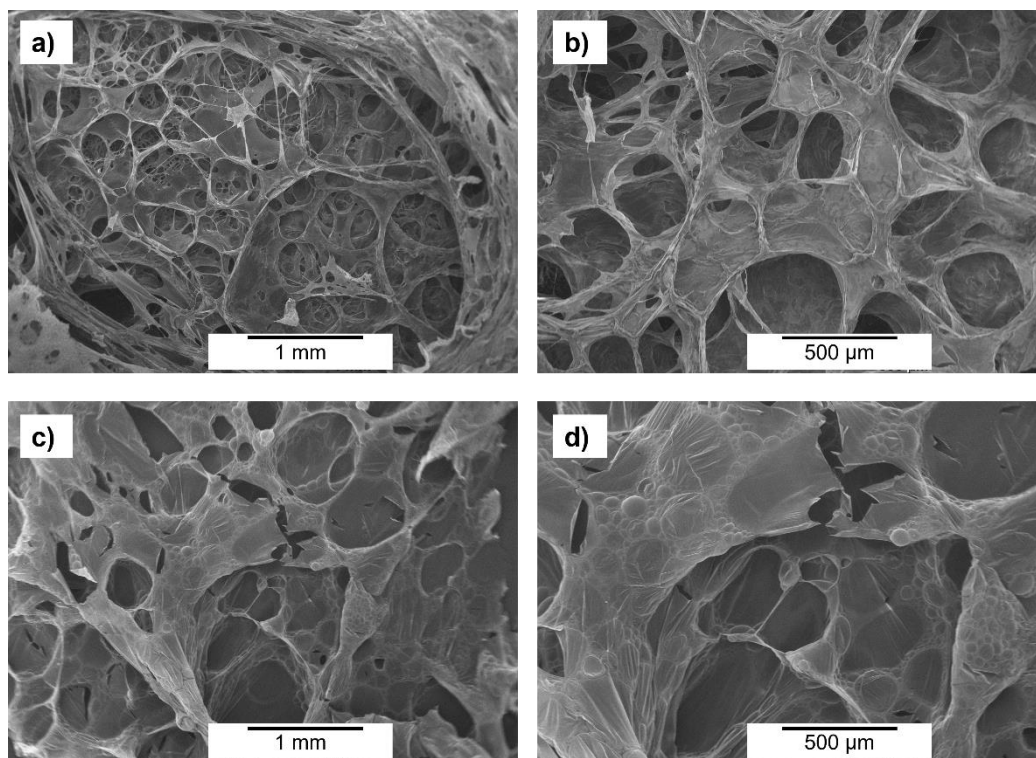


Figure 5. SEM micrographs of a)-b) freeze-dried and c)-d) air-dried P(AAm-co-4St)-stabilised foam subtracted from ViEDRA at the copolymer bulk $c = 174$ ppm.

CONCLUSIONS

Aqueous 0.1 M NaCl solutions containing P(AAm-co-St) as model drag reduction agents were foamed. The foaming capability of P(AAm-co-St) solutions increased with increasing amount of hydrophobic styrene moieties (from 0 to 4 mol.%) in the copolymer backbone and with increased polymer solution concentration. Foaming 174 ppm P(AAm-co-4St) solution in the pipe-flow test facility led to removal of 55% copolymer, which accumulated in the foam phase; high molecular weight fractions of the copolymers were prone to enrich in the foam phase. These findings suggested that drag reduction agents can be removed or recovered from return fluids after drag reduction applications by sparging the fluids, which is more chemical saving as compared to other potential DRAs recovering methods, such as changing temperature, pH or using additives. The self-standing liquid foams containing the copolymers were very stable and could be dried without collapsing, resulting in macroporous P(AAm-co-St). This

observation may lead to exploring the usefulness of removed DRAs as macroporous materials for other applications.

ASSOCIATED CONTENT

Supporting Information

Supporting observations such as photographs of foam produced in ViEDRA and freeze-dried foam (PDF)

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Author Contributions

EM and AB conceptualised the work. EM and JS performed all experimental work, EM and JS analysed the data. EM, QJ and AB wrote the manuscript and designed the figures. AB supervised the work. All authors contributed to manuscript review and editing.

Funding Sources

EM gratefully acknowledges financial support by the Institute of Materials Chemistry of University of Vienna (grant number 371300).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors acknowledge the financial support from the Faculty of Chemistry, University of Vienna (Austria). EM and JS acknowledge Lukas Brandfellner for kind technical support with gel permeation chromatography analysis.

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Supporting Information

Micellar Aggregation of Poly(Acrylamide-co-Styrene): Towards 'Self-Removing' Polymers from Solution

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SUPPLEMENTARY FIGURES

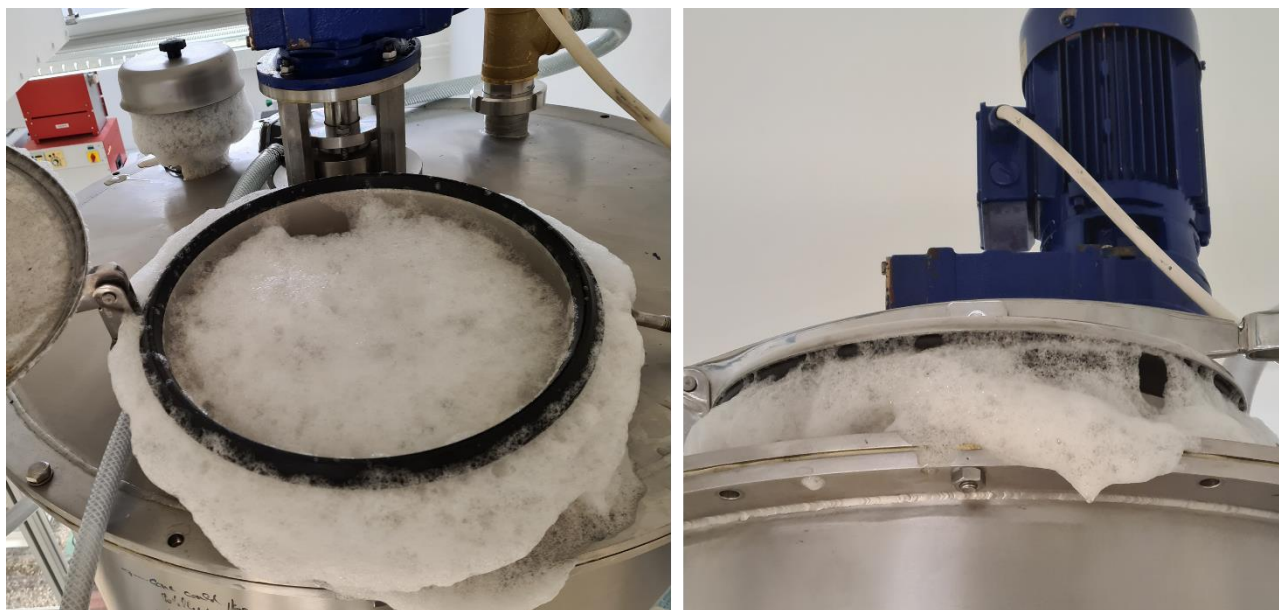


Figure S1. Foam over-flooding of the 300 L ViEDRA mixing tank by foaming 220 L of as-synthesised P(AAm-co-4St) 0.1 NaCl aqueous solution.



Figure S2. The extracted free-standing aqueous (0.1 M NaCl) foam stabilised by as-synthesised P(AAm-co-4St).

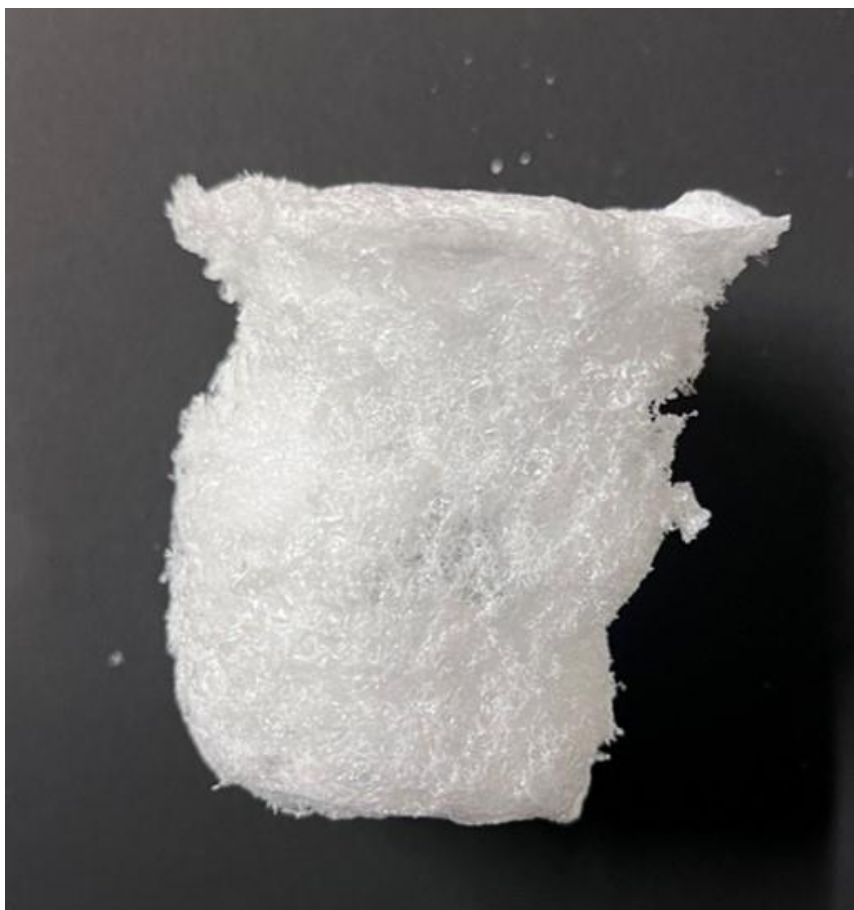


Figure S3. The freeze-dried P(AAm-co-4St) foam.

Poly(acrylamide-co-styrene): A Macrosurfactant for Oil/Water Emulsion Templating toward Robust Macroporous Hydrogels

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Cite This: *Macromolecules* 2023, 56, 3213–3223



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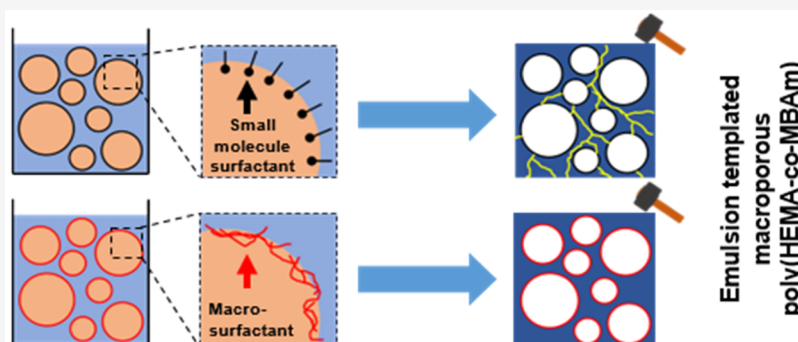
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ABSTRACT: Large amounts of relatively expensive small-molecule surfactants, between 6 and 25%, are typically required for the formulation of oil/water high or medium internal phase emulsion (H/MIPE) templates. We synthesized an amphiphilic “macrosurfactant” copolymer poly(acrylamide-co-styrene) via micellar polymerization. As-synthesized poly(acrylamide-co-styrene) still associated with 0.01 wt % cetyltrimethylammonium bromide (CTAB) can be used to produce stable toluene or cyclohexane-in-water H/MIPEs already at concentrations of 0.1 wt %. Emulsion templates containing 2-hydroxyethyl methacrylate (HEMA) and *N,N*-methylenebis(acrylamide) (MBAm) in the aqueous continuous phase can be polymerized to produce macroporous poly(HEMA-co-MBAm)/HIPEs. Our poly(HEMA-co-MBAm)/HIPEs synthesized in templates stabilized with much lower emulsifier content were mechanically more robust, in dry and swollen state, as compared with poly(HEMA-co-MBAm)HIPEs reported in the literature.

INTRODUCTION

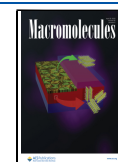
Hydrophobically driven self-assembly of small-molecule surfactants into association colloids is one of the most prominent aggregation phenomena thus representing the basis of diverse technological processes.^{1,2} Small-molecule surfactants are commonly used as emulsifiers in the formulation of water/oil or oil/water high and/or medium internal phase emulsions (HIPEs/MIPEs). M/MIPEs containing monomers as minority yet continuous phase can be polymerized to yield high porosity macroporous polymer monoliths after removal of the internal/templating phase.³ HIPEs are commonly defined as concentrated emulsions with an internal phase volume ratio >70%, while emulsions containing 30 to 70 vol % internal phase are termed MIPEs.⁴ Porous polymer monoliths synthesized by emulsion templating method are called poly(merized)H/MIPEs. Previously, it was demonstrated that the unique features of emulsion templating for the synthesis of porous polymers are the wide range of co/monomer systems^{5,6} that can be used in emulsion templates and the control exerted over the emulsion structure,⁷ which after polymerization results in polyH/MIPEs with controllable porosity, pore size, surface area,⁸ degree of interconnectivity,⁹

and mechanical properties.¹⁰ The open porous nature of polyH/MIPEs facilitates efficient fluid transport through their monolithic structure.^{11,12} Hydrogel-based polyH/MIPEs¹³ exhibit considerable water retention and sorption capabilities,¹⁴ and when combined with high porosity and pore interconnectivity, the polyH/MIPEs are valuable for diverse applications—ranging from tissue engineering^{15–17} to adsorbents.¹⁸ However, large amounts of relatively expensive surfactants are required to form stable water/oil (w/o),^{19,20} oil/water (o/w),^{13,21} and oil/oil (o/o) emulsion templates,^{22,23} which are required to successfully synthesize polyHIPEs. Small-molecule surfactants remaining in the polymer structure plasticize the resulting polymer foams, causing poor mechanical properties¹⁹ and deformation of the pore structure.²⁴ Thus, removal of surfactants is necessary to

Received: December 13, 2022

Revised: March 25, 2023

Published: April 4, 2023



prevent surfactant leakage during use, resulting in additional processing costs.¹⁹

Amphiphilic (block) copolymers, termed “macrosurfactants”,^{25–29} have emerged as efficient emulsifiers. Macrosurfactants exhibit very low critical micelle concentrations (CMC's)—in the concentration range from 10^{-9} to 10^{-4} mol/L²⁶—which is much lower compared to the CMC's typical for low molecular weight surfactants ranging from $\sim 10^{-5}$ to 1 mol/L.³⁰ The great advantage of macrosurfactants is that they enable to reduce the required emulsifier amount to stabilize HIPEs. Amphiphilic polymers were explored as sole building block for the synthesis of hydrogel polyHIPEs via surfactant-free (but not particulate stabilized)^{31,32} emulsion templating.^{33,34} Other advantages of macrosurfactants include their vast array of functionalities^{1,17} and improved mechanical properties of resulting polyHIPEs.^{17,35,25} Poloxamers, triblock copolymers of poly(ethylene oxide) and poly(propylene oxide) (PEO–PPO–PEO, commercially available as Pluronics), have been used to stabilize HIPEs.^{17,21} Zhang and Silverstein³⁶ used reactive Pluronic F-127, functionalized with dimethacrylate (F-127-DMA), as a (co)monomer and surfactant (0.6 wt %) to produce polyHIPEs that absorb both hydrophobic and hydrophilic fluids. Reactive F-127-DMA was also used to improve water sorption of hydrogel polyHIPEs.¹⁷ Bi- and triblock copolymers poly(styrene (St)-*co*-PEO) and poly(St-*co*-PEO-*co*-St) have been synthesized and used as very effective macrosurfactants^{35,37} for stabilization of water-in-methyl methacrylate (MMA) and divinylbenzene (DVB) HIPEs, which could not be stabilized using the commonly used small-molecule surfactant sorbitan monooleate (Span 80).³⁵

While much research did focus on producing versatile block copolymer macrosurfactants to provide desired surface functionalities to emulsion templated macroporous polymers,¹⁸ developing effective macrosurfactant emulsifiers with high emulsion stabilization efficiency already at very low concentrations, which is of particular relevance for H/MIPE formulations, remains largely unexplored. The concept of “supramolecular chemistry” offers the bottom-up fabrication of controlled-structure materials being governed by reversible noncovalent interactions.^{38,39} These assembled materials are composed of colloidal building blocks and have more complex, hierarchical structures with advanced properties.¹ Thus, colloids capable of self-assembly into structures hold great promise for various applications, including polymer drag reduction in pipe flows,⁴⁰ fabrication of porous polymers,⁴¹ drug delivery,⁴² or manufacture of sensors.⁴³

We synthesized poly(acrylamide-*co*-styrene) (poly(AAm-*co*-St) macrosurfactants with different molar ratios of acrylamide to styrene via micellar copolymerization, which offers advantages of scalability and ease of synthesis. Oil/water HIPE and MIPE templates containing 2-hydroxyethyl methacrylate (HEMA) and *N,N*-methylenebis(acrylamide) (MBAm) in the continuous aqueous phase were formulated using low emulsifier concentrations, down to 0.1 wt % of poly(AAm-*co*-St). Macrosurfactant-stabilized M/HIPEs were polymerized into poly(HEMA-*co*-MBAm)/HIPEs, and we characterized their physical, morphological, and mechanical properties in dry and wet state.

■ EXPERIMENTAL SECTION

Materials. Acrylamide (AAm) ($\geq 99\%$, Sigma-Aldrich) was purified twice via recrystallization from acetone ($\geq 99.5\%$, Donau-chem). Styrene (St) ($\geq 99\%$), $K_2S_2O_8$ ($\geq 99\%$), cetyltrimethyl-

ammonium bromide (CTAB, $\geq 98\%$), toluene ($\geq 99.5\%$), cyclohexane ($\geq 99.5\%$), 2-hydroxyethyl methacrylate (HEMA, $\geq 99\%$), *N,N*-methylenebis(acrylamide) (MBAm, $\geq 99\%$), polyethylene glycol *tert*-octylphenyl ether (Triton X-405, 70% in H_2O), ammonium persulfate (APS, $\geq 98\%$), *N,N,N',N'*-tetramethylethylenediamine (TEMED), formamide ($\geq 99\%$), and D_2O (99.9 atom % D) were purchased from Sigma-Aldrich and used without further purification. Methanol ($\geq 99.8\%$) and poly(vinyl alcohol) (PVA, $M_w = 15$ kg/mol) were purchased from Fisher Scientific and used as received. An inert atmosphere during copolymer synthesis was produced using nitrogen ($\geq 99.999\%$, Messer). Purification of (co)polymers was performed using dialysis (Bio Design, Thermo Fisher Scientific) with a molecular weight cutoff (MWCO) of 8000 Da. All experiments in aqueous solutions were performed using deionized water (conductivity of $0.055 \mu S/cm$, Water Purifier, Elga, UK).

Preparation of Poly(acrylamide-*co*-styrene). Poly(acrylamide-*co*-styrene) P(AAm-*co*-St) copolymers were prepared by aqueous micellar copolymerization as previously described.⁴ Briefly, 3.50 g (9.60 mmol) of CTAB was dissolved in 50 mL of deionized water followed by addition of 74.54 mg (0.72 mmol), 149.08 mg (1.44 mmol), 260.89 mg (2.52 mmol), or 409.97 mg (3.96 mmol) of St to achieve a 2, 4, 7, or 11 mol % hydrophobe content in the copolymers, respectively. AAm 2.50 g (35.17 mmol) was dissolved in the reaction mixture, and the polymerization was initiated by injecting dropwise 2 mL of aqueous $K_2S_2O_8$ (88.25 mg, 0.33 mmol) initiator solution at 80 °C. The homopolymer—poly(acrylamide) (PAAm)—was also synthesized using the same protocol, except for the addition of St, as a reference and its structure analyzed using NMR. After 24 h reaction time, the (co)polymer was precipitated in methanol under moderate mixing to remove most CTAB. P(AAm-*co*-St) copolymers that were used without further purification are termed as-synthesized P(AAm-*co*-St) throughout the article. P(AAm-*co*-St) copolymers termed purified were redissolved in deionized water and precipitated in methanol two more times followed by dialysis against ~ 4 L of deionized water for 10 days. All polymers were recovered by lyophilization.

The copolymers are called P(AAm-*co*-2St) and P(AAm-*co*-4St); the numbers stand for the molar ratio of St/AAm, which was either 2, 4, 7, or 11 mol %.

Toluene/Water Interfacial Tensions. Interfacial tensions between toluene/water (γ_{ow}) were measured using the Wilhelmy plate method (K100, Krüss GmbH, Germany) at 20 °C. Aqueous solutions of CTAB, purified P(AAm-*co*-4St) with and without added CTAB, and as-synthesized P(AAm-*co*-4St) of varying concentrations ranging from 0.001 to 1 wt % were used. Deionized water was used as reference and to prepare the solutions.

H/MIPE Templates and Synthesis of PolyH/MIPEs. PAAm or P(AAm-*co*-St) (co)polymers were dissolved in water by stirring overnight at room temperature to prepare stock solutions. The stock aqueous solutions were diluted to reach concentrations of 0.001–0.1 wt %. Toluene-in-water (o/w) H/MIPEs were prepared by addition of toluene as organic internal phase dropwise into the aqueous continuous phase containing the (co)polymers under vortexing to reach internal phase ratios of 50% and 75%. This group of emulsions was used to screen (co)polymers and to determine the required concentrations to effectively stabilize emulsions.

H/MIPE templates used for synthesis of macroporous poly-(HEMA-*co*-MBAm)/H/MIPE hydrogels were prepared by adapting a previously reported method.^{14,44} The aqueous phase consisted of P(AAm-*co*-4St), the monomers HEMA and MBAm, as cross-linker (with molar ratios of MBAm/HEMA of 14, 21, and 25 mol %), and initiator APS (and CTAB). Once all components were dissolved, cyclohexane—used as internal phase because of its lower boiling point and to ease comparison with literature—was added dropwise over 20 min while vortexing. Vortexing continued for an additional 10 min to enable formation of uniform o/w emulsion templates. Finally, the reducing agent TEMED was added into the emulsion template and shaken vigorously by hand to initiate the redox polymerization. The emulsion was polymerized at room temperature for 1 h. The templating cyclohexane phase was removed from synthesized polyH/

Table 1. Formulations of O/W HIPEs (E1–E3) and MIPEs (E4–E6) Stabilized by a Mixture of Purified P(AAm-co-4St) and CTAB and Formulations of HIPEs (E7–E9 and E7'–E9') and MIPEs (E10–E12) Stabilized by As-Synthesized P(AAm-co-4St) (All Values in wt %^a)

	aqueous phase								oil phase
	H ₂ O	purified P(AAm-co-4St)	as-synthesized P(AAm-co-4St)	CTAB	HEMA	MBAM	APS	TEMED	cyclohexane
E1	20.54	0.15		0.10	7.53	1.22	0.24	0.12	70.1
E2	20.39	0.15		0.10	7.03	1.72	0.34	0.17	70.1
E3	20.33	0.15		0.10	6.82	1.93	0.38	0.19	70.1
E4	28.72	0.10		0.10	10.37	1.63	0.32	0.16	58.6
E5	28.51	0.10		0.10	9.66	2.34	0.46	0.23	58.6
E6	28.42	0.10		0.10	9.36	2.64	0.52	0.26	58.6
E7	20.64		0.15		7.53	1.22	0.24	0.12	70.1
E8	20.49		0.15		7.03	1.72	0.34	0.17	70.1
E9	20.43		0.15		6.82	1.93	0.38	0.19	70.1
E7'	20.69		0.10		7.53	1.22	0.24	0.12	70.1
E8'	20.54		0.10		7.03	1.72	0.34	0.17	70.1
E9'	20.48		0.10		6.82	1.93	0.38	0.19	70.1
E10	28.82		0.10		10.37	1.63	0.32	0.16	58.6
E11	28.61		0.10		9.66	2.34	0.46	0.23	58.6
E12	28.52		0.10		9.36	2.64	0.52	0.26	58.6

^aAll components in wt % with respect to the total emulsion weight.

MIPE monoliths in a vented oven overnight at 60 °C, followed by drying for 48 h in a vacuum oven at 25 °C. H/MIPE recipes used to synthesize polyH/MIPE monoliths are summarized in Table 1. The H/MIPEs are classified into two series: H/MIPEs stabilized by purified P(AAm-co-4St) with added CTAB (P(AAm-co-4St)–CTAB complexes) and denoted as E1–E6; H/MIPEs stabilized by as-synthesized P(AAm-co-4St) (P(AAm-co-4St) containing traces of CTAB, less than 0.01 wt % as determined by CHNS analysis) and denoted as E7–E12 (Table 1). Each polyH/MIPE was reproduced at least three times; however, for mechanical testing we produced six monoliths.

Microstructures of H/MIPEs and PolyH/MIPEs. The microstructures of o/w H/MIPEs were examined by optical microscopy (Microscope Leica, DM2700 M, Wetzlar, Germany). Scanning electron microscopy (SEM, JCM-6000, JEOL GmbH, Echting, Germany) was used to investigate the morphology of polyH/MIPEs. Fractured polyH/MIPE surfaces were gold-coated (JFC-1200, JEOL GmbH, Echting, Germany) to provide electrical conductivity. The image analysis software package (ImageJ, <https://imagej.nih.gov/ij/download.html>) was used to further analyze SEM images and determine pore d_p and pore throat d_{pt} diameters of polyH/MIPEs.

Density and Porosity of PolyH/MIPEs. The skeletal density ρ_s of polyH/MIPEs was determined using helium pycnometry (Accupyc 1330, Micrometrics, Dunstable, UK) and their foam (envelope) density ρ_f in an envelope density analyzer (Geopyc 1360, Micrometrics, Dunstable, UK). A total of nine replicate measurements were conducted and averaged, and the porosity P (%) of the macroporous polymers calculated as follows:

$$P (\%) = \left(1 - \frac{\rho_f}{\rho_s} \right) \times 100 \quad (1)$$

Mechanical Properties of PolyH/MIPEs. Compression tests were performed on monolithic poly(HEMA-co-MBAm)HIPEs in a dual column universal testing frame (Instron 5969, Instron Ltd., Buckinghamshire, UK) equipped with a 1 kN load cell. Monolithic polyH/MIPEs were cut into disks with diameters of 23 mm and height of 10 mm. The dry samples were compressed by 70% of their original height at a speed of 1 mm/min, and stress–strain curves were recorded. Fully water swollen polyH/MIPEs P8, P8', and P11 were tested under cyclic compression (loading, unloading, and reloading) at a speed of 1 mm/min applying 50% strain. Elastic moduli E_c were determined from the slopes of the linear region of the stress–strain

curves. Crush strengths σ_c were determined from the intercept between the linear elastic region and the plateau stress region. At least five, in some cases up to 16, specimens were tested to obtain statistically relevant values of E_c and σ_c with associated standard deviation.

Dynamic Water Vapor Sorption. Dynamic water vapor sorption (DVS) measurements were performed using a dual vapor gravimetric sorption analyzer (Surface Measurement Systems UK Ltd.). Prior to measurement, slides of polyH/MIPE samples were conditioned at 0% relative humidity (RH) in a dry air atmosphere until no further mass change was detected. Water vapor sorption measurements were performed at 90% RH and 25 °C as a function of time. At least three sample pieces were characterized, and data were plotted as change in mass Δm over time t .

Water Sorption. The water swelling capacity Q of polyH/MIPEs synthesized from H/MIPEs E7–9, E7'–9', and E10–12 stabilized by as-synthesized P(AAm-co-4St) was characterized by determining the mass change $\Delta m (= m_s - m_d)$ during swelling for up to 18 h. The water uptake was followed by weighting at least five samples and measuring their dimensions in time intervals until no further change was observed. The swelling capacity is defined as

$$Q = \frac{m_s - m_d}{m_d} \quad (2)$$

where m_s is the mass of a swollen sample and m_d is the dry sample mass. We also use water sorption^a capacity, which is defined as mass increase (m_s) of the water-swollen polyH/MIPE over the original mass of the dry polyHIPE hydrogel (m_d), to aid comparison with literature. The swelling experiments were performed on freshly prepared samples (original) and on previously compressed samples to showcase the mechanical robustness of polyH/MIPEs.

RESULTS AND DISCUSSION

Properties of P(AAm-co-St). The chemical structure of P(AAm-co-St) and PAAm homopolymer was analyzed using ¹H NMR (see Figure S1), which showed that the amounts of St incorporated in the copolymer backbone were in good agreement with the initial amounts of St in the reaction mixture. In our previous study,⁴⁰ we demonstrated that for purified copolymer samples most CTAB was successfully removed by dialysis, leaving only a Br content of <0.01 wt % in the purified polymer. PAAm, P(AAm-co-2St), and P(AAm-co-

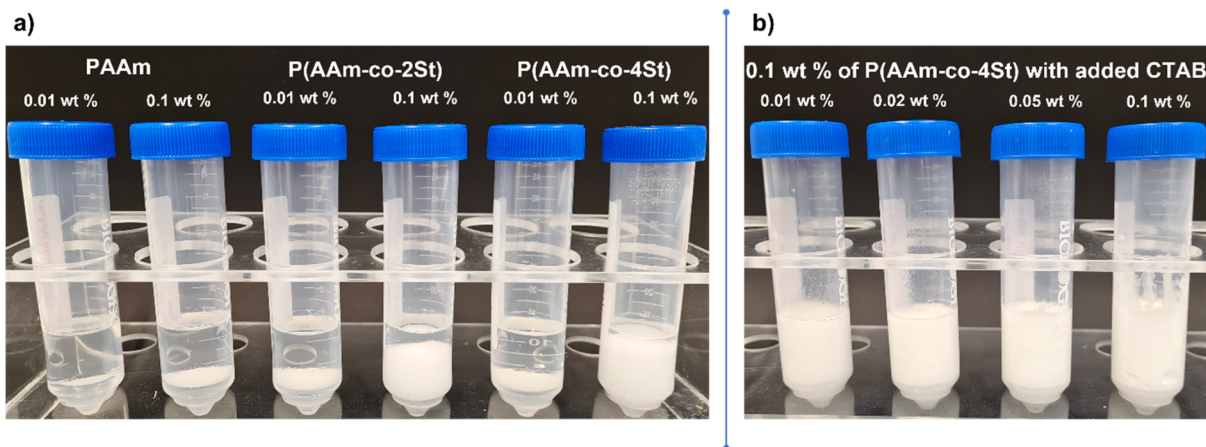


Figure 1. (a) 75/25 vol % of toluene/water HIPEs stabilized by homopolymer PAAm, copolymers P(AAm-co-2St), and P(AAm-co-4St) at polymer concentrations of 0.01 and 0.1 wt %. (b) 75/25 vol % of toluene/water HIPEs stabilized by mixture of purified P(AAm-co-4St) at constant polymer concentration of 0.1 wt % with increasing CTAB concentrations: 0.01, 0.02, 0.05, and 0.1 wt %. Photographs were taken 2 days after emulsification.

4St) have M_w of single chains of 1110 ± 190 , 590 ± 33 , and 370 ± 13 kg/mol, respectively, which were analyzed in formamide using static light scattering (SLS, see Figure S2).

Emulsification. The required concentrations of P(AAm-co-St) to effectively stabilize o/w emulsions comprising 50 vol % toluene as internal phase were determined. The (co)polymer concentrations investigated ranged from 0.001 to 0.1 wt %; increasing the (co)polymer concentration resulted in higher emulsification effectiveness, i.e., the emulsion volume in o/w mixtures increased (Figure S3b,c). The PAAm homopolymer exhibited poor emulsification performance of the o/w mixture likely because the homopolymer preferably remained in the aqueous phase rather than adsorbing at the o/w interface to enable emulsification (Figure S3a). Hydrophobically modified PAAm (P(AAm-co-St)), even containing only 2 mol % St, improved the emulsification effectiveness resulting in a significantly increased emulsion volume (see Figure S3b). At a polymer concentration of 0.1 wt % all oil was emulsified, but some water remained at the bottom of the vial. The styrene part of the copolymer enabled polymer adsorption at the o/w interface. The influence of hydrophobe content in P(AAm-co-St) on emulsification effectiveness could not be assessed in this initial screening step. HIPEs consisting of 75 vol % toluene as oil internal phase were prepared with macrosurfactant concentrations of 0.01 and 0.1 wt % (Figure 1a). It is clear that a macrosurfactant (copolymer) concentration of 0.01 wt % is ineffective for the emulsification of toluene in water, regardless of their hydrophobe content. However, increasing the copolymer concentration to 0.1 wt % results in the formation of significant o/w emulsion volumes. In this case, the copolymer containing 4 mol % styrene is a superior emulsifier, resulting in a greater emulsion volumes. The o/w emulsions stabilized with 0.1 wt % P(AAm-co-2St) and P(AAm-co-4St) contained spherical droplets occupying the majority of the emulsion volume (see Figures S4 and S5). It is worth mentioning that copolymers containing more than 4 mol % styrene were water insoluble; nevertheless, we tested the ability of P(AAm-co-St) containing 7 and 11 mol % of styrene to stabilize HIPEs, but the resulting emulsions phase separated within hours (Figure S6).

We also observed that purified P(AAm-co-4St) was not effective to emulsify the entire toluene volume of the 75:25 vol/vol toluene/water mixture at a c of 0.1 wt %; a small

toluene volume was seen to rest on top of the emulsion (Figure 1a). We performed interfacial tension γ_{wo} measurements for toluene and aqueous solutions of CTAB, purified P(AAm-co-4St) solely and with added CTAB, and as-synthesized P(AAm-co-4St) as a function of concentration (Figure S7). The addition of 0.1 wt % of purified and as-synthesized P(AAm-co-4St) reduced the interfacial tension of water/toluene interface from $\gamma_{wo} = 32 \pm 1$ mN/m to 22 ± 2 and 0.2 ± 0.1 mN/m, respectively, while at the same concentration pure CTAB reduced the γ_{wo} to 2.7 ± 1 mN/m. γ_{wo} of a mixture of 0.1 wt % purified P(AAm-co-4St) and varied CTAB concentrations (0.01, 0.05, 0.1, and 1 wt %) ranged between 0.3 and 2 mN/m. Tadros⁴⁵ showed that emulsions stabilized by a poly(vinyl alcohol) (PVA) and CTAB mixture displayed lower coalescence rates compared to those obtained with PVA or CTAB alone. Tadros stated that polymer–surfactant complexes formed, which probably created a rigid film at the o/w interface stabilizing the emulsions. Therefore, we added CTAB at concentrations of 0.01 (0.31 mM), 0.02 (0.62 mM), 0.05 (1.55 mM), and 0.1 wt % (3.1 mM) as a coemulsifier along with 0.1 wt % P(AAm-co-4St). CTAB was primarily chosen because we used it in the synthesis of P(AAm-co-St). In all cases, homogeneous o/w HIPEs were produced and stable for at least 2 days (Figure 1b). Experiments showed when using solely CTAB at a concentration of 0.1 wt % (3.1 mM) as emulsifier for toluene/water (75:25 vol %) mixtures no HIPEs could be produced; instead, it resulted in an aqueous foam layer resting on a w/o emulsion (determined by droplet test) on water (Figure S8). When using cyclohexane as dispersed phase, it was impossible to produce stable o/HEMA+MBAm in water HIPE templates using only CTAB as emulsifier (Figure S9). On the contrary, it was shown that 0.07 to 0.14 wt % CTAB was sufficient to stabilize w/styrene–divinylbenzene (DVB) HIPE templates for preparation of poly(St-co-DVB)-HIPEs.⁴⁶ Replacing the internal oil phase from toluene to cyclohexane did not affect the microstructure of the resulting HIPEs (Figure S10).

Morphology and Physical Properties of the PolyH/MIPE Monoliths. Cyclohexane-in-HEMA/MBAm dissolved in water HIPE and MIPE templates were stabilized with P(AAm-co-4St) at a concentration of 0.15 and 0.1 wt %, respectively, and additional CTAB at a concentration of 0.1 wt % (3.1 mM). Stable emulsion templates could be produced

and polymerized, which after removal of the oil and water phase resulted in pure white polyH/MIPE monoliths. The skeletal ρ_s and foam densities ρ_f of the polyHIPEs synthesized from E1–E3 were identical within the experimental error (Table 2), resulting in porosities of about 90%. Decreasing the

Table 2. Skeletal ρ_s and Foam Density ρ_f , Porosity P , Average Pore d_p , and Pore Throat d_{pt} Diameters of PolyH/MIPEs Synthesized from H/MIPEs E1–E12

sample	ρ_s (kg/m ³)	ρ_f (kg/m ³)	P (%)	d_p (μ m)	d_{pt} (μ m)
P1	1372 $\pm$ 47	138 $\pm$ 23	90 $\pm$ 2	21 $\pm$ 12	7 $\pm$ 2
P2	1362 $\pm$ 37	139 $\pm$ 27	90 $\pm$ 2	25 $\pm$ 13	7 $\pm$ 3
P3	1362 $\pm$ 33	137 $\pm$ 11	90 $\pm$ 1	20 $\pm$ 10	6 $\pm$ 2
P4	1292 $\pm$ 4	190 $\pm$ 10	85 $\pm$ 1	50 $\pm$ 31	14 $\pm$ 4
P5	1295 $\pm$ 4	200 $\pm$ 24	85 $\pm$ 2	52 $\pm$ 33	11 $\pm$ 3
P6	1300 $\pm$ 8	197 $\pm$ 14	85 $\pm$ 1	36 $\pm$ 19	12 $\pm$ 4
P7	1344 $\pm$ 26	140 $\pm$ 21	90 $\pm$ 2	31 $\pm$ 14	7 $\pm$ 3
P8	1309 $\pm$ 58	140 $\pm$ 13	90 $\pm$ 2	28 $\pm$ 9	6 $\pm$ 2
P9	1343 $\pm$ 22	153 $\pm$ 17	90 $\pm$ 1	25 $\pm$ 10	6 $\pm$ 2
P7'	1284 $\pm$ 20	136 $\pm$ 3	85 $\pm$ 3	110 $\pm$ 50	7 $\pm$ 2
P8'	1287 $\pm$ 15	125 $\pm$ 9	87 $\pm$ 3	150 $\pm$ 70	6 $\pm$ 2
P9'	1296 $\pm$ 16	131 $\pm$ 6	90 $\pm$ 2	90 $\pm$ 40	6 $\pm$ 2
P10	1292 $\pm$ 4	176 $\pm$ 15	86 $\pm$ 1	29 $\pm$ 10	8 $\pm$ 3
P11	1290 $\pm$ 12	180 $\pm$ 13	86 $\pm$ 1	29 $\pm$ 9	7 $\pm$ 2
P12	1308 $\pm$ 20	178 $\pm$ 6	87 $\pm$ 1	26 $\pm$ 12	5 $\pm$ 2

dispersed cyclohexane phase volume ratio in MIPEs E4–E6 led to an increased foam density of the polyMIPEs of 200 $\pm$ 20 kg/m³, corresponding to a porosity of 85%. The higher porosities of the polyH/MIPEs as compared to the internal phase ratios of their emulsion templates result from the removal of water from the polymer phase of the as-polymerized poly(HEMA-co-MBAm) macroporous hydrogel.

The pore structure of dried polyHIPEs consisted of spherical pores with an average pore size of about 20 μ m (Table 2), which was partially interconnected, indicating that pore throats formed by the rupture of the faces enclosing the internal phase during drying (Figure 2). Typically, the formation of open pore throats in emulsion templated macroporous polymers requires a certain amount, e.g., 5%,¹⁹ of surfactant. In our work, the concentration of small molecule surfactant, CTAB, was only 0.4% with respect to the entire emulsion volume. The presence of polymer/surfactant complex as rigid films covering

the droplets might also have hindered the formation of pore throats.

In contrast to polyHIPEs, polyMIPEs produced by polymerization of o/w MIPE templates containing 65 vol % internal phase possessed an open-porous pore structure with only few pore throats still being covered by polymer faces. PolyMIPEs had average pore sizes of 52 $\pm$ 33 μ m interconnected by pore throats in size of around 12 μ m. Because MIPEs contained a lower macrosurfactant concentration with respect to the emulsion volume as compared to the HIPEs, much less of the rigid polymer–surfactant complex film covering the emulsion droplets formed, allowing for pore throat formation during the polymerization of MIPEs.

Mechanical Properties. We conducted compression tests on dried polyH/MIPE monoliths produced from E2 and E5 containing 21 mol % of MBAm with respect to HEMA (Figure 3). The stress–strain curves are typical for porous organic materials, exhibiting a linear elastic region, from which the elastic moduli of the porous polymers were determined, followed by a plateau region at a strain >5% and a compaction region at a strain >50%. The elastic moduli and crush strengths of the polyHIPEs were lower than those of polyMIPEs (Table 3). This was due to the lower foam density of the polyHIPEs as compared to the polyMIPEs (Table 2).

To compare the mechanical properties of dried polyHIPEs synthesized from HIPEs stabilized by macrosurfactant with those produced from HIPEs stabilized by small molecule surfactants, we attempted to produce reference poly(HEMA-co-MBAm)HIPEs following published procedures¹⁴ using redox polymerization at 20 $^{\circ}$ C. However, the resulting samples shrank significantly and, therefore, could not serve as reference for mechanical properties (Figures S11–S13). As such, we compared our measured elastic moduli with those reported for poly(HEMA-co-MBAm)HIPEs in the literature;¹⁴ $\sim$ 6 MPa for polyHIPEs with a foam density of 0.13 g/cm³ and cross-linked using similar amounts of MBAm (17, 22, and 25 mol %). Our poly(HEMA-co-MBAm)HIPEs possessing the identical foam density within error had more than 200% higher elastic moduli.

All results discussed above were obtained from polyH/MIPEs synthesized from emulsion templates stabilized with purified P(AAm-co-St) and additional CTAB (0.1 wt % with respect to emulsion). Purification of the copolymer from CTAB used for its synthesis by dialysis was laborious and time-consuming, only to add CTAB again. Therefore, we explored

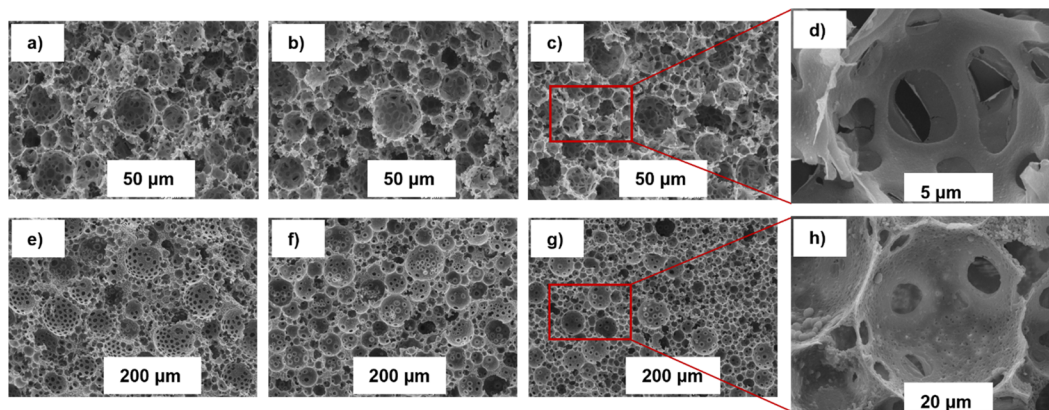


Figure 2. SEM micrographs of polyHIPEs (a–d) and polyMIPEs (e–h), which were synthesized by polymerization of H/MIPEs stabilized by a mixture of purified P(AAm-co-4St) and CTAB. Images (a–c) represent polyHIPEs produced from E1–E3, and images (e–g) represent polyMIPEs formed from E4–E6. The micrographs (d) and (h) represent a typical structure of pore throats for polyHIPEs and polyMIPEs.

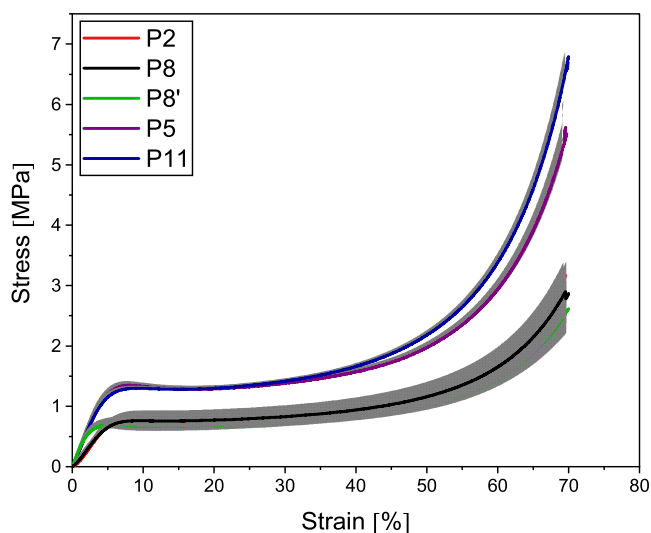


Figure 3. Compression stress–strain curves (solid lines represent mean averaged curves and shaded areas their standard deviation) of poly(HEMA-*co*-MBAm)/HIPE monoliths. PolyHIPE and polyMIPE monoliths were produced from HIPEs (E2) and MIPEs (E5) stabilized by a mixture of purified P(AAm-*co*-4St) and CTAB. PolyHIPE and polyMIPE monoliths were produced from HIPEs (E8 and E8') and MIPEs (E11) stabilized by as-synthesized P(AAm-*co*-4St) still containing 0.01 wt % CTAB with respect to the macrosurfactant as determined by elemental analysis.

Table 3. Elastic Moduli E_c and Crush Strengths σ_c of Dry and Fully Swollen PolyHIPE Monoliths Synthesized from HIPE Formulation E2, E8, and E8' and of PolyMIPEs Synthesized from MIPE Formulation E5 and E11

sample	dry		water swollen	
	E_c (MPa)	σ_c (MPa)	E_c (kPa)	σ_c (kPa)
P2	16.0 ± 2.4	0.80 ± 0.05		
P8	17.3 ± 2.0	0.77 ± 0.14	270 ± 30	22 ± 3
P8'	31.9 ± 1.5	0.70 ± 0.1	400 ± 60	33 ± 3
P5	27.7 ± 3.5	1.50 ± 0.06		
P11	28.9 ± 2.7	1.33 ± 0.02	440 ± 70	37 ± 7

the possibility of using the as-synthesized copolymer, which was precipitated from the aqueous synthesis medium using methanol, directly for the stabilization of the emulsions. Elemental analysis revealed that the as-synthesized copolymer still contained 0.01 wt % CTAB (Table S1). HIPEs stabilized with 0.15 wt % P(AAm-*co*-4St) contained 1.5×10^{-5} wt % (0.5 μ M) CTAB, while MIPEs stabilized with 0.1 wt % P(AAm-*co*-4St) contained 1.0×10^{-5} wt % (0.3 μ M) CTAB (Figure S14). After the polymerization, the resulting polyH/MIPEs had porosities of 90% and 85%, respectively (Table 2), indicating that the as-synthesized P(AAm-*co*-4St) was as effective in stabilizing emulsion templates during polymerization as compared to the surfactant–polymer complex formed by addition of CTAB to purified copolymer despite the much lower CTAB concentration in the as-synthesized copolymer.

PolyHIPEs produced from emulsion templates stabilized by as-synthesized P(AAm-*co*-4St) (E7–E9) possessed a partially interconnected pore structure consisting of spherical pores with pore throats partially covered by thin polymer faces, some of which did rupture. Pore sizes of these polyHIPEs ranged from 25 ± 10 to 31 ± 14 μ m, while the average pore throat size was around 6 μ m. PolyMIPEs produced by polymerization

of E10–E12 stabilized by as-synthesized P(AAm-*co*-4St) possessed an open-porous structure (Figure 4), characterized by average pore sizes of around 28 μ m and average pore throat sizes of around 6 μ m. The concentration of the as-synthesized P(AAm-*co*-4St) was reduced to 0.1 wt % to examine the influence of macrosurfactant on the morphology of polyHIPEs, i.e., the interconnectivity of their pore structure. HIPEs E7'–E9' stabilized with only 0.1 wt % P(AAm-*co*-4St) polymerized into polyHIPEs resulted in a much more interconnected pore structure, e.g., 100% open porous (P7'–P9') versus 12%, 29%, and 59% open, closed, and partially ruptured films covering pore throats within P7–P9, respectively (Figures 4a–c and 4e,f).

The polyHIPE synthesized from E8 stabilized by as-synthesized P(AAm-*co*-4St) had identical elastic moduli E_c and crush strengths σ_c as the polyHIPEs prepared from E2 stabilized by the purified copolymer, to which CTAB was added (Table 3). The same holds true for the polyMIPEs produced from E11 stabilized by as-synthesized P(AAm-*co*-4St), which exhibited identical E_c and σ_c within the error as compared to polyMIPE made from E5. PolyHIPE P8' had an identical E_c as polyMIPE P11, 80% higher than polyHIPE P8, which can be explained by the fact that the entire polyHIPEs P8' were open porous, and no polymer was lost in thin films covering the “pore throats” as in P8, meaning all polymer is located in edges (struts), leading to a higher stiffness. Because the emulsion droplets in the templates were covered by the P(AAm-*co*-4St)–CTAB complex, the pore throats in P8 can be anticipated to be covered by films consisting of the polymer–CTAB complex, which were extremely thin (as indicated by many ruptured films) and, thus, did not contribute to the stiffness of the polyHIPEs. Nevertheless, polyHIPE P8' had the same σ_c as polyHIPEs P8 and P2. The stiffer but more brittle behavior of P8' as compared to P8 was noticed already during drying, causing breaking of a number of P8' specimens (Figure S15). The higher elastic moduli of our poly(HEMA-*co*-MBAm)HIPEs, P8 and P8', as compared to the ones reported in the literature^{12,14} could likely be due to the much lower macrosurfactant amount used to stabilize our emulsion templates, providing a viscoelastic film and, thus, reduced the plasticizing effect caused by any remaining small molecule surfactant in the resulting polyHIPEs.

Water Sorption. We probed the water swelling capacity of polyHIPE and polyMIPE synthesized from E8, E8', and E11, respectively, stabilized by as-synthesized P(AAm-*co*-4St) (Video S1). These dried polyH/MIPEs had water sorption capacities of 8.5 ± 1.0 , 9.3 ± 1.1 , and 6.2 ± 1.2 (Figure 5a), corresponding to water sorption values ($= m_s/m_d$) of $950 \pm 100\%$, $1020 \pm 120\%$, and $720 \pm 120\%$, respectively. Kulygin and Silverstein¹⁴ reported water sorption values for poly(HEMA-*co*-MBAm)HIPEs of up to 800%. These polyHIPEs reached maximum water sorption after 45 h, whereas our polyH/MIPEs reached their equilibrium ratio (Q_E) after only 2 h. Golub and Krajnc⁴⁷ reported water sorption values for poly(HEMA-*co*-MBAm)HIPEs cross-linked with 20 mol % MBAm with respect to HEMA in buffer solution of 750%.

The water swelling capacity of both polyH/MIPEs synthesized from E7–E9, E7'–E9', and E10–E12 stabilized by as-synthesized P(AAm-*co*-4St) as a function of MBAm/HEMA molar ratio (Figure 5b) marginally decreased with increasing degree of cross-linking. For poly(MBAm-HEMA)HIPEs P7–P9 and P7'–P9' the water sorption values decreased from $1100 \pm 90\%$ to $980 \pm 50\%$ and from $1070 \pm$

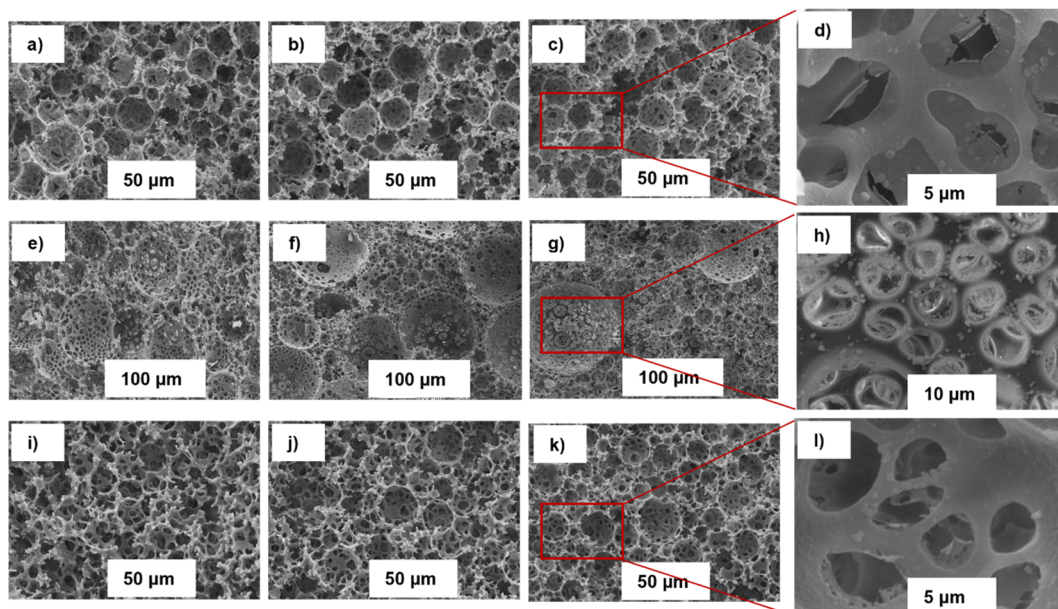


Figure 4. SEM micrographs of polyHIPEs (a–d) and polyMIPEs (e–h) synthesized by polymerization of emulsion templates stabilized by as-synthesized P(AAm-co-4St) containing traces of CTAB. Images (a–d) represent polyHIPEs produced from E7–E9, images (e–h) represent polyHIPEs produced from E7–E9, and images (i–k) represent polyMIPEs formed from E10–E12. The micrographs (d), (h), and (k) represent a typical structure of pore throats for polyHIPEs and polyMIPEs.

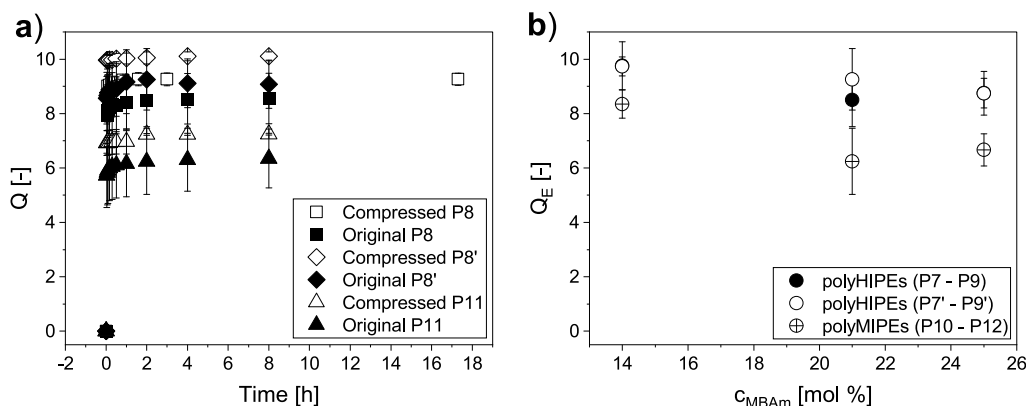


Figure 5. Water swelling ratio (Q) as a function of time (a) of dried original and previously damaged (compression tested) polyH/MIPEs synthesized from HIPE E8 and MIPE E11, respectively, stabilized by as-synthesized P(AAm-co-4St) and (b) equilibrium water swelling ratio (Q_E) as a function of cross-linker (MBAm) concentration of polyH/MIPEs. Q_E represents the swelling ratio of completely swollen polyH/MIPEs.

40% to $950 \pm 80\%$, in contrast to previously reported poly(HEMA-co-MBAm)HIPEs, for which water sorption values increased with increasing degree of cross-linking up to $\sim 810\%$ for poly(HEMA-co-MBAm)HIPEs with MBAm ratios from 17 to 25 mol %.¹⁴ The water uptake of these hydrophilic polyH/MIPEs is a combination of the swelling of the cross-linked poly(HEMA) and water imbibition into the open pore space of the polyHIPE structure. Irrespectively of the cross-linking density, the cross-linked poly(HEMA) making up the polyH/MIPEs itself absorbed only 25 ± 1 to $32 \pm 1\%$ water at 90% RH within 60 min as determined by DVS (Figure S16). The absorbed water could be removed again within 20 min. The determined water uptake is in line with reported data for bulk poly(HEMA-co-MBAm), for which swelling levels off at 32% above a cross-linking density of 4 mol % MBAm.⁴⁸

The swollen polyH/MIPE hydrogels were subjected to cyclic compression tests (Figure 6). The polyH/MIPE hydrogels had much reduced elastic moduli and strengths as

compared to the corresponding specimens in their dry state (Table 3) and follow a similar trend as the dry specimens except for polyHIPE hydrogel P8', which had a higher wet crush strength as P8. During compression, water was forced out of the porous hydrogels but was sucked back into the macroporous hydrogels during unloading (Video S2): 98% of the water was resorbed during one loading/unloading cycle. After unloading, the polyHIPEs lost 1.7% and polyMIPEs 5.6% of their original height. Repeated loading of the hydrogel polyH/MIPEs followed the original loading curves.

Surprisingly, the shape and volume of dry crushed polyH/MIPEs could be restored upon soaking in water (Video S3). Damaged compressed polyHIPEs had water sorption capacities of $\sim 1050\%$ ($1010 \pm 15\%$ (P8), $1100 \pm 20\%$ (P8')) and the polyMIPEs of $800 \pm 50\%$ (P11). These damaged porous polymers retained their integrity and swelling capacity despite a number of broken edges (struts) (Figure 7).

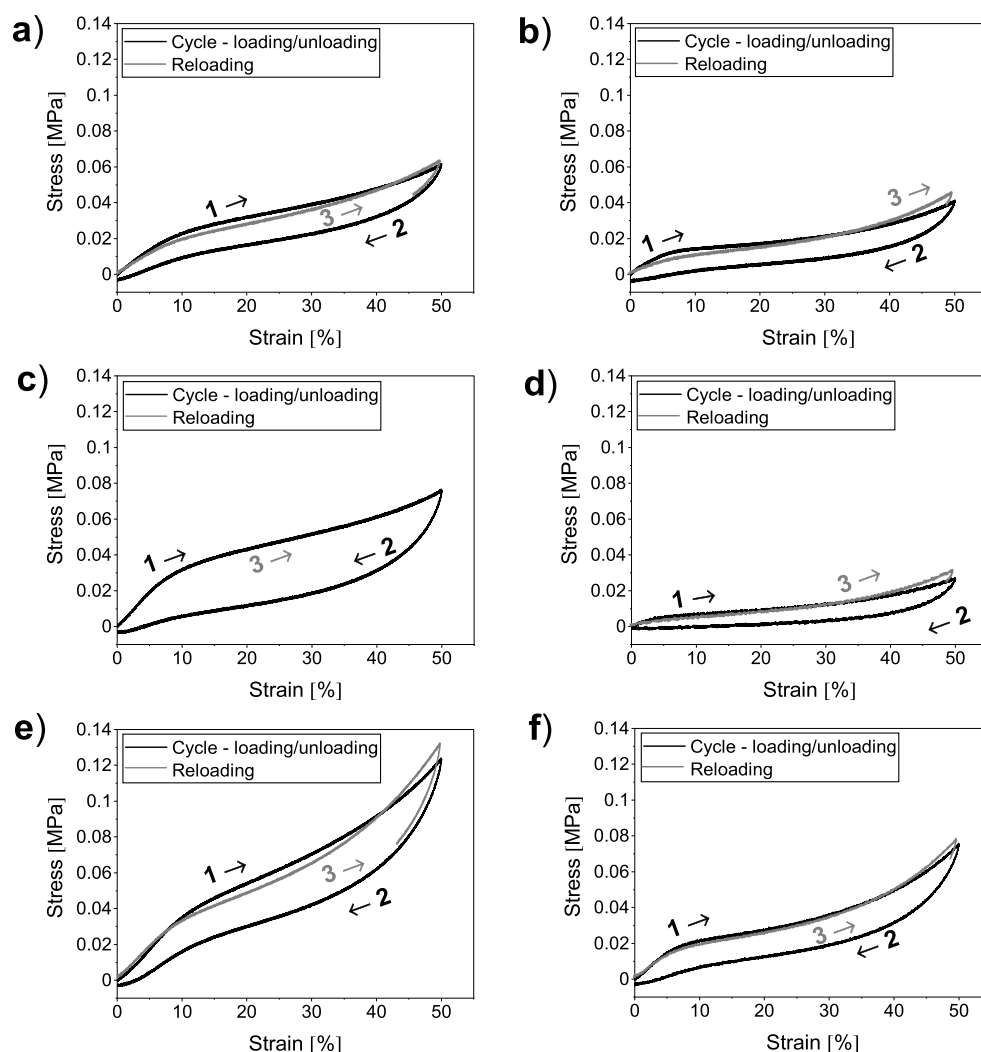


Figure 6. Compression loading, unloading, and reloading stress–strain curves of swollen monolithic polyH/MIPE hydrogels, produced from HIPEs E8, E8', and MIPE E11, stabilized by as-synthesized P(AAm-co-4St): (a) undamaged swollen polyHIPE P8, (b) previously compression loaded, damaged, and reswollen polyHIPE P8, (c) undamaged swollen polyHIPE P8', (d) previously compression loaded, damaged, and reswollen polyHIPE P8', (e) undamaged swollen polyMIPE, and (f) previously compression loaded, damaged, and reswollen polyMIPE.

The polyHIPEs ($E_c = 270 \pm 30$ kPa, $\sigma_c = 22 \pm 3$ kPa) and polyMIPEs ($E_c = 440 \pm 70$ kPa, $\sigma_c = 37 \pm 7$ kPa) that were previously compressed, damaged, and then reswollen in water had only slightly lower mechanical properties (Figure 6) than the undamaged but swollen macroporous hydrogel counterparts. The lower mechanical properties of these polyH/MIPE hydrogels are due to the number of broken edges (struts) present in the damaged materials.

CONCLUSIONS

Poly(acrylamide-co-styrene) was synthesized with different molar ratios of acrylamide to styrene via micellar copolymerization and explored as polymeric emulsifiers. We provide evidence that P(AAm-co-St) when associated with a low amount of molecular surfactant (CTAB) is an efficient emulsifier at concentrations as low as 0.1 wt % with respect to the total HIPE formulation. CTAB either can be added to purified P(AAm-co-St) or remains in low concentration (0.01 wt %) associated with this copolymer after synthesis. We demonstrated that P(AAm-co-St) is an effective emulsifier at much lower concentrations as compared with conventionally used polymeric surfactants, including Pluronic F-127 and F68.

The use of only 0.1 wt % of the copolymer with hydrophobe (styrene) content of 4 mol % and 1.5×10^{-5} wt % cosurfactant CTAB enabled the formulation of stable cyclohexane-in-HEMA/MBAm dissolved in water H/MIPE templates that could be successfully polymerized. The resulting high porosity (up to 90%), macroporous, partially and fully interconnected poly(HEMA-co-MBAm) contained spherical pores, characterized by an average pore size of about 20 μ m. The openness of the throats was affected by the P(AAm-co-4St) concentration used to stabilize the emulsion templates prior to polymerization. A higher macroemulsifier concentration (0.15 wt %) with added CTAB used to stabilize the emulsion templates probably formed rigid surfactant polymer complexes, which were still present in the face area surrounding the templated pores. Some of these faces ruptured during template removal, causing interconnectivity in the polyHIPEs. Lowering the macrosurfactant concentration in the emulsion templates resulted in poly(HEMA-co-MBAm)HIPEs with fully interconnected pores. Their elastic moduli exceeded those of partially interconnected polyHIPEs. Our poly(HEMA-co-MBAm)HIPEs possessed much higher elastic moduli (32 MPa) and water sorption capacities exceeding those of

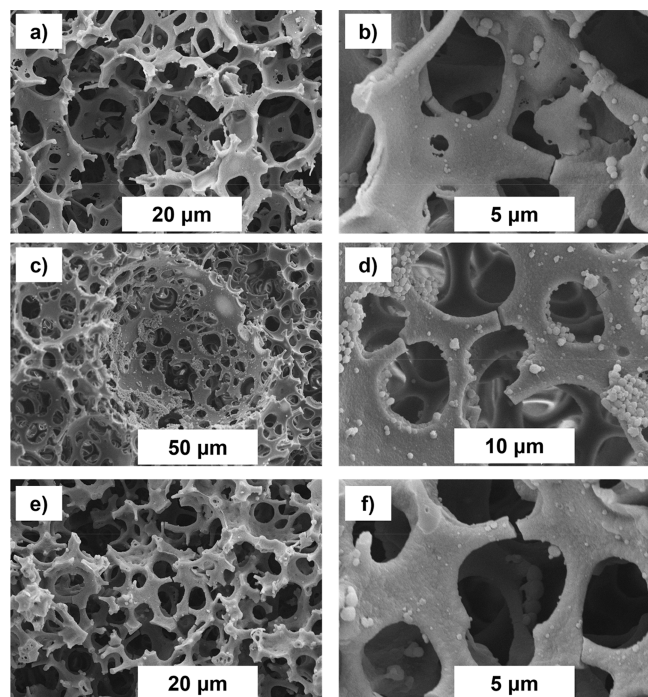


Figure 7. SEM micrographs of polyHIPEs (a–d) and polyMIPEs (e, f) synthesized by polymerization of E8, E8', and E11 H/MIPE templates. Prior to the SEM analysis samples were compressed, damaged, then reswollen in water, and dried again.

comparable polyHIPEs reported in the literature. Even in the hydrogel form, i.e., when fully water swollen, our polyH/MIPEs had very attractive mechanical properties under cyclic compression loading as desired for superporous hydrogels. Our report highlights the beneficial nature of using low concentrations of a polymeric emulsifier in combination with low amounts of a molecular cosurfactant (CTAB) for emulsion templating applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.2c02504>.

Elemental analysis, ^1H NMR, and SLS experimental procedure and results; supporting data, such as photographs of emulsions and polyHIPEs, toluene–water interfacial tensions, and microscope pictures of emulsions (PDF)

Video S1 (MP4)

Video S2 (MP4)

Video S3 (MP4)

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Author Contributions

E.M., Q.J., and A.B. conceptualized the work, E.M. and J.S. performed all experimental work, E.M. analyzed the data, and J.S. analyzed the SEM data. E.M., Q.J., and A.B. wrote the manuscript and designed the figures. Q.J. and A.B. supervised the work. All authors contributed to manuscript review and editing.

Funding

E.M. gratefully acknowledges financial support provided by the Institute of Materials Chemistry of University of Vienna (Grant 371300).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the financial support from the Institute of Materials Chemistry and Research of the Faculty of Chemistry, University of Vienna (Austria). We are grateful to Mag. Johannes Theiner for technical assistance with elemental analysis and to Prof. Dominik Eder, Dr. Niuscha Lasemi, and Dr. Davide Ret for providing resources and technical support with SLS measurements. We also acknowledge the help of Dr. Katrin Weiland and Dr. Hande Barkan-Öztürk for their assistance with DVS and density measurements as well as Prof. Christian Gruber and Nataša Tomašević for providing access to their freeze-dryer while ours was on repair.

■ ADDITIONAL NOTE

^aWe use sorption capacity rather than absorption capacity because both the open pore space and the polymer itself contribute to the overall water uptake, which cannot be distinguished by our measurements.

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Supporting Information

Poly(acrylamide-co-styrene): A macro-surfactant for o/w emulsion templating towards robust macroporous hydrogels

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EXPERIMENTAL SECTION

Characterisation of poly(acrylamide-co-styrene). ^1H NMR spectra were recorded in D_2O using a 600 MHz NMR (Bruker BioSpin, Rheinstetten, Germany) and the data processed using TopSpin 4.0.9. Following equation was used to determine the amount of incorporated styrene in P(AAm-co-St):

$$St \text{ (mol\%)} = \frac{2I_{7.3 \text{ ppm}}}{3I_{1.5-1.8 \text{ ppm}} + 2I_{7.3 \text{ ppm}}} \times 100$$

S1

where $I_{7.3 \text{ ppm}}$ is an integral of a triplet representing the protons of phenyl groups ($-\text{C}_6\text{H}_5$) and $I_{1.5-1.8 \text{ ppm}}$ an integral of protons representing methylene ($-\text{CH}_2-$) groups in the polymer backbone.

Static Light Scattering. Static light scattering (SLS) experiments were conducted using a compact goniometer system (ALV/CGS-3, Langen, Germany) equipped with a 22 mW helium-neon laser (632.8 nm). The detailed procedure is published elsewhere.¹ Briefly, the polymer was dissolved in formamide to obtain non-associated polymer solutions. Firstly, stock solutions were prepared by shaking at 200 rpm using an orbital shaker (PSU-10i, Biosan) for 48 h, followed by dilutions to reach concentrations from 0.01 to 0.2 wt.%. The apparent weight-average molecular weight M_w was determined plotting a minimum five concentrations using the Zimm data reduction method.

Elemental analysis. Elemental micro-analysis was conducted at the faculty's Microanalysis Services department. The detailed procedure is published elsewhere.¹ Briefly, an automatic Elemental Analyser EA 3000 (Eurovector) was used for simultaneous determination of C, H, N and S with sample amounts between 1.0 and 1.5 mg. Halogenes can be detected down to 0.01 wt.%.

S2

Dynamic vapour sorption. Dynamic vapour sorption measurements were performed using Dual Vapour Gravimetric Sorption Analyzer (Surface Measurement Systems UK Ltd.). Measurements were performed at 90% relative humidity as a function of time. Every sample was characterised 2 – 3 times and data plotted as change in mass Δm over time t .

SUPPLEMENTARY FIGURES AND TABLES

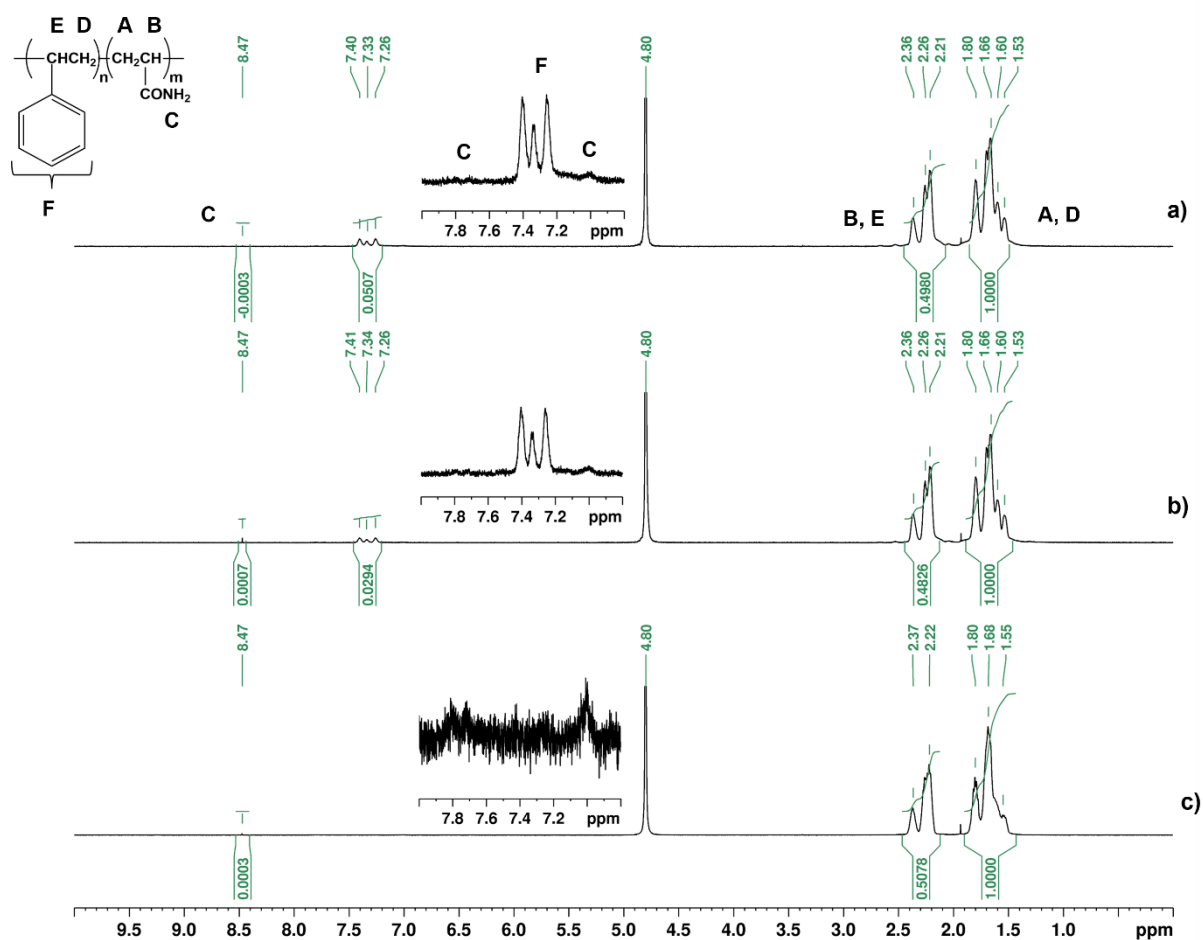


Figure S1. ^1H NMR spectra of a) P(AAm-co-4St), b) P(AAm-co-2St), and c) homopolymer PAAm acquired in D_2O .

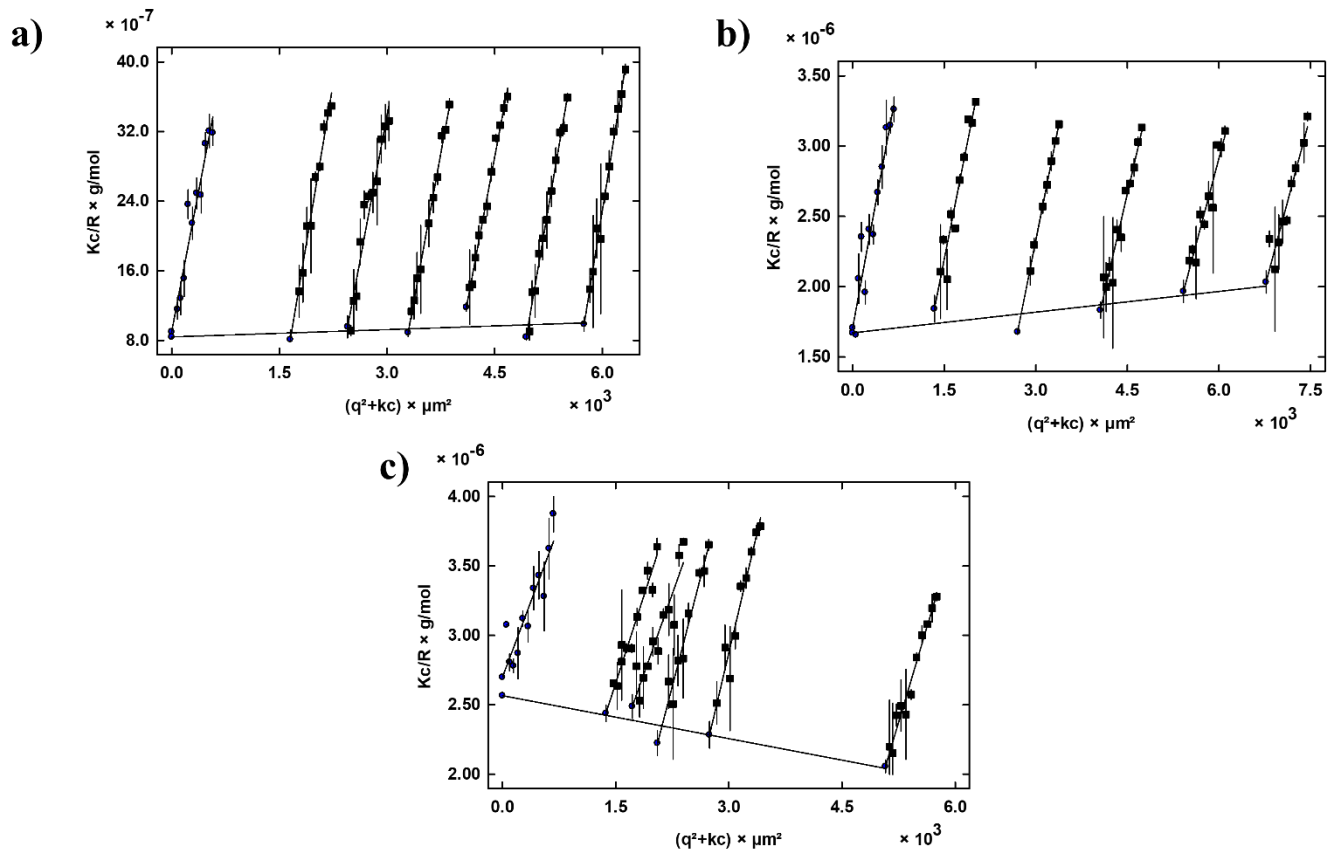


Figure S2. Static light scattering SLS data obtained in formamide and analysed using Zimm method for: a) homopolymer PAAm, b) P(AAm-co-2St), and c) P(AAm-co-4St).

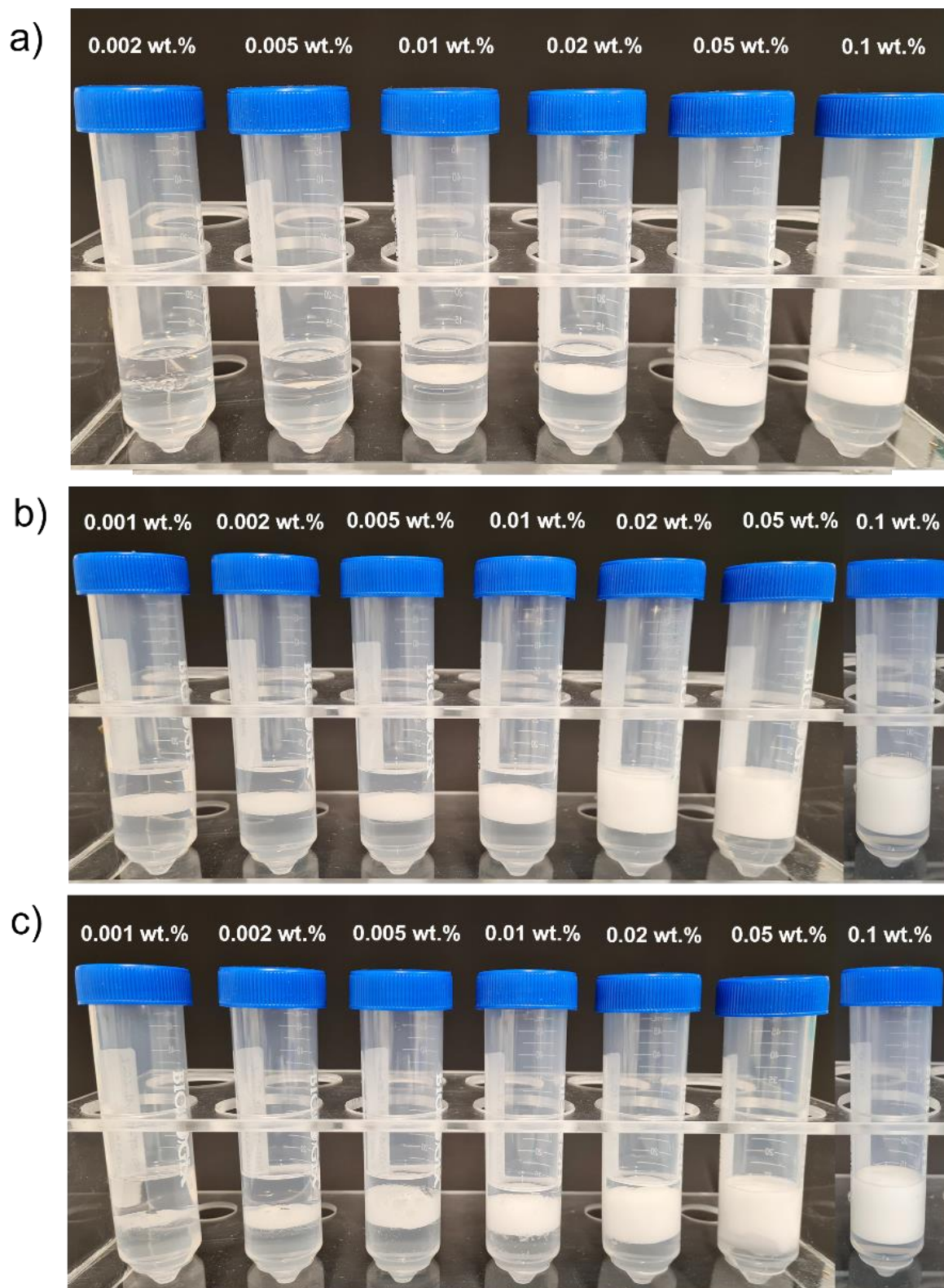


Figure S3. Emulsions comprising 50 vol.% toluene and 50 vol.% water stabilised by: a) homopolymer PAAm, copolymers b) P(AAm-co-2St), and c) P(AAm-co-4St) at different polymer concentrations. Polymer concentrations ranged from 0.001 wt % to 0.1 wt %.

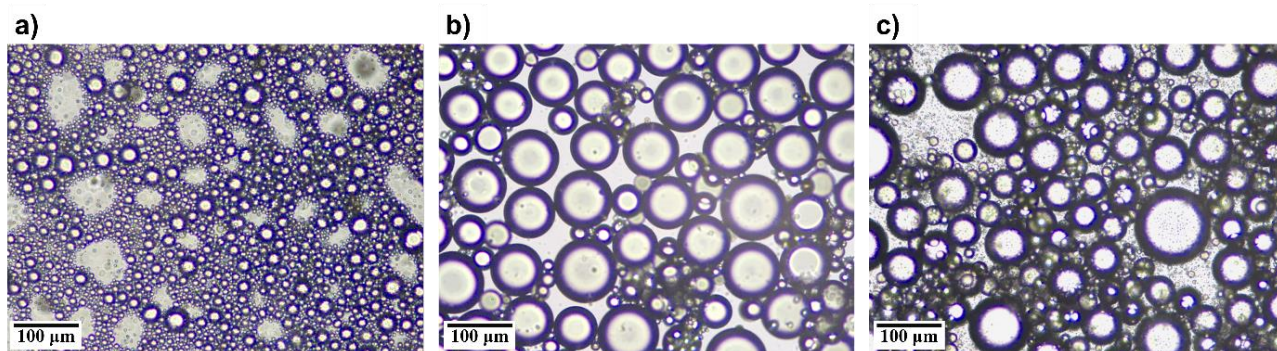


Figure S4. Microstructure of toluene/water 50/50 vol % emulsions recorded using optical microscope.

The emulsions were stabilised by polymers at concentration $c = 0.1$ wt %: a) homopolymer PAAm, b) P(AAm-co-2St), and c) P(AAm-co-4St).

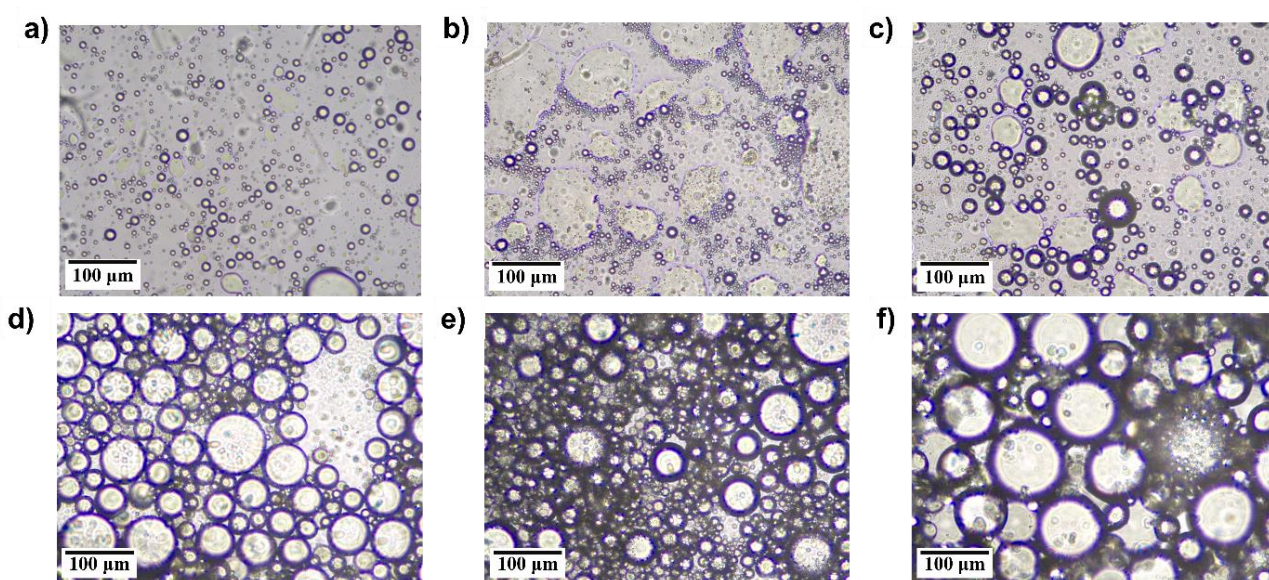


Figure S5. Microstructure of toluene/water 75/25 vol % emulsions recorded using optical microscope.

The emulsions were stabilised by polymers: a) homopolymer PAAm at $c = 0.01$ wt %, b) homopolymer PAAm at $c = 0.1$ wt %, c) P(AAm-co-2St) at $c = 0.01$ wt %, d) P(AAm-co-2St) at $c = 0.1$ wt %, e) P(AAm-co-4St) $c = 0.01$ wt %, f) P(AAm-co-4St) $c = 0.1$ wt %.

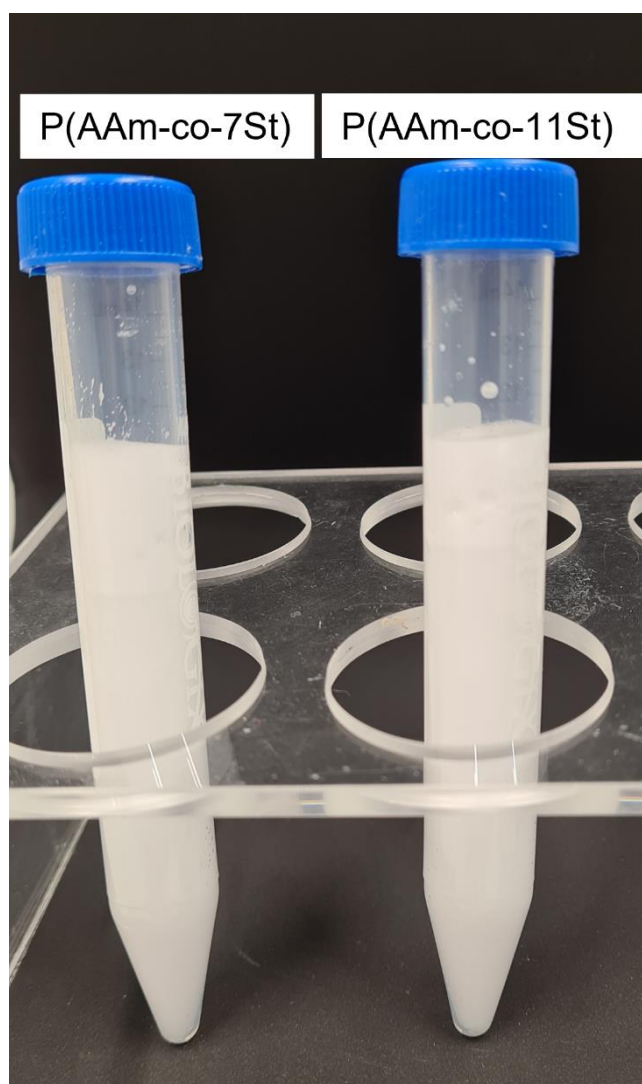


Figure S6. Water/toluene HIPEs with an emulsion phase volume ratio of $\sim 75\%$ stabilised by P(AAm-co-7St) and P(AAm-co-11St) at concentration of 0.15 wt.%. Please note on top of the emulsion rests a significant amount of aqueous foam, which removed some water from the external phase.

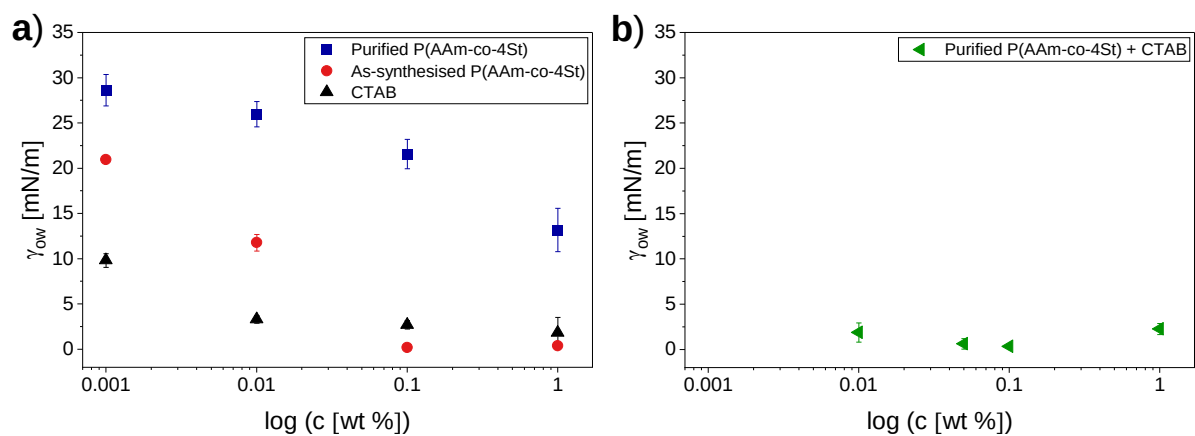


Figure S7. Interfacial tension γ_{ow} between toluene and water as function of log concentration in wt % for: a) purified P(AAm-co-4St), as-synthesised P(AAm-co-4St) and CTAB; b) purified P(AAm-co-4St) at concentration 0.1 wt.% with added CTAB at concentrations 0.01, 0.05, 0.1 and 1 wt.%.

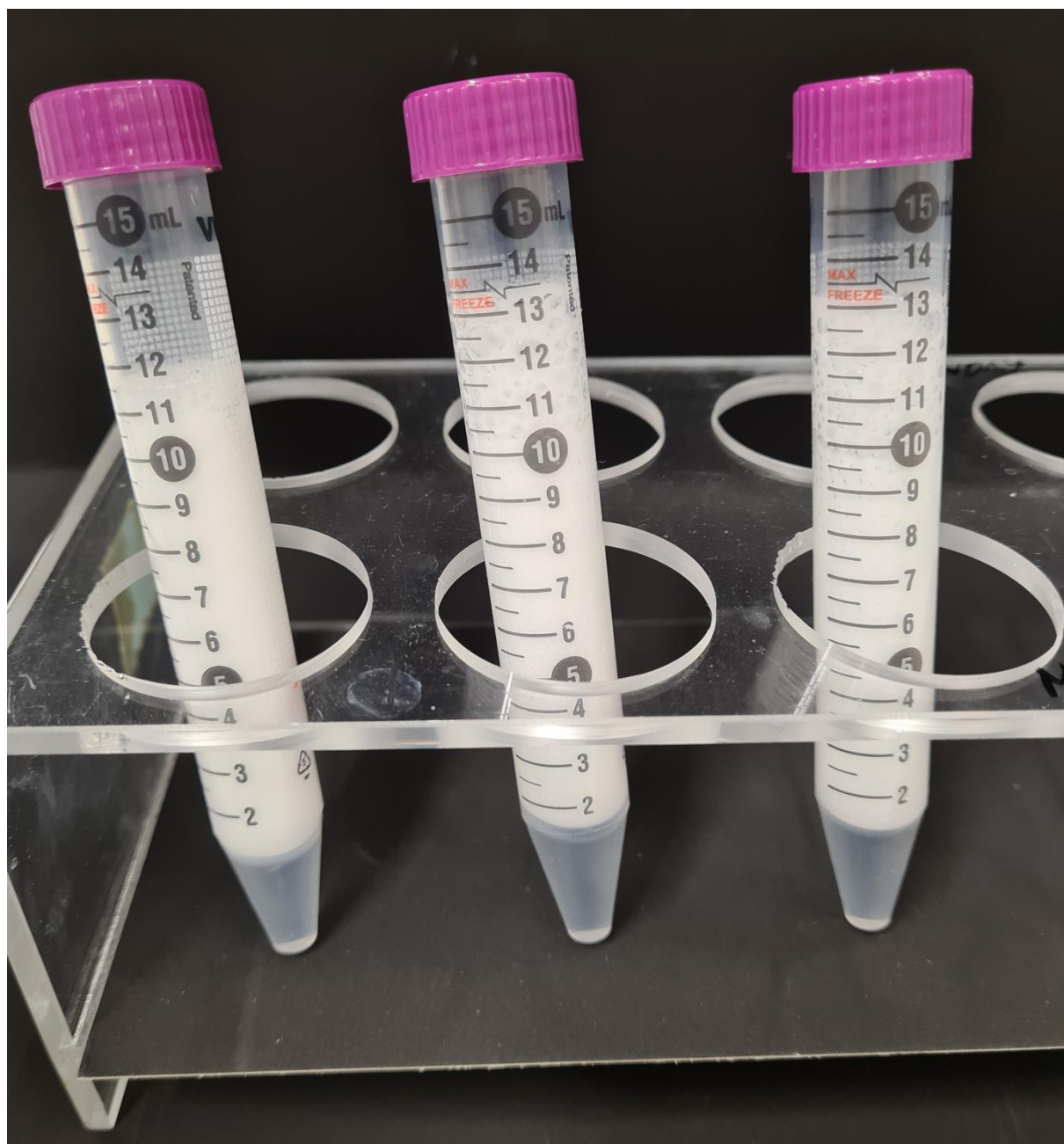


Figure S8. Three repetitions of 75/25 vol.% of toluene/water HIPEs stabilised solely by CTAB at concentration of 0.1 wt.%. Photographs were taken 24 h after emulsification.

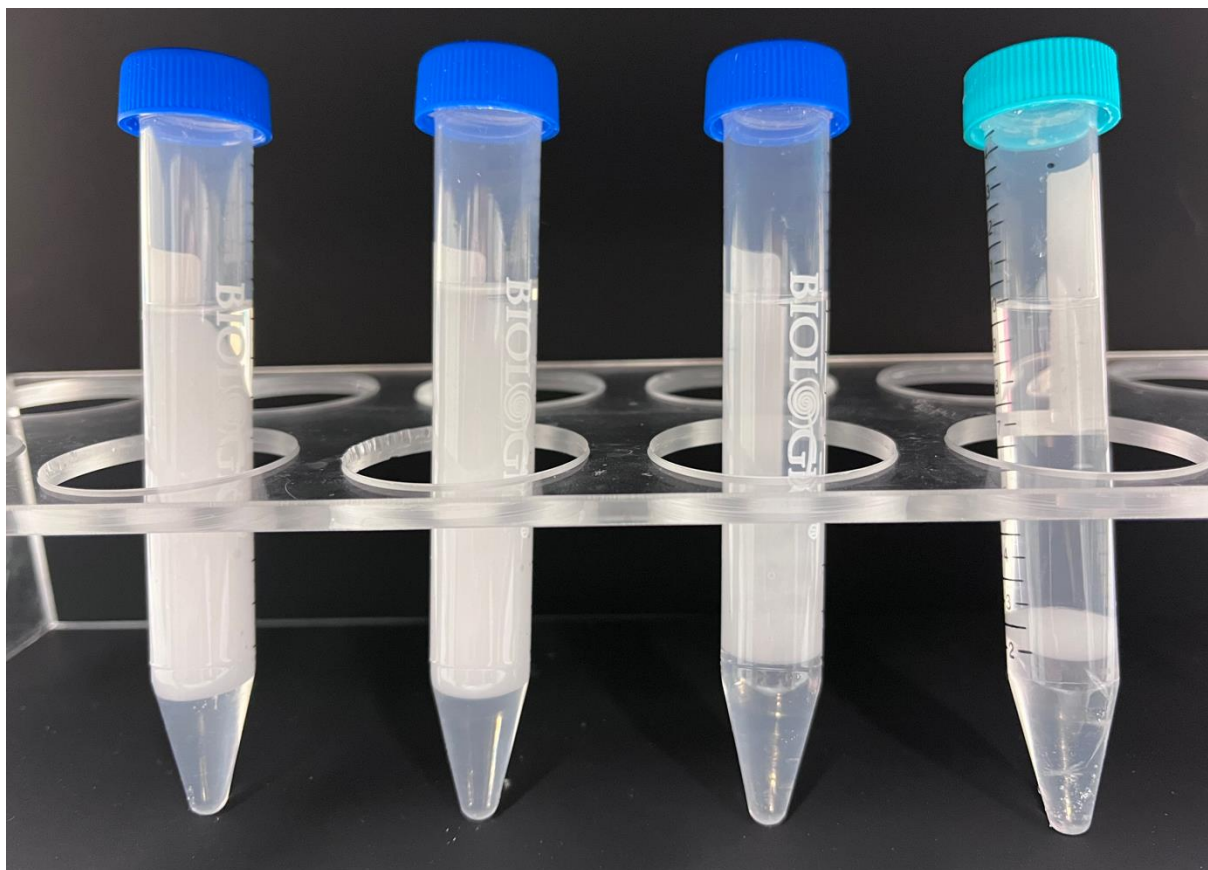


Figure S9. Four attempts to produce HIPEs from cyclohexane-in-HEMA/MBAm templates stabilised by CTAB at $c = 0.1$ wt.%.

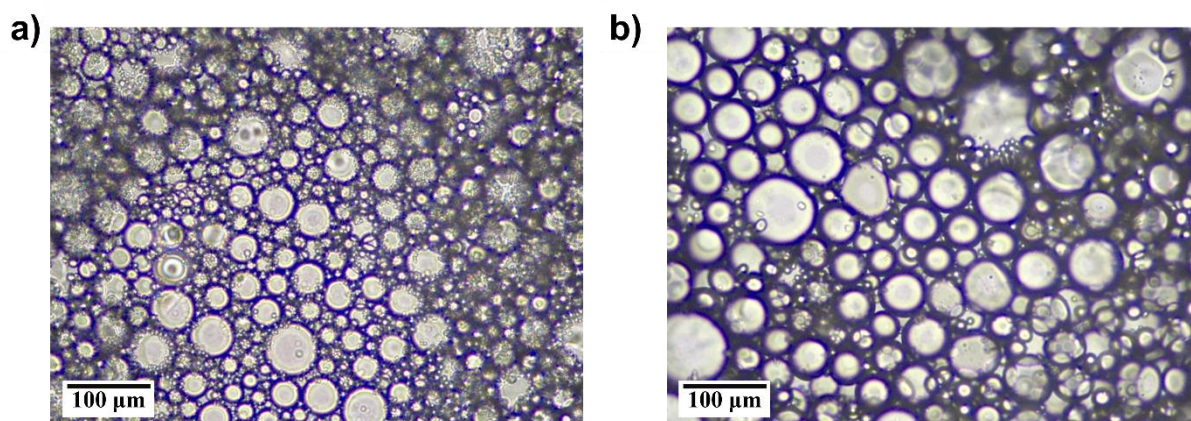


Figure S10. Microstructure O/W 75/25 vol % emulsions recorded using optical microscope. The emulsion were stabilised by mixture of purified P(AAm-co-4St) of $c = 0.1$ wt % and CTAB of $c = 0.02$ wt %. Oil phase was: a) cyclohexane, and b) toluene.

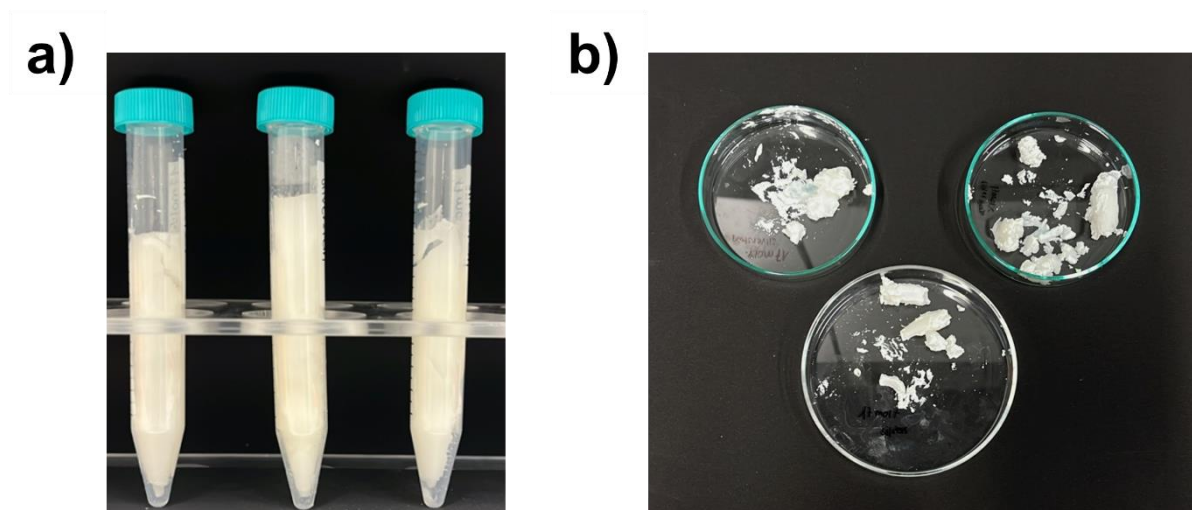


Figure S11. PolyHIPEs reproduced from literature² with 17 mol% of MBAM: a) samples after synthesis, and b) samples after drying.

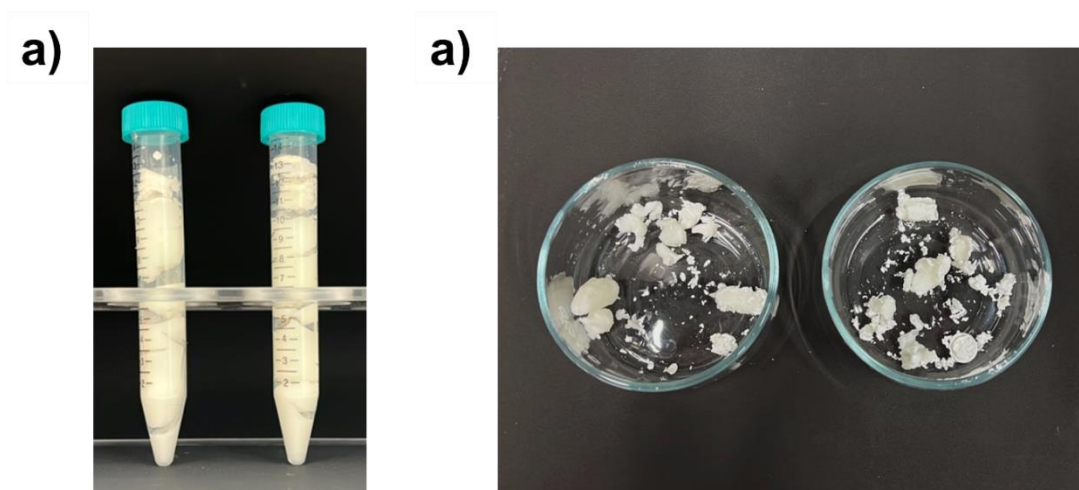


Figure S12. PolyHIPEs reproduced from literature² with 22 mol% of MBAM: a) samples after synthesis, and b) samples after drying.

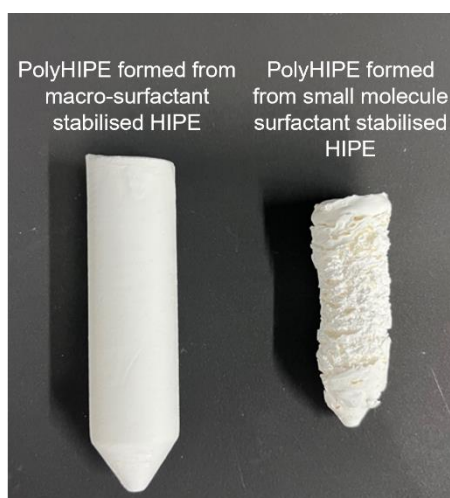


Figure S13. Left: polyHIPE monolith produced from HIPE (S2) stabilised by as-synthesised P(AAm-co-4St). Right: polyHIPE monolith reproduced from literature² stabilised by PVA at $c = 0.73$ wt % and small molecule surfactant Triton X-405 at $c = 6.38$ wt %.

Table S1. Elemental composition of as-synthesised P(AAm-co-4St) obtained using CHNS-O analysis

Sample	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	Br (wt.%)
as-synthesised P(AAm-co-4St)	48.20 ± 0.88	7.35 ± 0.01	18.09 ± 0.32	< 0.02	25.26 ± 0.62	0.01

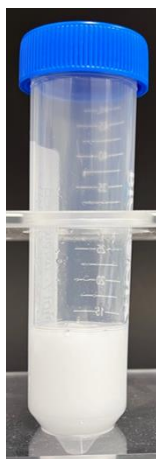


Figure S14. HIPE comprising 75/25 vol % of toluene/water stabilised by unpurified P(AAM-co-4St) at polymer $c = 0.1$ wt %.

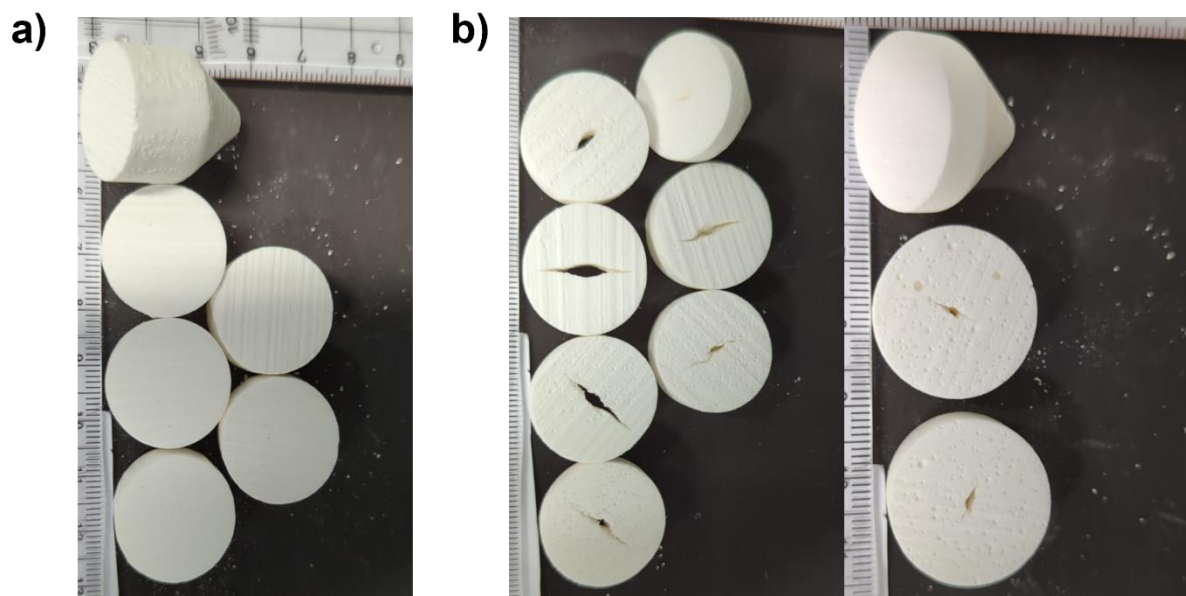


Figure S15. PolyHIPEs synthesised from poly(HEMA-co-MBAm) templates stabilised by a) 0.15 wt.% (P8) and b) 0.1 wt.% (P8') of as-synthesised P(AAm-co-4St) in a scale of approximately 40 mL.

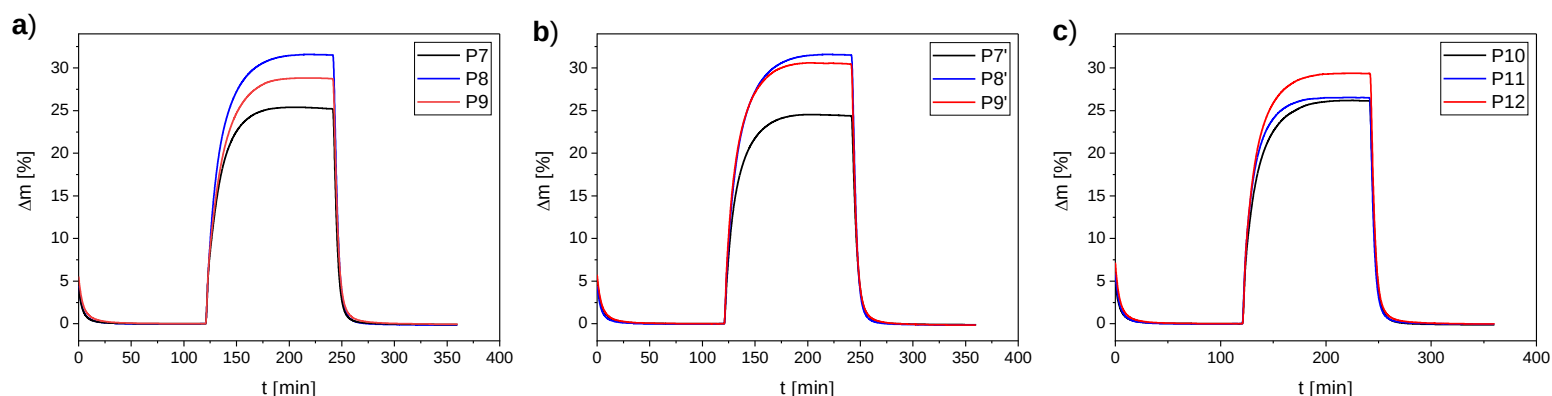


Figure S16. Change in mass Δm over time t for polyHIPEs a) P7-P9, b) P7'-P9', and polyMIPEs, c) P10-P12 at 90 % relative humidity.

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