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RAFT/MADIX Polymerization**

Aurora Mejia, Laurent Rodriguez, Charlène Schmitt, Nathalie Andreu,
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Aurora Mejia, Laurent Rodriguez, Charlène Schmitt, Nathalie Andreu, Cédric Favero, et al.. Synthesis and Viscosimetric Behavior of Poly(acrylamide- co -2-acrylamido-2-methylpropanesulfonate) Obtained by Conventional and Adiabatic Gel Process via RAFT/MADIX Polymerization. ACS Omega, 2019, 4 (6), pp.11119-11125. 10.1021/acsomega.9b00975 . hal-02187645

HAL Id: hal-02187645

<https://hal.science/hal-02187645>

Submitted on 6 Jan 2021

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Synthesis and Viscosimetric Behavior of Poly(acrylamide-co-2-acrylamido-2-methylpropanesulfonate) Obtained by Conventional and Adiabatic Gel Process via RAFT/MADIX Polymerization

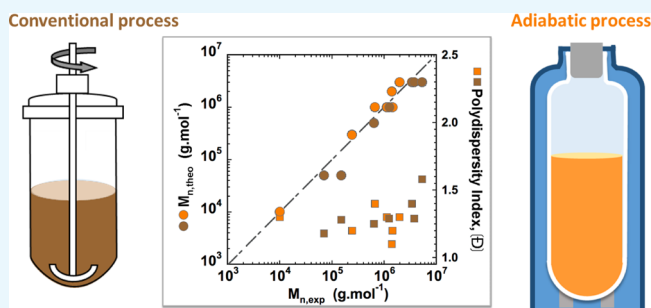
Aurora Mejia,[†] Laurent Rodriguez,^{†,‡,§} Charlène Schmitt,[†] Nathalie Andreu,[†] Cedrick Favéro,[‡] Olivier Braun,[‡] Guillaume Dupuis,^{‡,§} Elise Deniau,^{†,§} Stéphanie Reynaud,^{*,†,§} and Bruno Grassl^{†,§}

[†]CNRS/UNIV PAU & PAYS ADOUR/E2S UPPA, Institut des sciences analytiques et de physicochimie pour l'environnement et les matériaux (IPREM), UMR 5254, 64000 Pau, France

[‡]SNF S.A.S., ZAC de Milieux, 42163 Andrézieux Cedex, France

[§]Poweltec, ZAC RUEIL 2000, 3 Rue Paul Heroult, 92500 Rueil Malmaison, France

ABSTRACT: High molar masses homopolymers of both acrylamide (AM) and 2-acrylamido-2-methylpropanesulfonate (AMPS) as well as poly(AM-*stat*-AMPS) exhibiting a large range copolymer composition has been obtained via the optimization of a purely adiabatic gel process. Monomer concentrations ranging from 2.0 to 3.47 M have been successfully tested while keeping the control of the molar masses up to 5×10^6 g mol⁻¹. The products have been characterized in terms of molecular mass and viscosimetric properties.



INTRODUCTION

Polyacrylamides (PAMs) exhibit strong hydrogen bonding and water solubility, and the most interesting about this polymer is associated with its properties that lead to a multitude of uses in diverse industries. PAMs act as primary flocculants or coagulants in water clarification and mining application.¹ They are useful in the paper industry and may be used as flooding aids in secondary oil recovery from the producing oil well.² Other applications include agriculture, textile, and cosmetics. Acrylamide-based (AM-based) monomers are known for their high polymerizability properties, which rank them as top-grade candidates for the synthesis of ultrahigh molecular weight (co)polymers.³ 2-acrylamido-2-methylpropanesulfonate (AMPS) is a hydrosoluble and reactive acrylamide-based monomer, having the potential to improve the main chain stability in harsh environments such as temperature and salinity.⁴ The ultrahigh molecular weight (UHMW) polyacrylamide-based polymer are industrially obtained via conventional radical polymerization resulting in large molar mass distribution⁵ that may affect the final properties.

Reversible-deactivation radical polymerization (RDRP)⁶ is a synthetic route that yields functional polymers with controlled architecture and narrow molar mass distribution. The control of polymerization is provided via a reversible capping and de-capping of the growing (radical) polymer chain. During the process, the concentration of the growing radical species is low enough to consider the termination reaction negligible. The three most effective RDRPs include nitroxide-mediated polymerization (NMP),^{7–10} atom transfer radical polymerization (ATRP),¹¹ and reversible addition fragmentation chain

transfer (RAFT)¹² polymerization. The macromolecular design by the interchange of xanthate (MADIX)^{13,14} process may be assimilated to the RAFT system by using xanthates as a chain agent transfer.

All these approaches have been optimized by several groups for the synthesis of UHMW homo- and copolymers of acrylamides in the aqueous phase. So far, aqueous phase NMP leads to the synthesis of polyacrylamide (PAM) with a limited range of molar masses,¹⁰ that is, below 1×10^5 g mol⁻¹. Higher molar masses, up to 5.9×10^5 g mol⁻¹, were reached by using ATRP for the polymerization of different acrylamide-based monomers mediated by tris[2-(dimethylamino)ethyl]amine (Me₆TREN)/CuCl as a catalyst.¹⁵ In both cases, the control of polymerization was kept and the dispersities remained below 1.5 even for the highest molar masses. The RAFT process remains the controlled polymerization route in which the highest polyacrylamide molar masses are obtained. Recently, UHMW has been obtained via photomediated-RAFT polymerization. Homopolymers of *N,N*-dimethylacrylamide (DMA) have been obtained and controlled by a trithiocarbonate (TCT) or a xanthate iniferter using a UV light source. The reaction mixture volumes of few milliliters as well as the limited monomer concentration (from 1 to 2 M) have been studied. Molar masses reaching 8.57×10^6 g mol⁻¹ and dispersities below 1.2 were obtained.¹⁶

Received: May 7, 2019

Accepted: June 10, 2019

Published: June 25, 2019

Table 1. Comparison of the Adiabatic Gel Process (AGP) and Conventional Gel Process (CGP) for RAFT/MADIX Polymerization of Poly(AM-*stat*-AMPS)^a

theoretical [AMPS]/[AM]	CGP				AGP		
	polymer	$\bar{M}_{n(th)}$ ($\times 10^3$; g/mol)	$\bar{M}_{n(exp)}$ ($\times 10^3$; g/mol)	\bar{D}	$\bar{M}_{n(th)}$ ($\times 10^3$; g/mol)	$\bar{M}_{n(exp)}$ ($\times 10^3$ g/mol)	\bar{D}
100/0	#1	10	8.5	1.30	45	150	1.30
	#2	306	240	1.20	850	1240	1.30
	#3	975	660	1.40	2050	3730	1.30
	#4	310	200	1.20			
70/30	#5	2290	1970	1.30			
25/75	#6	1350	1430	1.20	45	70	1.20
	#7				440	640	1.30
	#8				2600	3430	1.40
5/95	#9	770	1120	1.30			
0/100	#10	930	1400	1.10	2500	5030	1.60

^aAll the polymers have been processed using PAM₇-X as a transfer agent, but entry #1 was obtained with Rhodixan and entries #2 and #3 with PAMPS₅₀-X.

Table 2. Experimental Conditions for the Copolymer Synthesis under Conventional Gel Conditions

theoretical [AMPS]/[AM]	experimental conditions under the conventional gel process (CGP)					
	$\bar{M}_{n(th)}$ ($\times 10^6$ g mol ⁻¹)	[M] ₀ (M), wt %	transfer agent (M)	[APS]/[PAM ₇ -X] (mol/mol)	yield (%) ^a	exp. polymer [AMPS]/[AM] ^b
100/0						
#1	0.01	1.6, 33.7%	Rhodixan 4×10^{-2}	0.12	99	100/0
#2	0.30	2.0, 45.8%	PAMPS ₅₀ -X 1.3×10^{-3}	0.17	97	
#3	1.00	2.0, 45.8%	PAMPS ₅₀ -X 4.0×10^{-4}	0.17	95	
#4	0.30	2.0, 45.8%	PAM ₇ -X 1.3×10^{-3}	0.17	98	
70/30	3.00	1.87, 42.8%; 0.8, 5.6%	PAM ₇ -X 1.6×10^{-4}	0.20	86	70/30
25/75	1.00	0.56, 17.3%; 2.27, 16.1%	PAM ₇ -X 1.95×10^{-4}	0.20	90	25/75
5/95	1.00	0.19, 2.7%; 2.27, 16.1%	PAM ₇ -X 1.9×10^{-4}	0.20	81	5/95
0/100	2.00	2.0, 14.2%	PAM ₇ -X 1.3×10^{-4}	0.17	95	0/100

^aVia SEC characterization. ^bVia NMR characterization, see the [Experimental Section](#).

However, for economic reasons, the polymerization of acrylamide in a concentration as high as possible has been desired as well as a better control of the macromolecular size and composition to target a specific physicochemical behavior. Considering the acrylamide monomer, its polymerization in an aqueous solution at a concentration above 10 wt %, is accompanied by the formation of a gel reaction medium while polymerization is being performed. Read et al. took advantage of this feature to perform the gel polymerization of acrylamides while controlling the molar masses by using the RAFT/MADIX.¹⁷ UHMW of polyacrylamides has been obtained by controlling the reaction temperature via a thermostated bath at low temperature. The MADIX system allows the synthesis of homopolymers and copolymers of acrylamide (AM) with molar masses above 1×10^6 g mol⁻¹ while keeping the distribution below 1.55. However, the limited range of copolymer composition have been obtained, as an example, copolymers of AM and up to 25 mol % of 2-acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS) were elaborated.

Our work proposes an innovative alternative in terms of processes and materials as compared to the previous works. Our strategy was to obtain ultrahigh molar masses of homopolymers of both AM and AMPS as well as poly(AM-*stat*-AMPS) copolymers exhibiting a large range of [AM]/[AMPS] ratio, with the RAFT/MADIX gel from conventional

to purely adiabatic gel processes. As compared to polymers obtained by Read et al.¹⁷ under a conventional gel process (CGP), we were able to extend the copolymer composition. Taking advantage of the sulfonated comonomer and the synthesis of a high molar mass copolymer, the viscosimetric behavior in aqueous salt solution of the copolymers poly(AM-*stat*-AMPS) and poly(AMPS) has been studied. Our results obtained via the adiabatic RAFT/MADIX gel process met the industrial expectation in terms of experimental conditions, such as the product can be handled as a solid and the energy required to synthesize and dry the product is reduced, and polymer specifications by controlling both the macromolecular dimensions and compositions.

RESULTS AND DISCUSSION

All polymerization processes have been performed simultaneously in the conventional gel process (CGP) and in the adiabatic gel process (AGP) by RAFT/MADIX (co)-polymerization, and the results are compared (Table 1).

While Destarac et al.¹⁷ obtained statistical copolymers of AM and AMPS with 0 and 25 mol % of AMPS with the CGP conducted at 10 °C, this work first extends the synthesis strategy to obtain the whole range of copolymer composition, that is, with 0, 5, 25, 70, and 100 mol % of AMPS (Table 1).

All the conditions have been reported in Table 1 with the molar masses and dispersities in the [Experimental Section](#). The

lowest PAMPS molar mass was obtained using Rhodixan as the transfer agent in the alcoholic reaction medium (Table 1, entry 1). This low molar mass polymer exhibits a polymerization degree of 50 (as obtained by ^1H NMR analysis) and is in accordance with the molar mass obtained via the SEC analysis and reported in Table 1. It is called PAMPS50-X and has been employed as the RAFT transfer agent to perform homopolymers of AMPS of higher molar masses (Table 1, entries 2 and 3). Due to the hydrophilic nature of the PAMPS₅₀-X agent, the polymerization reactions have been performed in a purely aqueous medium, and ammonium persulfate (APS) has been used as the initiator. The control of the $[\text{AMPS}]_0/[\text{PAMPS}_{50}\text{-X}]/[\text{APS}]$ ratios allowed the synthesis of PAMPS exhibiting molar masses of 3×10^6 and $10 \times 10^6 \text{ g mol}^{-1}$ and dispersities below 1.3 and above 95% conversion. Moreover, the molar masses are in accordance with the expected theoretical ($\bar{M}_{n(\text{th})}$) values calculated from the eq 1 where m_M and m_{RAFT} are the molar masses of the monomer and RAFT agent, respectively, d is the number of radicals formed from the initiator, and f is the initiator efficiency and was taken equal to 0.7.

$$\bar{M}_{n(\text{th})} = \frac{[\text{M}]_0 - [\text{M}]_f}{[\text{RAFT}]_0 + df([\text{I}]_0 - [\text{I}]_f)} m_M + m_{\text{RAFT}} \quad (1)$$

In a last attempt (Table 1, entry 4), a fourth PAMPS has been performed using PAM₇-X as the transfer agent, an oligomer of AM containing seven monomer units. The experimental conditions of PAMPS obtained previously (Table 2, entry 2) have been reproduced. The results showed that the polymer exhibits the same molar mass and dispersity either with PAMPS₅₀-X or PAM₇-X, all other conditions remain the same. Therefore, all other polymers have been performed using the PAM₇-X agent in the purely aqueous medium for a better comparison with the previous works reported in the literature. A feed composition of the AMPS molar fraction $f_{\text{AMPS}} = 0, 0.5, 0.25, 0.7,$ and 1 and a monomer concentration ranging from 2.0 M ($f_{\text{AMPS}} = 1$) to 4.2 M ($f_{\text{AMPS}} = 0$) for the copolymers were the parameters to be varied. It is worth mentioning that the pH value was adjusted to 6.5–8.0 if necessary before adding the RAFT/MADIX agent to the reactive mixture to avoid the acid form of AMPS. Whatever the composition was, the polymers reached the theoretical molar masses and were above $1 \times 10^6 \text{ g mol}^{-1}$ with a dispersity below 1.4.

To go further on the development of the synthesis of poly(AM-*stat*-AMPS) copolymers, we decided to take advantage of the exothermic process of the AM polymerization and performed the reaction under an adiabatic chemical process by which polymerization occurs without the transfer of heat or matter between the reactor system and its surroundings. This process is called the adiabatic gel process (AGP). The success of polymerization within these conditions is ensured by a low rate of reaction at the initial temperature versus a high rate of reaction when the temperature increases due to the exothermic reaction to reach the adiabatic reaction temperature. The latter is the temperature value allowing a complete conversion without a heat loss. The process takes advantage of the heat of polymerization,^{18,19} which is 33.5 KJ mol⁻¹ for AMPS and $79.5 \pm 0.7 \text{ KJ mol}^{-1}$ for AM allowing the self-heating process of the medium. The challenge using this process was to keep the control of polymerization to reach UHMW of PAM, PAMPS, and poly(AM-*stat*-AMPS) (co)-polymers by keeping low dispersities. Under our work,

polymerization has been carried out at a starting temperature in which the polymerization rate is negligible, that is below 15 °C. The adiabatic temperature is known to vary with the nature and concentration of the monomer, and the values have been reported in the Experimental Section. Whatever the polymer composition is, the adiabatic temperature ranges from 75 to 100 °C. As expected from the heat of the polymerization of each monomer, the adiabatic temperature increases with the AM content, and all other parameters remain the same. All the polymerization processes have been performed within 20 min; the latter is calculated from the start of the temperature increase (above 20 °C) until the beginning of the temperature decrease after having reached the adiabatic value. The oxidant/reducing agent pair sodium persulfate/sodium formaldehyde sulfoxylate dihydrate was used as the initiator to spontaneously start polymerization at room temperature. The monomer concentration and molar ratio of the initiator/RAFT agent were optimized and adapted to the target molar mass. Under the adiabatic method, the polymerization reaction takes place in a Dewar flask, and the reaction mixture heats itself until adiabatic reaction temperature, which is the temperature reached when the reaction goes to completion without a heat loss. After completion, the temperature decreases and a viscous gel is obtained. The latter is cut, blended, and dried in an oven at 45 °C for 24 h. This last step has been optimized under microwave irradiation decreasing the drying step down to 25 min without altering the polymer as obtained by ^1H NMR analysis for the chemical composition and by SEC analysis for the molar masses and distribution (Figure 1).

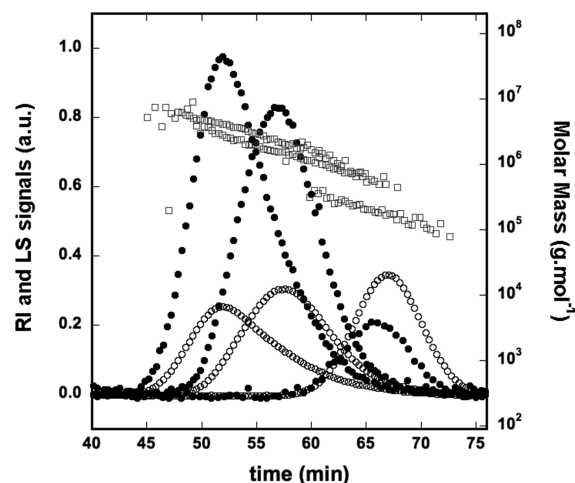


Figure 1. SEC analyses of entries #1, #2, and #3 obtained via the AGP process (see Table 1) with the refractive index detector (circle open), light scattering detector (solid circle), and molar masses (box) against time.

The polymerizations of both AM and AMPS has been studied via the AGP, and the results have been compared to the above data reported for the CGP. As the conventional, the adiabatic gel process allows the syntheses of UHMW PAM, PAMPS, and poly(AM-*stat*-AMPS) (co)polymers with controlled molar masses and low dispersities. Targeted molar masses ranging from 0.5×10^6 to $3 \times 10^6 \text{ g mol}^{-1}$ were successfully reached, and the adiabatic conditions did not affect the results. Both of the methods, CGP and AGP, have been compared in terms of molar mass control and dispersity values. As shown in Figure 2, all the data exhibit good agreement

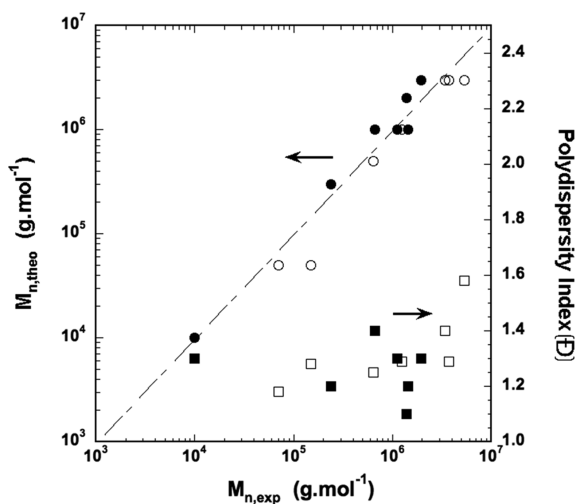


Figure 2. Molar mass and molar mass distribution (D) of the poly(AM-*stat*-AMPS) series reported in Table 1 obtained by AGP (open symbol) and CGP (close symbol).

between the theoretical and the experimental molar masses obtained at quantitative yields (see Table 2 in the Experimental Section). The results show that RAFT/MADIX polymerization leads to a perfect control of molar masses either in the conventional or adiabatic gel process up to $3 \times 10^6 \text{ g mol}^{-1}$. In the same manner, both methods lead to an extremely low disparity as regards to the molar mass values, and all the polymers exhibit a value below 1.4, but pure PAM of $3 \times 10^6 \text{ g mol}^{-1}$ molar mass obtained via AGP at the highest rate and temperature of the series.

Viscosimetric properties of AMPS copolymers have been widely studied within the context of enhanced oil recovery applications.²⁰ Other works deal with their polyelectrolyte properties in the aqueous phase with and without added salt, as a function of the counter-ions and polymer molar masses.^{21–27} Within the present work, poly(AM-*stat*-AMPS) copolymers with $f_{\text{AMPS}} = 0.25$ and 1 cover a wide range of molar masses and exhibit narrow dispersities, which make them ideal

candidates to establish the Mark–Houwink–Sakurada (MHS) Law. The MHS equation is defined as $[\eta] = KM_w^\alpha$ where $[\eta]$ is the intrinsic viscosity, the constant K is the characteristic of the polymer and solvent, and the MHS exponent α is a function of the shape of the polymer coil in a solution. In Figure 3a, intrinsic viscosities of poly(AM-*stat*-AMPS) copolymers have been reported as a function of the added salt concentration. Figure 3b shows intrinsic viscosities ($[\eta]$) against molar masses of the corresponding polymer series in the aqueous solution with 1.8 M NaNO₃ to minimize the polyelectrolyte effects.

The data are strictly linear over the range of molar masses studied. The following MHS equations (eqs 2 and 3) are obtained for poly(AM-*stat*-AMPS) copolymers with $f_{\text{AMPS}} = 0.25$ and 1, respectively.

$$[\eta] = 8 \pm 1 \times 10^{-3} \times M_w^{0.78 \pm 0.05} \quad (2)$$

$$[\eta] = 3.6 \pm 0.1 \times 10^{-4} \times M_w^{0.92 \pm 0.01} \quad (3)$$

The copolymer poly(AM-*stat*-AMPS) with $f_{\text{AMPS}} = 0.25$ shows an exponential $\alpha = 0.78 \pm 0.05$, which is the signature of flexible chains in a good solvent. Homopolymers of AMPS exhibit the greater value of α for a more extended conformation. Previous works reported by Fisher et al.^{23,24} reported similar α values in CsCl ($\alpha = 0.91$ to 1.0), whereas lower values are obtained in NaCl (0.77 to 1). These results may be explained by the use of a larger anion with a higher value of polarizability (nitrate ion) as compared to the chloride one as already observed in previous works reported in the literature^{23,24} with the comparison of both cesium and sodium cations.

The behavior of the intrinsic viscosity versus the added salt concentration follows a well-known trend.²⁸ The viscosity of polyelectrolyte solutions is proportional to the square root of the added salt up to 0.25 and 1.8 M poly(AM-*stat*-AMPS) copolymers with $f_{\text{AMPS}} = 0.25$ and 1, respectively, although the viscosity may be considered as constant for higher salt concentrations with the disappearance of any polyelectrolyte

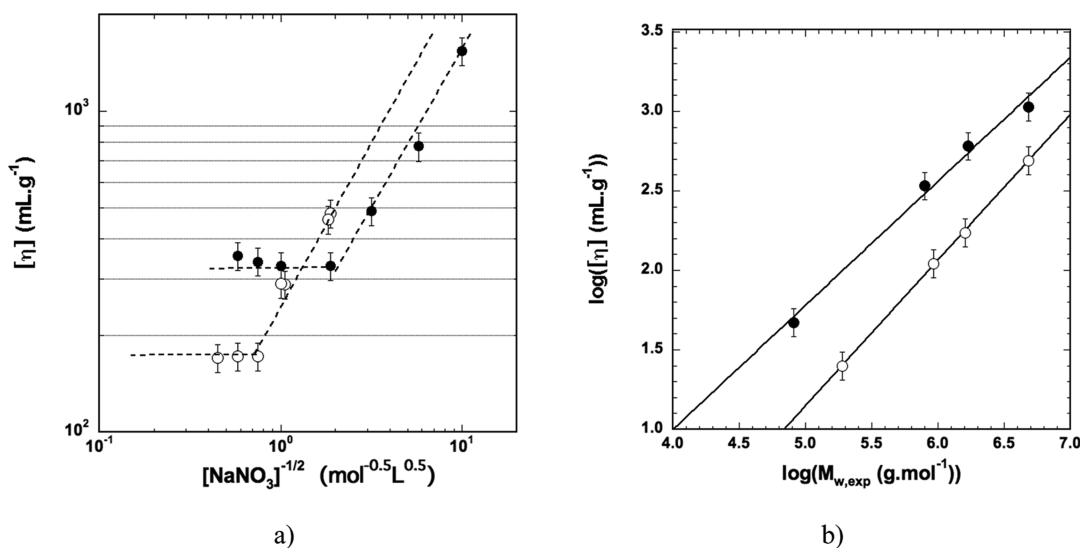


Figure 3. (a) Intrinsic viscosities of poly(AM-*stat*-AMPS) with $f_{\text{AMPS}} = 0.25$ ($\bar{M}_n 6.4 \times 10^5 \text{ g mol}^{-1}$) (circle open) and $f_{\text{AMPS}} = 1$ ($\bar{M}_n 1.240 \times 10^6 \text{ g mol}^{-1}$) (circle solid) vs the salt concentration and $C_s^{-0.5}$. (b) Intrinsic viscosities against molar masses of the both polymer series with 1.8 M NaNO₃.

effect, and the behavior is thus assimilated to a neutral polymer in the good solvent.

CONCLUSIONS

Within this work UHMW of poly(AM-*stat*-AMPS) copolymers have been synthesized via RAFT/MADIX polymerization either in conventional or purely adiabatic gel processes. Following the latter, we were able to perform polymerization to a much higher volume and monomer concentration, from 2.0 to 3.47 M, than that reported so far within the literature while keeping the control of the molar masses up to 5×10^6 g mol⁻¹, with a narrow dispersity and a feed composition ranging from f_{AMPS} of 0 to 1. The poly(AM-*stat*-AMPS) with $f_{\text{AMPS}} = 0.25$ and 1 have been considered as UHMW standards to study their viscosimetric behavior. The results are described as a function of the added salt content and molar masses in aqueous solution and showed the structural differences caused by the copolymer composition and the added salt concentration range where the polyelectrolyte effect occurs.

EXPERIMENTAL SECTION

Chemicals and Materials. The following chemicals were used without preliminary purification unless noted: acrylamide (AM) 99% ABCR, sodium 2-acrylamido-2-methylpropanesulfonate (AMPS, Sigma-Aldrich, 50 wt % in aqueous solution), ammonium persulfate (APS, Sigma-Aldrich, 98%), sodium persulfate (NaPS, Sigma-Aldrich, 99%), sodium formaldehyde sulfoxylate dihydrate (NAFS, Sigma-Aldrich, 98%), 2,2-azobis-(2-methylpropionamide) dihydrochloride (V-56, Fluka, 98%), ethanol (VWR, 99.8%), acetone (VWR, 98%), and water MilliQ 18.2 MΩ.

Macro-Transfer Agent Synthesis. PAM₇-X Synthesis. PAM₇-X was synthesized according to the protocol described by Read and al.;¹⁷ O-ethyl-S-1-methoxycarbonyl ethyl dithiocarbonate (Rhodixan A1) was previously synthesized according to patent number 2 814 168 20.

Rhodixan A1 (2.5 g, 12.0 mmol) was dissolved in 8 g of ethanol in a 50 mL round-bottom flask containing a magnetic bar and provided with an arrival of nitrogen, then powder acrylamide (6.038 g, 85 mmol), V-56 (149 mg, 0.55 mmol), and MilliQ water (15 g) were added. The reactive mixture was cooled on ice and degassed by bulling nitrogen for 30 min. Then, it was put in a water bath at 60 °C ($t = 0$ of polymerization). The reactive mixture was left under agitation and maintained under nitrogen flow for 3 h (AM conversion = 100% obtained by NMR analysis, $\bar{M}_{n,\text{NMR}} = 740$ g mol⁻¹).

After ethanol drying, the macroagent was isolated by precipitation in acetone and dried under microwave (MultiwavePro with Rotor 1DRY, Anton Paar).

PAMPS₅₀-X (AMPS Macroagent RAFT) Synthesis. Rhodixan A1 (0.087 g, 0.42 mmol) was dissolved in ethanol (1.246 g) in a 50 mL round-bottom flask containing a magnetic bar and provided with an arrival of nitrogen. AMPS 50 wt % (7.774 g, 17 mmol), V-56 (0.0249 g, 0.089 mmol), and MilliQ water (1.4 g) were added to the reaction flask. The reactive mixture was cooled down to 0 °C and degassed by nitrogen for 30 min. The reaction vessel was then heated under magnetic stirring up to 60 °C under nitrogen for 3 h (AMPS conversion = 96% obtained by NMR analysis, with, PD = 50, $\bar{M}_{n,\text{SEC}} = 85000$ g mol⁻¹).

After ethanol drying, the macroagent was isolated by precipitation in acetone and dried under microwave (MultiwavePro with Rotor 1DRY, Anton Paar).

Polymer Synthesis under a Conventional Gel Process. PAM Homopolymer Synthesis. PAM was synthesized according to the protocol described by Read et al.¹⁷

Typically, polymerization was performed as follows (target $\bar{M}_{n(\text{th})} = 10^6$ g mol⁻¹): AM (4.26 g, 60 mmol) and 1 mL of a 4×10^{-3} M aqueous solution of PAM₇-XA1 were dissolved in 28.5 mL of MilliQ water in a 100 mL round-bottom flask before cooling down to 0 °C and degassed with nitrogen for 30 min. A 1.4×10^{-3} M degassed solution (0.5 mL) of APS was then added to the reactive mixture. The reaction vessel was then heated under magnetic stirring up to 60 °C under nitrogen for 2 h. The polymer was isolated by precipitation in acetone and dried under microwave (MultiwavePro with Rotor 1DRY, Anton Paar). Yield 95% obtained by NMR analysis.

PAMPS Homopolymer Synthesis. Typically, polymerization was performed as follows (target $\bar{M}_{n(\text{th})} = 10^6$ g mol⁻¹): AMPS 50 wt % (11.00 g, 24 mmol) and 1 mL of a 4.8×10^{-3} M aqueous solution of PAM₇-X were dissolved in a 20 mL vial before cooling at 0 °C and degassed with nitrogen during 30 min. Two aqueous solutions of 3.3×10^{-3} M APS and NaFS were degassed, and 0.25 mL of each was then added to the reaction flask. The reactive medium was heated up to 60 °C under magnetic stirring and nitrogen for 2 h.

All polymers were isolated by precipitation in acetone and dried under microwave irradiation (MultiwavePro with Rotor 1DRY, Anton Paar). The sample was successfully heated under 200 W and air cooling for 10, 10, and 5 min and cooled down under air cooling, and no irradiation for 5 min between each step. The polymer was isolated by precipitation in acetone and dried under microwave (MultiwavePro with Rotor 1DRY, Anton Paar). Yield 95% obtained by NMR analysis.

Poly(AM-*stat*-AMPS) Statistical Copolymer Synthesis. Polymerization was performed as follows (target $\bar{M}_{n(\text{th})} = 10^6$ g mol⁻¹ and a 25:75 AMPS/AM theoretical composition): AM (16.12 g, 0.23 mol), 50 wt % AMPS (34.67 g, 0.087 mol), 1 g of a 3.3×10^{-2} M solution of PAM₇-X, and 62 g of a 0.1 g mol⁻¹ NaCl aqueous solution were added in a 250 mL round-bottom flask before cooling down to 0 °C and degassed by nitrogen during 30 min. Two solutions of 5.7×10^{-3} M APS and NaFS were degassed, and 1 g of each was simultaneously added to the reaction flask. The reactive medium was heated up to 60 °C under mechanical stirring and nitrogen for 16 h. The polymer was isolated by precipitation in acetone and dried under microwave (MultiwavePro with Rotor 1DRY, Anton Paar). Yield 90% obtained by NMR analysis.

All the copolymers were performed following the same experimental procedure by keeping equimolar concentrations of APS and NAFS. The initiator to the RAFT transfer agent ratio was experimentally optimized for each composition. Experimental conditions are summarized in Table 2.

Polymer Synthesis under an Adiabatic Gel Process. Polymerization processes were performed using a protocol adapted from Read et al.¹⁷ to be processed in adiabatic conditions.²⁹ Monomer concentrations were increased in comparison to the conventional method, whereas the monomer-to-agent RAFT ratio was maintained the same. Homopolymers and copolymers were synthesized following the same protocol. The synthesis of a copolymer was reported below as an example.

Table 3. Adiabatic Gel Process and Experimental Conditions with $[APS] = [NAFS]$

theoretical [AMPS]/[AM]	adiabatic gel process (AGP)						
	$\bar{M}_n^{(th)}$ ($\times 10^6$ g/mol)	$[M]_0$ (M), wt %	$[PAM_{7-X}]$ (M)	$[APS]/[PAM_{7-X}]$	yield (%) ^a	adiabatic temp. (°C) ^b	exp. polymer [AMPS]/[AM] ^c
100/0	0.05	2.0, 45.8%	9.1×10^{-3}	0.17	99	75–80	100/0
	1.00	2.0, 45.8%	4.6×10^{-4}	0.17	95		100/0
	3.00	2.0, 45.8%	1.5×10^{-4}	0.34	83		100/0
25/75	0.05	0.87, 19.9%; 2.6, 18.5%	7.67×10^{-3}	0.34	98	90–95	25/75
	0.5	0.87, 19.9%; 2.6, 18.5%	7.67×10^{-4}	0.34	98		26/74
	3.00	0.87, 19.9%; 2.6, 18.5%	1.28×10^{-4}	0.34	96		27/73
0/100	3.00	4.2, 29.8%	9.9×10^{-5}	0.34	96	95–100	0/100

^aVia SEC characterization, see the Experimental Section. ^bRecorded via an analogic probe PT100. ^cVia NMR characterization, see the Experimental Section.

Poly(AM-*stat*-PAMPS) Statistical Copolymer Synthesis. Polymerization was performed as follows (for a 25:75 AMPS/AM theoretical composition): AM (185 g, 2.6 mol), 50 wt % aqueous AMPS (399.8 g, 0.87 mol), and 415 g of deionized water were introduced in a 2 L beaker, and the mixture was cooled down to 5 °C. Then, a 50 wt % aqueous solution of NaOH was added to reach a pH value of 6.5–8.0, whereas the temperature was maintained below 15 °C. PAM_{7-X} was added to the mixture according to Table 2. The reaction mixture was cooled down to 0 °C before transferring in a 1 L Dewar flask and degassed by nitrogen. Initiator solutions were added to the mixture according to the quantity as reported in Table 3, whereas degassing was maintained until the reaction temperature starts to rise. The temperature reaches 90 °C before decreasing down to room temperature. The polymer gel was then cut and granulated using a granulator with grids to obtain gel particles with a diameter below 6 mm. These gel particles were dried in an oven at 45 °C overnight. The dry powder obtained is grinded and sieved to obtain a white powder with a particle diameter below 1 mm with less than 15% water content as measured by thermogravimetric analysis. The yields are reported in Table 3.

Instrumentation and Characterization. The number-average molar mass (\bar{M}_n) and dispersity (\mathcal{D}) were determined by size exclusion chromatography (SEC) using an Agilent 1260 Iso pump G1310B (Agilent technologies) equipped either with four Shodex OHPak columns (SB-807HQ, SB-805HQ, SB-803HQ, and SB-802HQ) or two columns (SB-807HQ and SB-805HQ) for molar masses above 5×10^5 g mol⁻¹ and two online detectors: a differential refractometer Waters 2410 (Waters Corporation) and a DAWN HELEOSII (Wyatt Technology Corporation) utilizing a 120 mW solid-state laser operating at 658 nm and fitted with a K5 cell. A 0.1 M NaNO₃ aqueous solution phosphate-buffered at pH = 8 was used as an eluent at a flow rate of 0.5 mL min⁻¹. Interdetector volumes, normalization, and calibration constant of the refractometer were determined by using bovine serum albumin ($dn/dc = 0.165 \pm 0.001$) and a polyoxyethylene standard ($M_w = 20\,000$ g mol⁻¹, $dn/dc = 0.135 \pm 0.001$). Polymer samples were prepared by diluting the reaction mixture in the SEC eluent to reach an approximate concentration of 0.2 to 1 g L⁻¹. After 24 h of orbital stirring, they were filtered through a 0.45 μm filter (mixture of cellulose esters–Millipore). Fifty microliters of these solutions was injected. The number-average molar mass and polydispersity were obtained from the data collected and analyzed using the ASTRA SEC software (version 6.1, Wyatt Technology Corporation). The calculation of the molar mass was carried out according to the Zimm fit

method. The refractive index increments, (dn/dc), for this system were determined according to our previous work³⁰ to be 0.185 ± 0.001 and 0.144 ± 0.001 mL g⁻¹ for PAM and AM, respectively, and 0.133 ± 0.001 and 0.113 ± 0.001 mL g⁻¹ for polyAMPS and AMPS, respectively. For the molar masses above 10^6 g mol⁻¹, the results have been characterized and confirmed by the SEC analysis with the characterization method developed elsewhere.³¹

Experimental compositions of copolymers were obtained by ¹H NMR analysis in D₂O of the purified product using a Bruker AVANCE 400 MHz. Spectra were analyzed with the Topspin software (version 3.5, Bruker). Polymer conversion has been obtained according to a previous methodology.³²

The measurement of viscosity η for dilute solutions of polymers was carried out on a capillary rheometer based on the Poiseuille law according to the protocol reported elsewhere.³³

AUTHOR INFORMATION

Corresponding Author

*E-mail: stephanie.reynaud@univ-pau.fr.

ORCID

Elise Deniau: 0000-0001-5857-6756

Stéphanie Reynaud: 0000-0001-9048-0842

Bruno Grassl: 0000-0002-1554-1411

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

SNF Floerger company, France is gratefully acknowledged for financial support of this work. The authors are grateful to Dr. Abdel Khoukh for his assistance in NMR measurements.

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