Electronic Supplementary Material (ESI) for Polymer Chemistry

Electronic Supplementary Information

Low temperature RAFT/MADIX gel polymerisation: access to controlled ultra-high molar mass polyacrylamides

Emmanuelle Read,[a] Aymeric Guinaudeau,[a] D. James Wilson,[b] Arnaud Cadix,[b] Frédéric Violleau[c] and Mathias Destarac *[a]

Contents of the Supplementary Information document:

---

[a] Université Paul Sabatier, Laboratoire Heterochimie Fondamentale et Appliquée, UMR-CNRS 5069,Bat 2R1, 118 route de Narbonne,31062 Toulouse Cedex9, France,. Fax: +33 (0)561558204; Tel:+33 (0)561556354 E-mail: destarac@chimie.ups-tlse.fr

[b] Solvay Novecare, Research and Innovation Centre - Paris, 52 rue de la Haie coq, 93308 Aubervilliers Cedex, France

[c] Université de Toulouse, Ecole d'Ingénieurs de Purpan, UPSP/DGER 115, 75, voie du TOEC, BP 57611, F-31076, Toulouse Cedex 03, France

To whom correspondence should be adressed : destarac@chimie.ups-tlse.fr

I. Experimental Section

Materials

2,2'-azobisisobutyronitrile (AIBN, Janssen Chemica, 98%) was recristallised twice from methanol before use. Acrylamide (AM, SNF, 50% in water stabilized with 100 ppm MEHQ), N,N-dimethylacrylamide (DMA, Aldrich, 99%), N-isopropylacrylamide (NIPAM, Aldrich, 97%), 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS, Aldrich, 50% in water) were used received. *O*-ethyl-*S*-(1-methoxycarbonyl)ethyl dithiocarbonate agent (Rhodixan A1®, Solvay), ammonium persulfate (APS, Acros, 98+%), sodium formaldehyde sulfoxylate dihydrate (NAFS, Acros, 98%) and L(+) ascorbic acid (AscAc, Acros, 99%), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50, Acros, 98%), ethyl acetate (pure for synthesis, Carlo Erba reagent), N,N-dimethylformamide (DMF, Aldrich, HPLC grade>99.9%), ethanol (VWR, 99.9%) and distilled water were used without prior purification.

A. RAFT/MADIX synthesis of AM-based polymers

Synthesis of PAM_7-XA1.

Rhodixan A1 (1.69 g, 8.1 mmol) was dissolved in 5.94 g of ethanol in a two-neck round-bottom flask. Then, AM (8 g, 56.3 mmol), V-50 (69.4 mg, 0.35 mmol) and distilled water (4.61 g) were added. The mixture was degassed by bubbling argon for 30 min while stirring. Then it was heated under argon atmosphere at 60°C for 3h until the completion of the reaction. The ethanol was evaporated under vacuum prior to freeze-drying the sample to give a light yellow powder. (AM conversion=100%, $M_{n, RMN}$=650 g mol^{-1})

Synthesis of P(AM-*stat*-AMPS)$_7$-XA1.

Rhodixan A1 (2.34 g, 11.2mmol) was dissolved in 6.52 g of ethanol. Then AM (5.40 g, 38 mmol), AMPS (5.74 g, 12.5 mmol) and V-50 (83.6 mg, 0.31mmol) were simultaneously added with 6.52 g of water. The mixture was degassed by bubbling argon for 30 min while stirring. Then it was heated under argon atmosphere at 60°C for 3h until the completion of the reaction. The ethanol was evaporated under vacuum prior to freeze-drying the sample. (AM conversion>99% , AMPS conversion>99%, F_{AMPS}=0.245, $M_{n, RMN}$=700 g mol^{-1})

Redox-initiated aqueous RAFT/MADIX polymerization of AM.

Typically, the polymerization was performed as follows: AM (8.00 g, 56.3 mmol), a 2% wt solution of PAM_7-XA1 (0.13 g, 0.040 mmol) were dissolved in 7.88 g of distilled water and placed in a thermostated bath set at 10°C while bubbling argon for 30min before injecting simultaneously 0.1 mL of 0.3% wt solutions in water of APS and NAFS. The reaction was let at 10°C under a stream of argon for 2h until completion of the reaction (AM conversion>99.9%, $M_{n,SEC}$=971 000 g mol^{-1}, Đ=1.12, dn/dc=0.185 mL g^{-1})

Redox initiated aqueous RAFT/MADIX statistical polymerization of AM and AMPS.

AM (4.25 g, 29.9 mmol), AMPS (4.58 g, 9.9 mmol) , a 5% wt solution of P(AM-*stat*-AMPS)$_7$-XA1 (0.05g, 0.004 mmol) were dissolved in 8.65 g of distilled water and placed in a thermostated bath set at 10°C. For 30 min, it was degassed by bubbling argon before injecting simultaneously 0.42 mL of 0.3% wt aqueous solutions of APS and NAFS. The reaction was let at 10°C under a stream of argon for 2h until completion of the reaction (AM conversion>99%, AMPS conversion>99%, $M_{n,SEC}$=1 170 000 g mol^{-1}, Đ=1.36, dn/dc (P(AM-*stat*-AMPS))=0.147 mL g^{-1})

Chain extension.

PAM-XA1 ($M_{n,th}$=4.10^5 g mol^{-1}) (0.32 g, 6.65x10^{-7} mol), AM (0.71 g, 5.00 mmol) were dissolved in 4.48 g of distilled water and placed in a thermostated bath set at 10°C. For 30 min, it was degassed by bubbling argon before injecting simultaneously 0.175 mL of 0.03% wt aqueous solutions of APS and NAFS. The reaction was let at 10°C under a stream of argon for 2h until completion of the reaction (AM conversion>99%, $M_{n,SEC}$=1 110 000 g mol^{-1}, Đ=1.09, dn/dc (P(AM))=0.185 mL g^{-1}).

B. RAFT/MADIX synthesis of DMA-based polymers

Synthesis of PDMA$_7$-XA1.

N,N-dimethylacrylamide (4.98 g, 50.0mmol), Rhodixan A1 (1.49 g, 7.20 mmol), AIBN (0.0114 g, 0.07mmol) and ethyl acetate (18.5 g, 210 mmol) were added at ambient temperature in a two-neck round-bottom flask. The mixture was degassed by bubbling argon for 30 min while stirring. Then it was heated under argon atmosphere at 60°C for 24h until the completion of the reaction. Finally the solvent was evaporated under vacuum. (DMA conversion=97.6%, $M_{n,RMN}$=1050 g mol^{-1})

Redox initiated aqueous RAFT/MADIX polymerization of DMA.

PDMA$_7$-XA1 5 % wt solution in water (0.124 mg, 0.055 mmol), DMA (5.99 g, 60 mmol) were mixed in distilled water (27.5 mL) in a schlenk flask and thermostated at 20°C. The mixture was gently degassed with argon for 30 min before injecting simultaneously 0.75 mL of 1.2%wt aqueous solutions of APS and NAFS. The reaction was let at 20°C under a stream of argon for 24h until completion of the reaction (DMA conversion>99.9%, $M_{n,\ SEC}$ =825 500 g mol^{-1}, Đ=1.11, dn/dc=0.087 mL g^{-1})

Redox initiated aqueous RAFT/MADIX statistical polymerization of DMA and AMPS.

For a polymerization with f_{AMPS}=0.09: DMA (6.04 g, 60.9 mmol), AMPS (2.76 g, 6.03 mmol) and a PDMA$_7$-XA1 5% wt solution in water (160 mg, 0.007 mmol) were mixed together in 25.7 mL of distilled water. The mixture was gently degassed with argon for 30 min before injecting simultaneously 1.09 mL of 1.2% wt solutions of APS and NAFS. The reaction was let at ambient temperature (T=20°C) under a stream of argon until completion of the reaction. (DMA conversion=99%, AMPS conversion=100%, $M_{n,\ SEC}$=1 110 000 g mol^{-1}, Đ=1.61, dn/dc=0.154 mL g^{-1}).

RAFT/MADIX block copolymerization of NIPAM and DMA:

Aqueous Synthesis of PNIPAM-XA1.

NIPAM (2.10 g, 18 mmol), PDMA$_7$-XA1 (248 mg, 0.23 mmol) and APS (42.0 mg, 0.18 mmol) were mixed with distilled water (7.35 mL) in a two-neck round-bottom flask and thermostated at 25°C during all the reaction. The mixture was degassed by bubbling argon for 30 min. Then 2 mL of a solution of AscAc (32.5 mg, 1.8 10^{-4} mol) was injected under a stream of argon. The reaction was stopped after 4 hours of stirring at 25°C.
The product was then freeze dried to give a white powder. (NIPAM conversion >99.9%, $M_{n,\ SEC}$ =13 000 g mol^{-1}, Đ=1.28, dn/dc=0.087 mL g^{-1}).

Redox-initiated RAFT/MADIX block copolymerization of DMA from PNIPAM-XA1.

PNIPAM-XA1 (40 mg, 0.004 mmol), DMA (4 g, 40 mmol) were placed in a schlenk flask with 11.8 mL of distilled water and degassed with argon for 30 min at 20°C. Then 0.12 mL of 0.6% wt aqueous solutions of APS and NAFS were simultaneously injected in the mixture. The reaction was let at 20°C under a stream of argon for 24h. (DMA conversion =100%, $M_{n,\ SEC}$=1 021 000 g mol^{-1} and Đ=1.51, dn/dc of P(NIPAM-*block*-DMA)=0.087 mL g^{-1}).

C. Instrumentation and measurements

NMR analysis. All ^{1}H NMR spectra were recorded on a Bruker AMX 300 at 300MHz in D_2O.

Size exclusion chromatography.

PAM and P(AM-*stat*-AMPS).

SEC was carried out on a Agilent 1100 HPLC system including a vacuum degasser and an isocratic pump monitored by an eclipse 2 system (Wyatt technonology), a guard column Shodex SB807-G and three columns Shodex OHpak in series (two SB-807 HQ (8mm*300mm, 35µm) and one SB-806M HQ (8mm*300 mm, 13µm)) coupled with a refractometer (OptilabRex, Wyatt technology), a UV detector (Agilent) set at 290 nm and a multi-angle laser light scattering detector (Dawn HeleosII + QELS, 18 angles, Wyatt technology). The eluent used was aqueous $NaNO_3$ 0.1M with 100ppm NaN_3.

Prior to injections, samples were diluted at a concentration of 0.5 mg mL^{-1}, stirred over a week and filtered through 0.45µm PTFE filters. Dn/dc of each sample according to its composition in AMPS was calculated with the Eq. 1 given below with dn/dc (AM)=0.185 mL g^{-1} and dn/dc (AMPS)=0.113 mL g^{-1} in the corresponding eluent at T=25°C.

For the chain extension of PAM, a column Shodex SB802.5 was added to the three previous described columns.

PDMA

SEC was carried out on a system comprising a Shodex KD-G guard column and two columns K-805L (8mm*300mm, 5µm) coupled with a refractometer (thermostated at 35°C (Optilab Rex, Wyatt technology), a UV detector (Prostar, Varian) set at 290 nm and a multi-angle laser light scattering detector (Mini Dawn, 3 angles, Wyatt technology). DMF/LiBr (10mM) was used as eluent at 55°C with a flow rate of 1 mL min^{-1}.Prior to injections, samples were diluted at a concentration of 5 mg mL^{-1}, stirred over a week and filtered through 0.45µm PTFE filters. Dn/dc (PDMA)=0.087 mL g^{-1}, dn/dc (PNIPAM)=0.087 mL g^{-1} at 35°C in the corresponding eluent. Dn/dc of block copolymers was calculated with Eq. 1 given below.

P(NIPAM-*block*-DMA)

The system is the same as for PDMA except for the columns**:** Shodex KD-G guard column and three columns Shodex KD-804 (8mm*300mm, 7µm), KD-802.5 (8mm*300mm, 6µm) and K-805L (8mm*300mm, 5µm).

P(DMA-*stat*-AMPS).

SEC was carried out on a system comprising two columns PL-aquagel-mixed OH-8µm (Agilent, 30 cm) coupled with a refractometer (Agilent) and a multi-angle laser light scattering detector (Mini Dawn TREOS, 3 angles, Wyatt technology). 15% methanol / 85% aqueous NaCl 100 mM, NaH_2PO_4 25 mM, Na_2HPO_4 25 mM buffer solution (pH=7) was used as eluent and samples were injected at 0.5 mg ml^{-1} and filtered through 0.45 µm PTFE filters. Dn/dc of each sample was calculated from Eq. 1 described below with dn/dc (DMA)=0.160 mL g^{-1} and dn/dc (AMPS)=0.133 mL g^{-1} in the corresponding eluent.

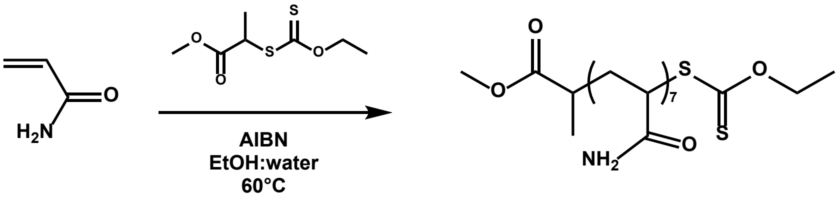
Note: dn/dc of P(A/B) copolymers was calculated according to the following equation 1:

$$dn/dc_{(A/B)} = W_A*(dn/dc)_A + W_B*(dn/dc)_B \qquad \text{(Eq. 1)}$$

where W_A and W_B are the mass fraction of monomers A and B in the copolymer, respectively.

II. Macro-MADIX agents characterization

A. PAM$_7$-XA1



Scheme 1: Synthetic pathway for the synthesis of PAM$_7$-XA1 macro-MADIX agent

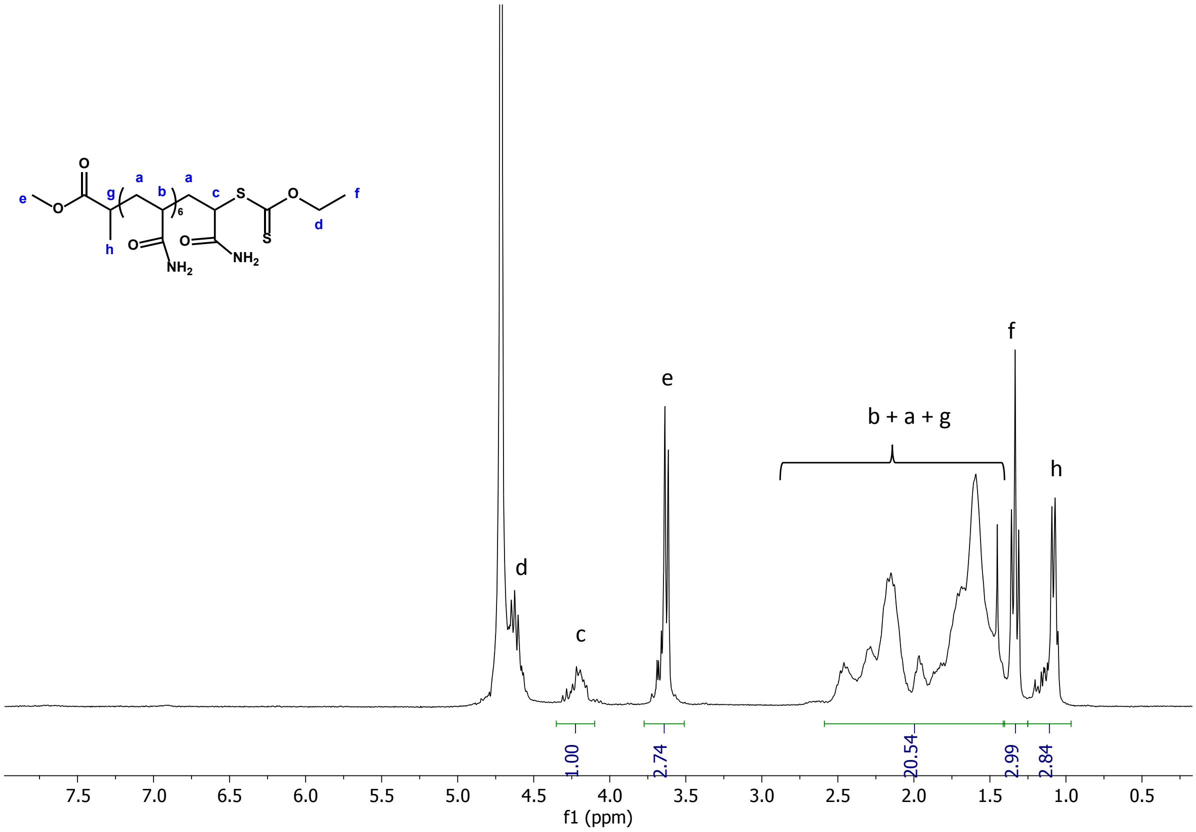
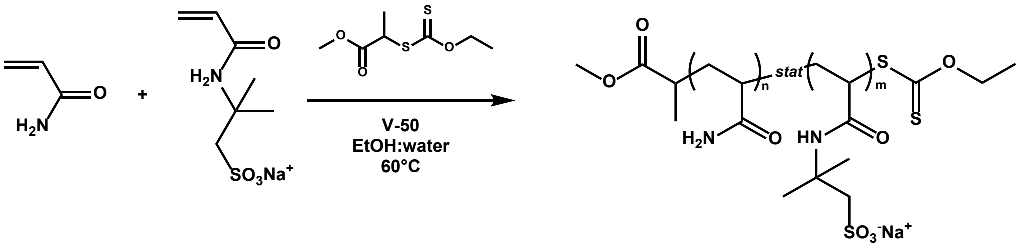


Figure S1 : ^{1}H NMR spectrum and assignements of signals for PAM$_7$-XA1 in D_2O

$$DP = \frac{\mathrm{b} + \mathrm{c}}{\mathrm{c}}$$

B. P(AM-*stat*-AMPS)$_7$-XA1



Scheme 2: Synthetic pathway for the synthesis of hydrophilic P(AM-*stat*-AMPS)$_7$-XA1 macro-MADIX agent

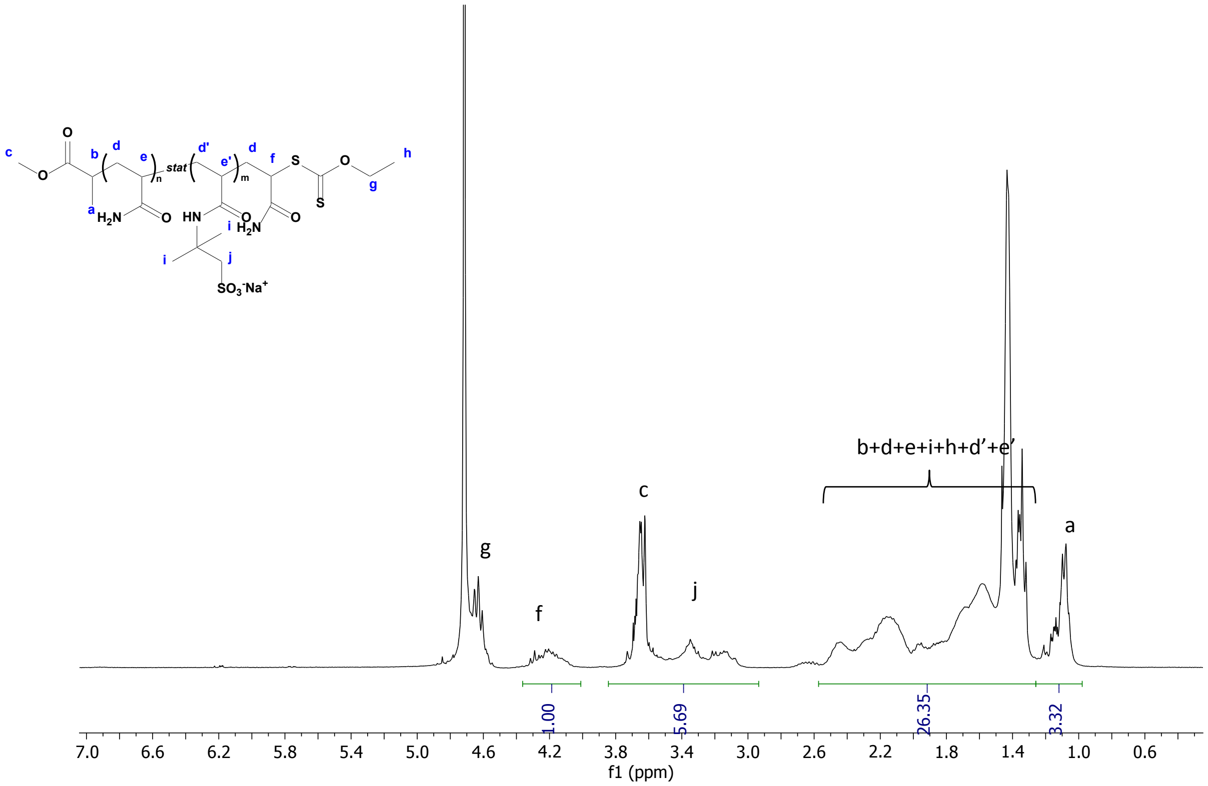
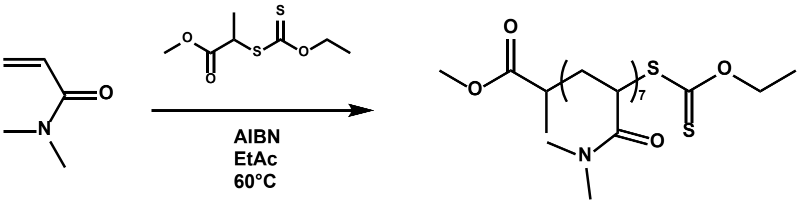


Figure S2 : ^{1}H NMR spectrum and assignements of signals for P(AM-*stat*-AMPS)$_7$-XA1 in D_2O

$$Mn = \mathrm{DP(AM)} * \mathrm{M(AM)} + \mathrm{DP(AMPS)} * \mathrm{M(AMPS)} + \mathrm{M(RHODiXAN)}$$

$$Mn = \mathrm{e} * \mathrm{M(AM)} + \mathrm{j}/2 * \mathrm{M(AMPS)} + \mathrm{M(RHODiXAN)}$$

C. PDMA$_7$-XA1



Scheme 3: Synthetic pathway for the synthesis of PDMA$_7$-XA1 macro-MADIX agent

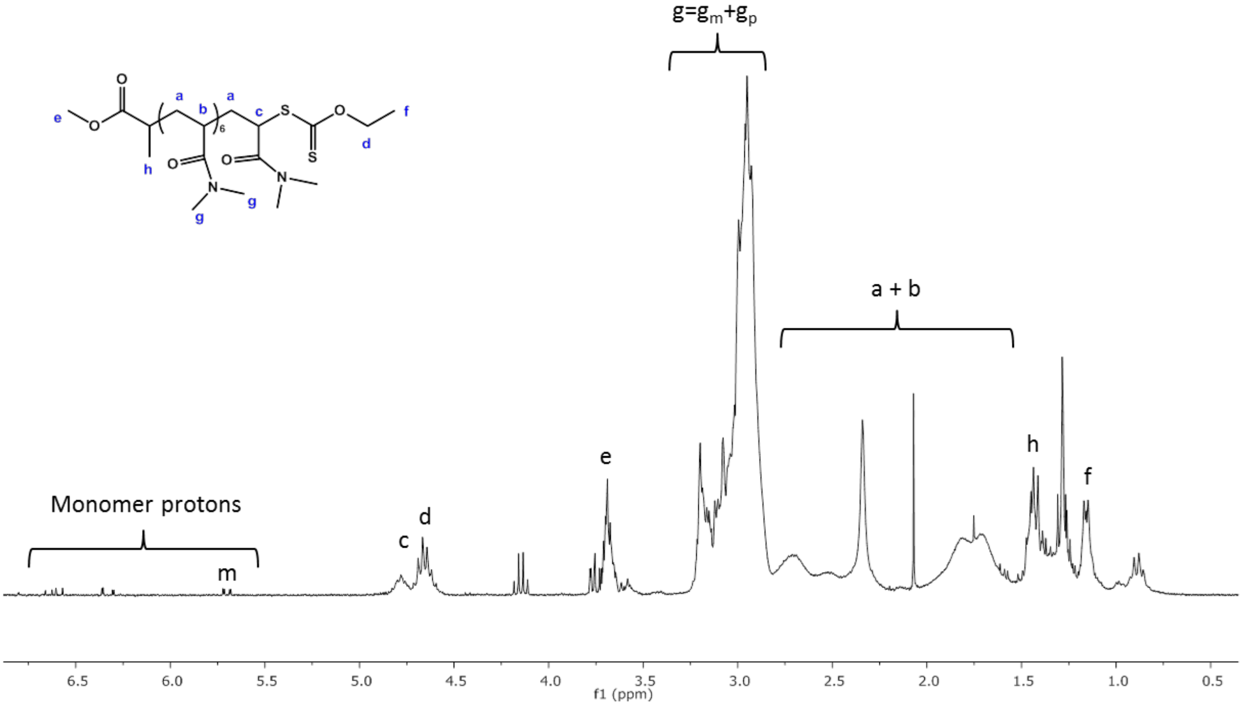


Figure S3 : ^{1}H NMR spectrum and assignements of signals for PDMA$_7$-XA1 in CDCl$_3$

DP calculation of PDMA$_7$-XA1: $DP = \frac{g-6m}{6c}$

III. Molar masses results

A. Homopolymers

Table 1. Aqueous RAFT/MADIX polymerization of AM.

[AM]$_0$=4.65 mol L^{-1}, [APS]$_0$=[NaFS]$_0$=8.21.10^{-5} mol L^{-1} (600ppm / AM monomer),T=10°C, t=2h, AM conv.=100%

PAM homopolymers

$M_{n,theo}$/[a] g mol^{-1}	$M_{n,SEC}$/[b] g mol^{-1}	$M_{w,SEC}$/[b] g mol^{-1}	Đ[b]	recovery[c] %
200 000	296 000	310 000	1.05	101
400 000	563 000	592 000	1.05	103
600 000	809 000	871 000	1.08	107
990 000	971 000	1 090 000	1.12	109
3 000 000	1 270 000	1 680 000	1.32	120
Xanthate free	946 000	1 790 000	1.89	86

[a] $M_{n,theo}$=([AM]$_0$/[PAM$_7$-XA1]$_0$)*M_{AM}*AM conv. + M(PAM$_7$-XA1),[b] determined by SEC-RI-MALS in 0.1M NaNO$_3$/100ppm NaN$_3$ with dn/dc=0.185 mL g^{-1}, [c] recovery is the ratio of the mass actually eluted over the initial mass of the sample

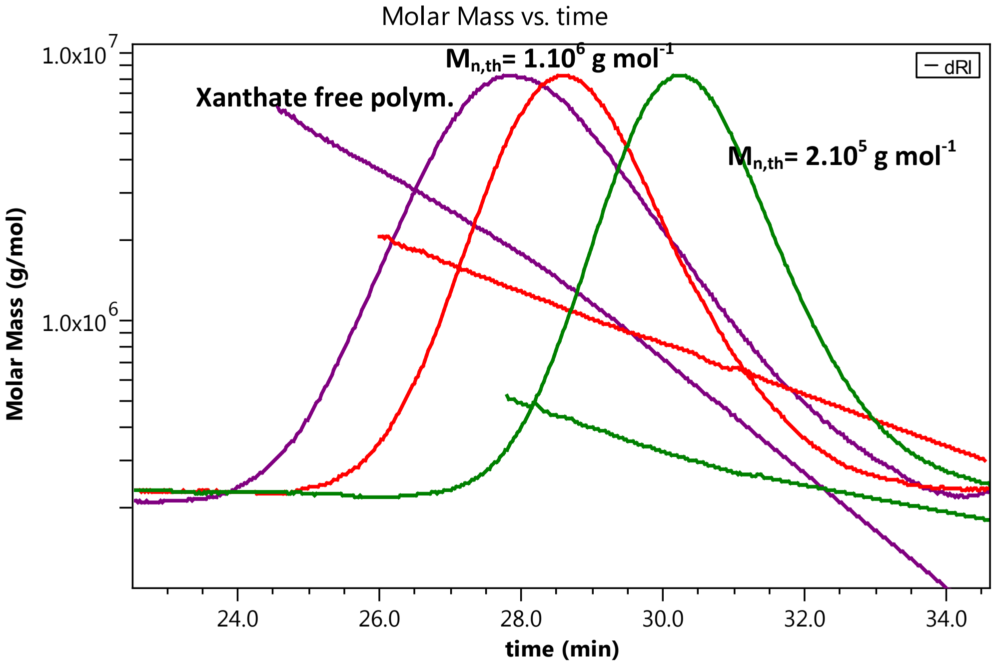


Figure S4 : Log(molar mass)= f(time) for PAM homopolymers under the overlay of chromatogram

Table 2. Aqueous RAFT/MADIX polymerization of DMA.

$[DMA]_0$=2 mol L^{-1}, $[APS]_0$=$[NaFS]_0$=1.14.10^{-3} mol L^{-1} (1500 ppm / DMA monomer),T=20°C, t=2h, DMA conv.=100%

PDMA homopolymers

$M_{n,theo}$/^{a} g mol^{-1}	$M_{n,SEC}$/^{b} g mol^{-1}	$M_{w,SEC}$/^{b} g mol^{-1}	Đ^{b}	recovery %
100 000	148 000	185 000	1.25	104
200 000	242 000	319 000	1.32	103
400 000	468 000	591 000	1.26	103
600 000	568 000	704 000	1.24	109
1 000 000	825 000	911 000	1.11	107
3 000 000	1 040 000	1 110 000	1.06	105

[a] Mn,theo=($[DMA]_0$/$[PDMA_7\text{-}XA1]_0$)*M_{DMA}*DMA conv. +M(PDMA -XA1),[b] determined by SEC-RI-MALS in DMF/LiBr (10 mM) with dn/dc=0.087 mL g^{-1}

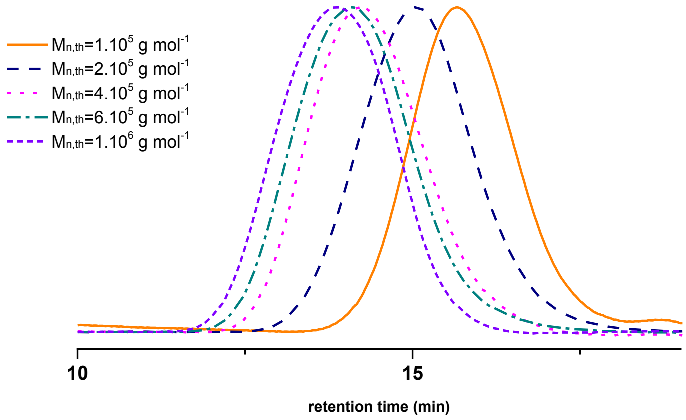


Figure S5 Overlay of SEC chromatograms of PDMA synthesized at 20°C in water using varying concentrations of $PDMA_7$-XA1

B. AMPS-based statistical copolymers

Table 3. Aqueous RAFT/MADIX polymerization of AM and AMPS

$[AM]_0$=1.91 mol L^{-1},$[AMPS]_0$=0.64 mol L^{-1} $[APS]_0$=$[NaFS]_0$=3.1.10^{-4} mol L^{-1} (280 ppm / AM +AMPS monomers),T=10°C, t=2H, AM and AMPS conv.=100%

P(AM_{75}-stat-$AMPS_{25}$)

$M_{n,theo}$/^{a} g mol^{-1}	$M_{n,SEC}$/^{b} g mol^{-1}	$M_{w,SEC}$/^{b} g mol^{-1}	Đ^{b}	recovery %
200 000	308 000	336 000	1.09	94
400 000	459 000	551 000	1.20	91
600 000	655 000	808 000	1.23	121
800 000	900 000	1 200 000	1.33	93
1 000 000	1 170 000	1 580 000	1.36	116
Xanthate free	3 940 000	7 100 000	1.80	79

[a] $M_{n,theo}$=(mAM_0/n(P(AM-*stat*-AMPS))$_7$-XA1)$_0$+ $mAMPS_0$/n(P(AM-*stat*-AMPS)$_7$-XA1)$_0$ + M(P(AM-stat-AMPS)$_7$-XA1),[b] determined by SEC-RI-MALS in 0.1 M $NaNO_3$/100 ppm NaN_3 with dn/dc=0.147 mL g^{-1}

Table 4. Aqueous RAFT/MADIX polymerization of DMA and AMPS

$[APS]_0=[NaFS]_0=2.3.10^{-3}$ mol L^{-1}(1800 ppm / DMA +AMPS monomers),T=20°C, t=2H, DMA and AMPS conv.=100%

P(DMA-stat-PAMPS)

	%AMPS	$M_{n,SEC}/^b$ g mol^{-1}	$M_{w,SEC}/^b$ g mol^{-1}	$Đ^b$	recovery %
Mn_{th}=1000kg mol^{-1a}	**9**	**1 110 000**	**1 790 000**	**1.61**	**73**
Xanthate free polym.	9	3 840 000	4 630 000	1.20	23
Mn_{th}=1000kg mol^{-1}	**20**	**1 020 000**	**1 580 000**	**1.55**	**70**
Xanthate free polym.	20	3 550 000	4 390 000	1.24	31
Mn_{th}=1000kg mol^{-1}	**33**	**983 000**	**1 500 000**	**1.53**	**67**
Xanthate free polym.	33	4 150 000	4 460 000	1.08	32
Mn_{th}=1000kg mol^{-1}	**50**	**960 000**	**1 420 000**	**1.48**	**58**
Xanthate free polym.	50	3 870 000	4 500 000	1.16	43

[a] Mn,theo=($mDMA_0/n(PDMA_7\text{-}XA1)_0$+ $mAMPS_0/n(PDMA_7\text{-}XA1)_0$ + $M(PDMA_7\text{-}XA1)$, [b] determined by SEC-RI-MALS in 15% methanol / 85% aqueous NaCl 100mM, NaH_2PO_4 25mM, Na_2HPO_4 25mM with ponderated dndc for each copolymer composition by using dn/dc (DMA)=0.160 mL $g^{-1}$and dn/dc (AMPS)=0.133 mL g^{-1}

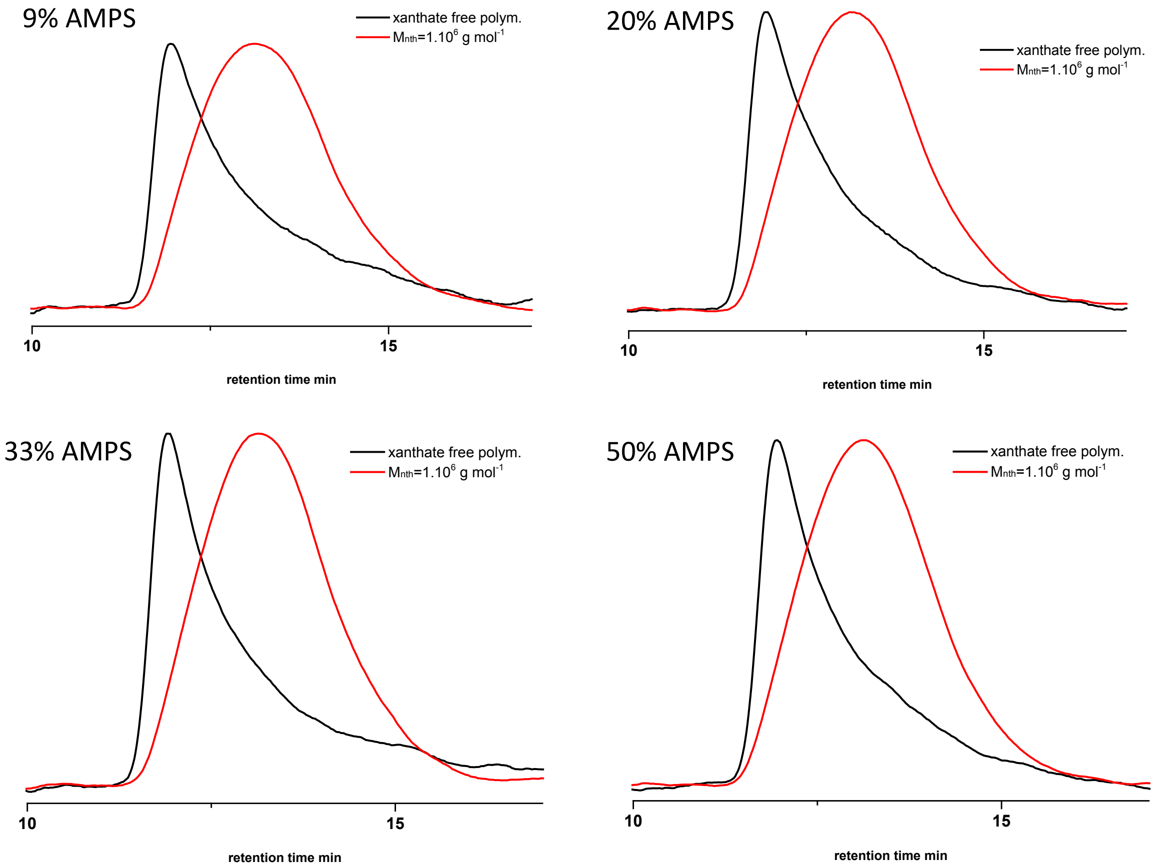


Figure S6 : Overlay of SEC chromatograms for P(DMA-*stat*-AMPS) for each AMPS composition for $M_{n,th}=1.10^6$ g mol^{-1} and xanthate free polymerization