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SEC Analysis of Poly(Acrylic Acid) and Poly(Methacrylic Acid)[a]

Igor Lacík,* Marek Stach, Peter Kasák, Vladislav Semak, Lucia Uhelská, Anna Chovancová, Günter Reinhold, Peter Kilz, Guillaume Delaittre, Bernadette Charleux, Isabelle Chaduc, Franck D'Agosto, Muriel Lansalot, Marianne Gaborieau, Patrice Castignolles, Robert G. Gilbert, Zachary Szablan, Christopher Barner-Kowollik, Pascal Hesse, Michael Buback

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Dr. Igor Lacík, Dr. Marek Stach,[#] Dr. Peter Kasák,[□] Dr. Vladislav Semak,[+] Dr. Lucia Uhelská, Anna Chovancová
Polymer Institute of the Slovak Academy of Sciences, Dúbravska cesta 9, 845 41 Bratislava 45, Slovakia
E-mail: igor.lacik@savba.sk

Dr. Günter Reinhold, Dr. Peter Kilz
PSS Polymer Standards Service GmbH, In der Dalheimer Wiese 5, D-55120 Mainz, Germany

Dr. Guillaume Delaittre,[⊥,¥] Prof. Bernadette Charleux[◁]
UPMC Univ. Paris 6, Sorbonne Universités and CNRS, Laboratoire de Chimie des Polymères, UMR 7610, 3 rue Galilée, 94200 Ivry, France

Dr. Isabelle Chaduc, Dr. Franck D'Agosto, Dr. Muriel Lansalot
Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Team LCPP, Bat 308F, 43 Bd du 11 Novembre 1918, BP 2077, 69616 Villeurbanne, France

Dr. Marianne Gaborieau, Dr. Patrice Castignolles
University of Sydney, School of Chemistry, Key Centre for Polymers & Colloids, Sydney NSW 2006, Australia; and University of Western Sydney, School of Science and Health, Australian Centre for Research on Separation Science, Molecular Medicine Research Group, Locked Bag 1797, Penrith NSW 2751, Australia

Prof. Robert G. Gilbert
The University of Queensland, Centre for Nutrition and Food Sciences, Queensland Alliance for Agriculture and Food Innovation, Brisbane, QLD 4072, Australia; and Tongji School of Pharmacy, Huazhong University of Science and Technology, Wuhan, Hubei 430030, China

Dr. Zachary Szablan,[$] Prof. Dr. Christopher Barner-Kowollik[⊥]
Centre for Advanced Macromolecular Design, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales (UNSW), Sydney NSW 2052, Australia

Dr. Pascal Hesse,[§] Prof. Dr. Michael Buback
Institute of Physical Chemistry, University of Goettingen, Tammannstraße 6, 37077 Goettingen, Germany

[a] **Supporting Information** ((bold)) is available online from the Wiley Online Library or from the author.

[#]Current address: ZF Boge Elastmetall Slovakia a.s., Strojárenská 2, 917 02 Trnava, Slovakia
[□]Current address: Center for Advanced Materials, Qatar University, P.O. Box 2713, Doha, Qatar
[+]Current address: EPFL, Institute of Chemical Sciences and Engineering, EPFL, CH-1015 Lausanne, Switzerland
[⊥]Current address: Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstrasse 18, 76128 Karlsruhe, Germany
[¥] Current address: Institute of Toxicology and Genetics, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[◁] Current address: Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Team LCPP Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France
[$]Current address: Vinidex Pty. Ltd., 254 Woodpark Road, Smithfield NSW 2164, Australia
[§]Current address: BASF SE, Polymer Process Development, 67056 Ludwigshafen, Germany

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Abstract. The accurate characterization of molar mass distributions of poly(acrylic acid), PAA, and poly(methacrylic acid), PMAA, by size-exclusion chromatography (SEC) is addressed. Two methods were employed: direct aqueous-phase SEC on P(M)AA and THF-based SEC after esterification of P(M)AA to the associated methyl esters, P(M)MA. P(M)AA calibration standards, P(M)AA samples prepared by pulsed-laser polymerization (PLP), and PAA samples prepared by reversible addition-fragmentation chain transfer (RAFT) were characterized in a joint initiative of seven laboratories, with satisfactory agreement achieved between the institutions. Both SEC methods provide reliable results for PMAA. In the case of PAA, close agreement of both SEC methods was only observed for samples prepared by RAFT polymerization with weight-average molar mass between 80 000 and 145 000 g mol^{-1} and for standards with peak molar masses below 20 000 g mol^{-1}. For higher molar masses of standards and for PLP-prepared PAA, the values from THF-based SEC are as much as 40 % below the molar masses determined by aqueous-phase SEC. This discrepancy may be due to branching or degradation of branched PAA during methylation. While both SEC methods can be recommended for PMAA, aqueous-phase SEC should be used for molar mass analysis of PAA unless the sample is completely unbranched.

Key-words: poly(acrylic acid); gel permeation chromatography (GPC); kinetics (polym.); poly(methacrylic acid); radical polymerization

1. Introduction

Poly(acrylic acid), PAA, and poly(methacrylic acid), PMAA, are important water-soluble polymers produced by radical polymerization. To adjust polymerization processes to the various applications in areas such as superabsorbents, drug delivery, coatings, thickeners, and water treatment,[1–3] the kinetics and mechanism of (M)AA polymerization in aqueous solution have been studied extensively.[4–6] The current picture has benefitted from the advent of pulsed-laser polymerizations (PLP) techniques[7,8] which, in conjunction with aqueous-phase size-exclusion chromatography (PLP–SEC), permit reliable measurements of the propagation rate coefficients, k_p, of both AA[9,10] and MAA.[10–13] Termination rate coefficients have also been measured by pulsed-laser techniques,[14,15] and used for modeling polymerization rates of MAA as well as of P(MAA) molar mass distributions.[16] Recent studies into reversible-deactivation radical homo-[17-19] and copolymerizations[20,21] underline the need for developing models for polymerization processes that are based on accurately known rate coefficients.[22–24]

Of fundamental importance is accurate information on the weight and number molar mass averages, $\overline{M}_w$, and $\overline{M}_n$, and on the molar mass distribution, MMD. The methods considered for MMD determination include SEC, matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS), analytical ultracentrifugation (AUC), and field-flow fractionation (FFF). MALDI-TOF MS was employed to characterize PAAs[25–27] as well as PMAAs[28] of low molar mass. Asymmetric FFF in conjunction with small-angle X-ray scattering was used to characterize PAAs of broad molar mass distribution.[29] However, SEC is by far the dominant method because of its availability, simplicity in data acquisition and

evaluation, and applicability to a broad range of molar masses. Two modes of SEC have been applied to P(M)AA: (1) aqueous-phase SEC on PAA[9,18–22,26,30−34] and PMAA[11,12,14,16,35] samples and (2) THF-based SEC after esterification of PAA[10,18,30,36–40] and PMAA[10,17,41] to the associated methyl esters. These methods require examination for their vulnerability towards sources of error related to the separation mechanism, to calibration aspects, to sample topology, and to potential side or incomplete reactions in case of the esterification route.

With aqueous-phase SEC, the presence of hydrogen bonding as well as hydrophobic and ionic interactions needs to be minimized to avoid non-size-exclusion phenomena.[42,43] In the case of P(M)AA analysis, suitable conditions for SEC separation require (i) hydrophilic column packing together with an eluent of pH ~ 9 to provide complete ionization of P(M)AA and thus avoid hydrogen bonding interactions, (ii) an inorganic salt to suppress the polyelectrolyte effect and, optionally, (iii) an increased temperature in order to lower the eluent viscosity.[9,11,12,14,16,22,30−35] For calibration, P(M)AA standards are commercially available as sodium salts with those for PAA exhibiting a broader distribution, $Đ = \overline{M}_w / \overline{M}_n < 2$, than the PMAA standards, $Đ < 1.2$.[44] Loiseau et al. prepared PAA standards by fractionation of polymer from conventional radical polymerization which were characterized by MALDI-TOF MS and light scattering.[26] Calibration against standards such as pullulans or poly(ethylene oxides)/poly(ethylene glycols)[19,22,32,45] may result in significant systematic errors as has been demonstrated for PAA samples by direct comparison of the data analysis via calibration using PAA and poly(ethylene glycol) standards.[26] In a detailed discussion of aqueous-phase SEC of PAA, Brüssau et al.[46] emphasized the importance of using accurate refractive index increments, d*n*/d*c*, for analysis via light scattering.

Non-size-exclusion phenomena are negligible in THF-based SEC of methylated P(M)AA samples.[47] Narrowly-distributed calibration standards are available for PMMA and universal

calibration may be applied, via the known Mark-Houwink-Sakurada (MHS) parameters, for SEC analysis of PMA.[48,49] Esterification of P(M)AA to P(M)MA is well known.[50] This early study reports that hydrolysis of PMA to PAA followed by esterification to PMA yields a sample of the same intrinsic viscosity as the original PMA, which suggests that these polymer analogous reactions do not affect the chain-length distribution of the samples. The esterification method has been frequently used for MMD characterization of P(M)AAs from radical polymerization,[10,17,30,36,41] of star-shaped PAA,[51] of P(M)AA with narrow MMD,[17,18,20,21,26,33,34,36–40,52] for converting poly(*N*,*N*-diphenylacrylamide) to PMA via PAA,[53] for preparation of various polymethacrylates,[54] of stereogradient PMMA[55] by esterification of stereoregular polyMAA, and of PAA gels with a hydrophobic shell.[56] Diazomethane is the most common methylating reagent for carboxylic acids due to its specificity and completeness in converting the carboxylic to methyl ester moieties.[57] Kawauchi et al. showed that esterification of PMAA by various primary, secondary, and tertiary halogenated compounds in the presence of 1,8-diazabicycloundec-7-ene resulted in various degrees of esterification.[54] By subsequent treatment with diazomethane, the degree of esterification with halogenated compounds may be determined.

It is generally assumed that esterification is not accompanied by side reactions which affect the degree of polymerization. Data which were independently obtained in two laboratories[10,11] by using both aqueous-phase and THF-based SEC on PLP-prepared PMAA and, after esterification, on PMMA samples, respectively, resulted in excellent agreement of the k_p values deduced from the position of inflection points on the MMDs. These k_p data represent the IUPAC-recommended benchmark k_p values for radical polymerization of MAA.[13] A few studies however raised doubt on the applicability of the esterification method to PAA. Brüssau et al. reported that methyl esterification was incomplete in the case of PAA.[46] Recently star-shaped PAA was subjected to esterification by trimethylsilyldiazomethane.[51] The authors

concluded from the ^{1}H NMR spectra that the conversion to the methyl ester was around 80%, with the majority of residual acid groups being transformed to ketones. The conversion of some carboxylic acid groups to ketone moieties should not significantly affect the SEC result. However, the k_p values from PLP−SEC carried out in conjunction with either aqueous-phase or THF-based SEC were not in satisfactory agreement.[30] Hence SEC characterization of PAA requires further attention. The following potential sources of error need to be particularly addressed: (1) uncertainties due to branching during AA polymerization, with transfer to polymer being known from acrylate studies to occur and to interfere with molar mass analysis by SEC,[58−61] (2) side reactions or incomplete reaction during esterification, (3) the accuracy of calibration due to the broader dispersity of PAA chromatography standards, and (4) the uncertainty of MHS parameters when using universal calibration for PMA analysis.

The present study reports on the measurement of molar mass distributions of P(M)AA by aqueous-phase SEC and, after methylation, by THF-based SEC. Three types of polymers differing in their mode of production were examined: SEC standards, PLP-made samples, and polymers from RAFT polymerization. Primary emphasis is on the MMD analysis of PAA, whereas the investigations into PMAA are made for the purpose of comparison. The manuscript has been prepared within a joint activity of the IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes in an effort to deduce reliable propagation rate coefficients by the IUPAC-recommended PLP-SEC technique. Seven laboratories participated in this study with the individual tasks being listed in **Table 1**: preparation of P(M)AA samples by PLP, preparation of PAA samples by reversible addition-fragmentation chain transfer (RAFT), esterification of P(M)AA to P(M)MA, and characterization of MMDs by aqueous-phase and by THF-based SEC. Pulsed laser polymerizations were carried out at the Georg-August University (GAU, Göttingen, Germany) and at the Polymer Institute SAS (PI SAS, Bratislava, Slovak Republic). The RAFT polymerizations of AA were carried out at the

Table 1. Tasks of the laboratories participating in preparation of the P(M)AA samples and in SEC characterization.

Laboratory	P(M)AA samples			SEC characterization				
	Chromatography standards	PLP-prepared	RAFT-prepared	Eluent	Columns	Calibration	Temperature [°C]	Flow rate [mL min^{-1}]
GAU	–	MAA1 MAA2 MAA3 AA1	–	–	–	–	–	–
PI SAS	Esterification and SEC analysis	AA2	–	0.1 M Na_2HPO_4	10 μm PSS Suprema guard and three PSS Suprema columns with pore sizes 100, 1000 and 3000 Å	P(M)AA	60	1.0
				THF	5 μm PSS SDV guard and three PSS SDV columns with pore sizes 100, 1000 and 100,000 Å	Polystyrene[a)] PMMA[b)]	40	1.0
PSS	–	–	–	0.1 M Na_2HPO_4	10 μm PSS Suprema guard and three PSS Suprema columns with pore sizes 100, 1000 and 3000 Å	P(M)AA	25	0.5
UPMC	–	–	–	THF	PL-gel 10 μm mixed, and Shodex KF 801L	Polystyrene[a)] PMMA[b)]	30	1.0
C2P2	–	–	AA-RAFT	THF	T6000M General Mixed Org, Malvern Instruments	Polystyrene[a)]	40	1.0
KCPC	–	–	–	0.1 M Na_2HPO_4	10 μm PSS Suprema guard and three PSS Suprema columns with pore sizes 100, 1000 and 100,000 Å	PMAA	50	1.0
CAMD	–	10 wt% AA	–	0.1 M Na_2HPO_4	10 mm PL mixed guard column and one PL OH mixed 8 μm column	PAA	25	0.5

[a)] characterization of PMA after methyl esterification of PAA using universal calibration
[b)] characterization of PMMA after methyl esterification of PMAA

Université de Lyon (C2P2, Lyon, France). Polymer samples were analyzed by aqueous-phase SEC at PI SAS, at the Polymer Standards Service (PSS, Mainz, Germany), and at the Key Center for Polymers & Colloids (KCPC, Sydney, Australia). The esterification of P(M)AA samples was performed at PI SAS, including esterification of the chromatography P(M)AANa calibration standards, at the Université Pierre et Marie Curie (UPMC, Paris, France), and at C2P2. THF-based SEC was performed at PI SAS, at UPMC, and at C2P2. Additional PAA samples were prepared by PLP and evaluated at the Centre for Advanced Macromolecular Design (CAMD, Sydney, Australia).

2. Experimental Section

2.1. Materials

Methacrylic acid (MAA, Fluka > 98%, stabilized with 0.025 % hydroquinone monomethylether), acrylic acid (AA, either Fluka or Aldrich > 99.0%), 4,4'-azobis(4-cyanopentanoic acid) (ACPA, Fluka, > 98%), 1,3,5-trioxane (Aldrich, > 99%), and 2,2-dimethoxy-2-phenylacetophenone (DMPA, Sigma-Aldrich, 99 %) were used as supplied. The AA used for preparing the PAA sample by irradiation with a pulse repetition rate of 500 Hz was distilled at 45 °C and reduced pressure using a minidistiller Büchi Glass Oven B-585 (Büchi Labortechnik AG, Switzerland). 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA) was obtained by reaction of ACPA with bis(thiobenzoyl) and bis(propylsulfanylthiocarbonyl) disulfide according to the literature.[62] Demineralized water was used for preparation of the monomer solutions and as the eluent for aqueous-phase SEC. Tetrahydrofuran (THF) of HPLC quality was used as received or was dried over KOH and distilled from copper(I) chloride under a nitrogen atmosphere. Trimethylsilyldiazomethane (a 2 mol L^{-1} solution in hexane, Aldrich)[36] and diazomethane, prepared according to the

literature,[57,63] were used as methylation agents. PAANa (produced by fractionation of PAA prepared by radical polymerization to low conversion)), PMAANa, PMMA, and polystyrene chromatography calibration standards were used as obtained from PSS (Polymer Standards Service, Mainz, Germany).

2.2. Pulsed-laser polymerizations

The 351 nm (XeF) line of an excimer laser (LPX 210i, Lambda Physik) with an incident laser energy of about 10 mJ per pulse was used for PLP of the MAA1, MAA2, MAA3, and AA1 samples. MAA samples were polymerized at 15 wt% monomer, 20 °C, a DMPA concentration of 1 x 10^{-3} mol L^{-1}, at pulse repetition rates of either 20 Hz (applying 300 and 200 pulses with samples MAA1 and MAA2, respectively) or 10 Hz (sample MAA3, where 300 pulses were applied). Sample AA1 was prepared at a pulse repetition rate of 100 Hz (using 30 pulses), at 10 wt% AA, 2 °C, and a DMPA concentration of 5 x 10^{-4} mol L^{-1}. To enable distribution of samples among several laboratories, a larger quantity of the P(M)AA samples, 20 to 90 mg, was prepared by carrying out up to 14 low-conversion (< 5%) PLP experiments under identical conditions. The MMDs and the associated first-derivative curves for sample AA1 as obtained from the individual polymerizations are shown together with the associated pooled sample in the Supplementary Information (**Figure SI1**) to demonstrate the good reproducibility of PLP sample preparation and SEC analysis. For AA2 sample, the excimer pulsed laser (ExciStar XS 500, Coherent) had an incident laser energy of 3 mJ per pulse. The polymerization temperature was 6 °C, monomer concentration 20 wt%, and DMPA concentration 2 x 10^{-3} mol L^{-1}. The AA2 sample was produced by applying 150 pulses at a repetition rate of 500 Hz (two repeated experiments). Additional PAA samples were prepared by PLP at CAMD at a monomer concentration of 10 wt% and six temperatures between 2 and 25 ºC, a DMPA concentration of 5 x 10^{-4} mol L^{-1}, and a pulse repetition rate of 100 Hz using the Continuum Surelite I-20-

Nd:YAG pulsed laser system at a wavelength of 355 nm with single pulse energies between 15 and 30 mJ at a beam diameter of 6 mm.[64] Pulsed laser polymerizations were carried out in quartz cells after oxygen removal, by purging with nitrogen, as described elsewhere.[11,30,64] Post-polymerization was suppressed by pouring the mixture after PLP into a sample vial containing hydroquinone monomethylether. Water and (M)AA were evaporated under high vacuum at ambient temperature. The degree of monomer conversion was determined by gravimetric measurement of the amount of polymer.

2.3. RAFT polymerization of AA in water

The procedure for RAFT polymerization of AA (samples AA-RAFT) was similar to the one previously reported in the literature for the synthesis of low molar mass PAA.[18] PAA samples were synthesized in water using CTPPA as a chain transfer agent and ACPA as a radical initiator. In a two-necked round-bottom flask equipped with a condenser, CTPPA (21 mg, 2.01 $\times 10^{-3}$ mol L^{-1}) and ACPA (2.2 mg, 2.01 $\times 10^{-4}$ mol L^{-1}) were dissolved in AA (7.63 g, 2.79 mol L^{-1}) and water (4 mL). 1,3,5-trioxane (1.57 mg, 4.64 $\times 10^{-1}$ mol L^{-1}) was added as internal reference for NMR analysis. Finally, water (26 mL) were added. After deoxygenation by bubbling nitrogen for 30 min, the resulting mixture was immersed in an oil bath and thermostated at 70 °C. The timed withdrawal of samples permitted analysis of monomer conversion as a function of time and of the evolution of molar masses and molar mass distributions as a function of monomer conversion. Monomer conversion was determined by ^{1}H NMR spectroscopy of the crude reaction medium diluted with D_2O by integration of the protons of 1,3,5-trioxane and the vinylic protons of the monomer. $\overline{M}_w$ and $\overline{M}_n$ values were determined after esterification by THF-based SEC using universal calibration.

2.4. Esterification of P(M)AA

P(M)AA was dissolved in a 1:1 v/v THF/H_2O mixture (5 mg mL^{-1}). The yellow solution of the methylation agent, diazomethane (PI SAS) or trimethylsilyldiazomethane (UPMC), was added dropwise, which resulted in the formation of N_2 bubbles and rapid decoloration upon reaction. The methylation agent was added until nitrogen production stopped and the color remained. The solution was subsequently stirred for 6 h until the yellow color disappeared due to evaporation of excess methylation agent. THF and H_2O were then evaporated at ambient pressure and the resulting polymeric film was dissolved in THF for SEC analysis. The completeness of esterification was verified by FTIR and by ^{1}H-NMR spectroscopy, which showed the absence of carboxylic acid groups within the detection limits of the analytical techniques (FTIR ~ 5 %, ^{1}H-NMR ~ 2 %). The P(M)AA samples from PLP were methylated directly after isolation, whereas the P(M)AANa chromatography standards were transformed into the acidic form prior to esterification. For this purpose, around 20 mg of P(M)AANa were dissolved to about 0.1 wt% in water and dialyzed using a regenerated cellulose Spectra/Por® dialysis membrane (MWCO 1000 Da, Spectrum Laboratories, Inc.) against 0.01 mol L^{-1} HCl followed by dialysis against water and subsequent P(M)AA isolation by lyophilization.

2.5. SEC in aqueous phase

Aqueous-phase SEC analysis was carried out as described elsewhere.[11] P(M)AA samples from PLP were analyzed in an aqueous solution of 0.1 mol L^{-1} Na_2HPO_4 (Table 1) at pH ~ 9, under which conditions the carboxylic groups of P(M)AA are ionized to eliminate hydrogen-bonded interactions. Moreover, the polyelectrolyte effect is circumvented. Slightly different flow rates and temperatures were employed in the individual laboratories (Table 1). Either Suprema columns from PSS or PL aquagel-OH columns (Polymer Laboratories Ltd, Shropshire, UK) were used. The SEC polymer samples were prepared at a concentration of 2 mg mL^{-1} at least 24 hours prior to SEC analysis. The PMAANa and PAANa calibration standards from PSS

were in the M_p range from 1.22 x 10^3 to 1.027 x 10^6 g mol^{-1} and 1.25 x 10^3 to 1.10 x 10^6 g mol^{-1}, respectively.

2.6. SEC in THF

Conventional THF-based SEC was used for P(M)MA analysis at PI SAS, UPMC, and at C2P2 (Table 1) employing SDV column packing and THF as the eluent. Narrowly-distributed PMMA standards from PSS were used for calibration of SEC for characterization of PMMA samples. Universal calibration was applied for characterization of PMA samples using narrowly-distributed polystyrene standards from PSS. The following MHS parameters were used: K = 1.14×10^{-4} dL g^{-1} and a = 0.716 for polystyrene,[48] and K = 1.95×10^{-4} dL g^{-1} and a = 0.660[48] or K = 1.02×10^{-4} dL g^{-1} and a = 0.719,[49] respectively, for PMA.

2.7. NMR spectroscopy

The conversion of AA in RAFT polymerization was determined by ^{1}H NMR spectroscopy in D_2O at ambient temperature (Bruker DRX 300). The ^{13}C NMR experiment used for analysis of quaternary carbons was performed at 333 K in D_2O/Na_2O (1 equivalent compared to carboxylic acid groups) solution with a Bruker DRX 400 spectrometer operating at 100.61 MHz (NMR Polymer Center of the Institut de Chimie de Lyon (FR5223)). The spectrum was recorded with a 10 mm SEX probe, ^{13}C selective with a z-gradient coil using the following conditions: 70° flip angle, TD 65 K, and 5.3 recycle time. Chemical shift values (δ) were given in reference to the shift of internal Tspd4 (trimethylsilyl-3-propionic acid, 2,2,3,3 sodium salt, δ_0 = –2.35 ppm).

3. Results and Discussion

3.1. SEC analysis of PMAA and PAA calibration standards.

Figure 1 shows the MMDs of the P(M)AANa calibration standards and of the associated methylated products. The abscissa scale refers to the sodium salt moiety as the repeat unit. Calibration standards with molar masses above 480 000 g mol^{-1} for PMAANa and above 193 000 g mol^{-1} for PAANa are not included in Figure 1, as the esterified samples of such high-molar-mass samples were not completely soluble in THF. The samples of lower molar mass did not cause any solubility problem. Good agreement of MMDs before and after esterification is seen for PMAANa (**Table 2**). The peak molar masses, M_p, of the starting material (nominal value as given by PSS) are very close to the M_p data deduced from aqueous-phase SEC and from THF-based SEC after methylation. Also contained in Table 2 are the $\overline{M}_w$ and $\overline{M}_n$ averages, where the agreement between the three data sets is satisfactory as well. The aqueous-phase SEC data reflect the quality of the 3rd polynomial fit used as calibration curve with the MMDs shown in Figure 1a along with the MMDs for PMMA obtained after esterification. The data in Figure 1a confirms previous findings about both aqueous-phase and THF-based SEC after esterification being suitable for molar mass analysis of PMAA. [13]

Figure 1b and Table 2 reveal that with PAA the agreement between the M_p values of the parent calibration standards is satisfactory for aqueous-phase SEC, but is poor for analysis of the methylated samples by THF-based SEC. This discrepancy is minor at low molar masses, but increases systematically towards higher masses and is up to 30 and 40 per cent, respectively, for molar mass standards of nominal M_p of 62 900 and 193 000 g mol^{-1}. The masses determined for the methylated samples are clearly below the ones from aqueous-phase SEC. Two sets of MHS parameters for PMA,[48,49] as deduced from experiments at 30 and 40 °C, respectively, were applied for analysis of PMA via universal calibration. The resulting M_p values differ by less than 10 % (see Table 2), which is within the range indicated by Couvreur et al. for PMA.[36] The reported MHS parameters have been determined for PMA from conventional free-radical

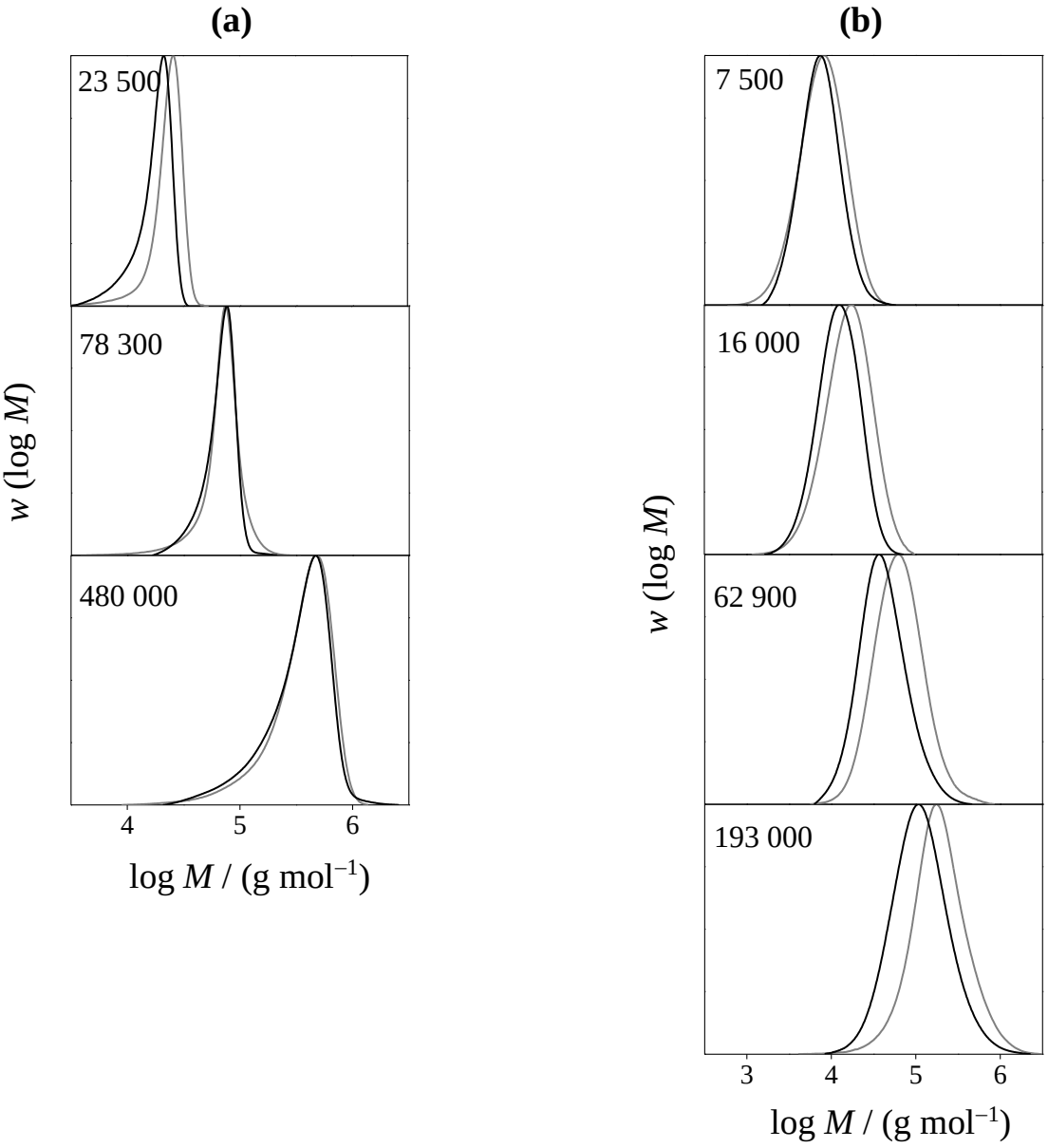

Figure 1. Molar mass distribution of polyMAANa (a) and polyAANa (b) calibration standards determined by aqueous-phase SEC (grey lines) and THF-based SEC after methyl esterification (black lines). The numbers represent the nominal values of molar mass at the peak maximum M_p (g mol^{-1}) as given by the manufacturer. The MMDs for the esterified poly(M)MA standards were transformed to (M)AANa repeat units to facilitate comparison between parent and methyl-esterified standards. The MMDs for polyMA were determined via universal calibration with the MHS parameters from ref.[48]

Table 2. Comparison of molar masses at the peak maximum, M_p, weight-average, M_w, and number-average, M_n, molar masses for P(M)AANa calibration standards (i) as given by the manufacturer, (ii) as determined by aqueous-phase SEC (two values are from repeated injections) and, (iii) by THF-based SEC applied after methyl esterification. The mass values refer to (M)AANa as the repeat units.

standard	molar mass ($\times 10^{-3}$ g mol^{-1})								
	nominal value			aqueous-phase SEC			THF-based SEC		
	M_p	$\overline{M}_w$	$\overline{M}_n$	M_p	$\overline{M}_w$	$\overline{M}_n$	M_p	$\overline{M}_w$	$\overline{M}_n$
PMAANa	23.5	20.5	19.2	25.7 25.8	23.8 23.8	20.7 20.9	21.3	18.4	15.9
	78.3	75.1	73.3	76.8 76.8	69.5 69.4	61.1 61.1	75.1	67.9	61.1
	480	421	380	479 477	448 446	333 330	472	408	273
PAANa	7.5	8.3	6.2	8.3 8.3	9.3 9.3	6.4 6.3	8.2[a)] 8.8[b)]	9.9[a)] 9.3[b)]	7.6[a)] 7.0[b)]
	16.0	18.1	12.8	17.4 17.5	19.3 19.1	12.9 12.8	13.9[a)] 14.6[b)]	16.2[a)] 15.5[b)]	12.2[a)] 11.4[b)]
	62.9	83.4	47.9	62.3 62.1	80.0 78.2	51.0 50.0	40.7[a)] 41.4[b)]	55.3[a)] 55.4[b)]	37.6[a)] 36.7[b)]
	193	245	153	179 176	249 252	138 144	119[a)] 116[b)]	160 [a)] 167[b)]	91.8[a)] 91.1[b)]

[a)] K = 1.95 x 10^{-4} dL g^{-1} and a = 0.660 from ref.[48]

[b)] K = 1.02 x 10^{-4} dL g^{-1} and a = 0.719 from ref.[49]

polymerization, i.e., for material with branched microstructure. MHS parameters of poly(*n*-alkyl acrylates) have been found to be different for branched and linear material in the case of poly(2-ethylhexyl acrylate) and poly(*tert*-butyl acrylate), but not in the case of poly(*n*-butyl acrylate).[60] The branching structure was shown to lead to approx. 20 % error in molar mass of

PMA determined by SEC (local dispersity around 1.2),[49] which may affect the accuracy of the MHS coefficients.

An influence of non-SEC phenomena for aqueous-phase SEC in the case of PAA is not very likely, as such effects should also occur with the SEC analysis of PMAA, where they are however absent. The discrepancy in molar masses seen with the PAA samples may be related to branching, which is the principal difference between PAA and PMAA. Branches arise from backbiting processes, by which mid-chain radicals are formed in acrylate radical polymerization[65] as has also been demonstrated for AA by PLP in aqueous solution[66] and by single-pulse PLP carried out in conjunction with electron paramagnetic resonance spectroscopy.[67] Branches are also seen by ^{13}C NMR spectroscopy with PAA produced via reversible-deactivation radical polymerization (RDRP).[36,68,69] In case of PMA, no significant effect of polymerization temperature on MHS parameters was found for polymer from MA bulk polymerizations between 20 and 86 °C, in which range the degree of short-chain branching largely differs. So far, it is not known whether this observation holds also for AA polymerization in aqueous solution. Different extents of short-chain branching may not significantly affect the MHS coefficients.[70] Long-chain branching, however, may affect the MHS parameters of PAA as is the case with PMA. Incomplete methylation cannot be the origin of the mismatch, as both FTIR and NMR analysis provide no indication of carboxylic acid groups remaining after treatment with the methylating agents.

The discrepancies between the PAA molar mass results from the two modes of SEC analysis may be related to branching, more precisely to long-chain branching. Long-chain branching affects the hydrodynamic volume of polymer chains, such that molecules of different masses may co-elute in case of different branching topology.[47,71] This may affect both aqueous-phase

SEC of PAA and THF-based SEC of PMA in different ways, and could explain the discrepancy between the measured molar masses since intermolecular chain transfer to polymer and/or random intramolecular transfer to polymer are affected by polymerization temperature. An alternative explanation assumes that some side reaction associated with bond scission occurs during methylation. The extent by which this side reaction occurs would increase with the number of branching points. Higher molar mass PAAs would thus be more vulnerable to this side reaction than shorter-chain PAAs. This is what the SEC data in Figure 1b and in Table 2 suggest. Thus the message from the SEC investigations into the PAA and PMA samples is that, apart from the situation of relatively low molar masses, i.e., for $\overline{M}_w$ well below 20 000 g mol^{-1}, the esterification pathway should be avoided and PAA samples should be directly analyzed by aqueous-phase SEC. This finding validates studies where short-chain PAA obtained by RDRP was characterized by the methylation/THF-SEC method.[36–40,72]

3.2. SEC characterization of PLP-prepared PMAA and PAA samples

The consequences of using one or the other SEC procedure for deducing propagation rate coefficients, k_p, of (M)AA will now be illustrated. The method of k_p measurement recommended by the IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes is PLP–SEC, pulsed-laser polymerization in conjunction with SEC. Benchmark k_p values have been collated for the bulk homopolymerizations of styrene,[73] methacrylates,[74–76] *n*-butyl acrylate,[77] methyl acrylate,[78] as well as for MAA polymerized in aqueous solution.[13] The accuracy of such k_p measurements essentially relies on the quality of SEC analysis. Thus, k_p measurement via PLP–SEC may be used to evaluate SEC analysis.

Figure 2 depicts the MMDs and associated first derivatives for PMAA samples prepared at 20 °C in aqueous solution containing 15 wt% MAA. Aqueous-phase SEC has been carried out

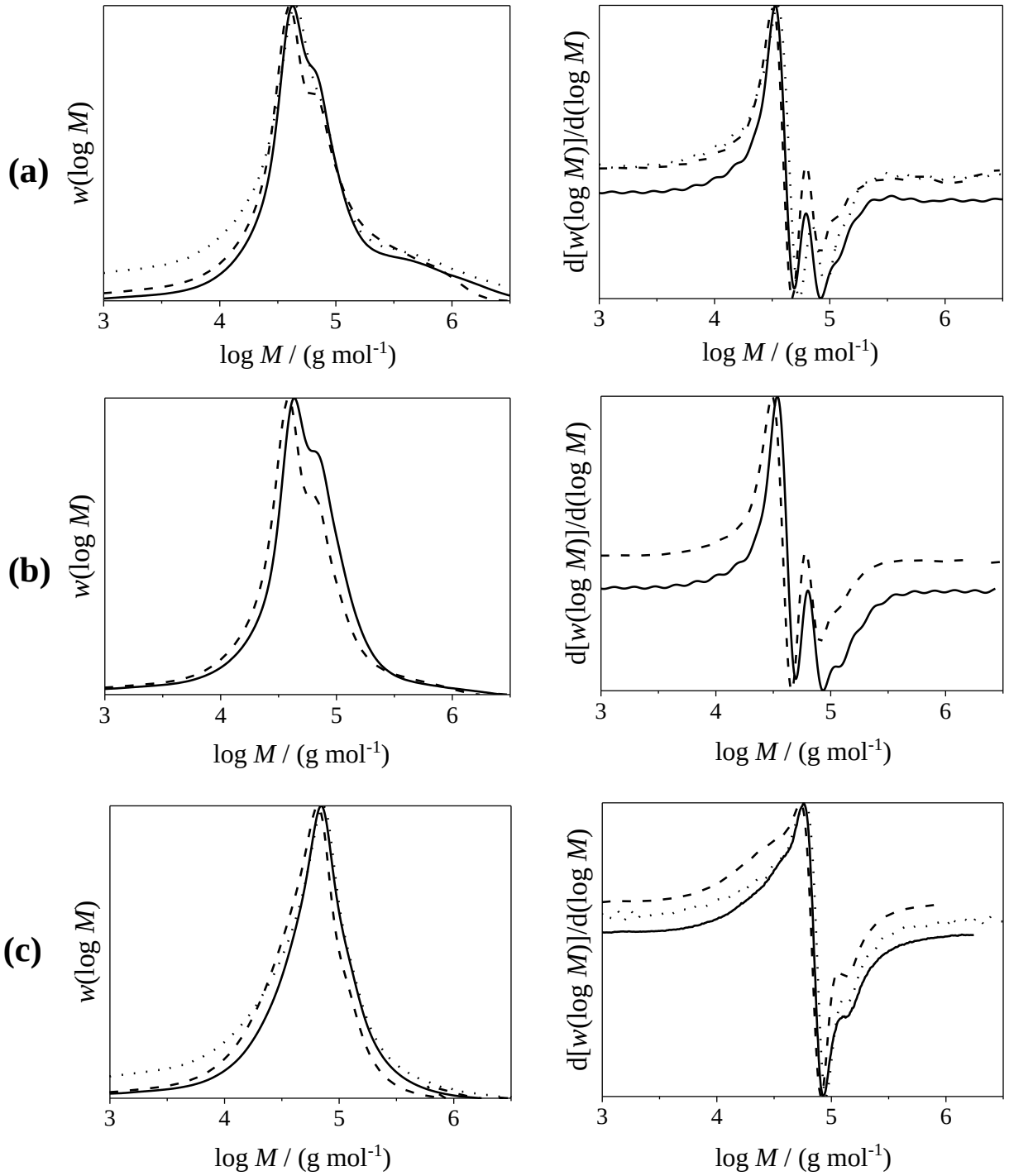

Figure 2. Molar mass distributions and associated first-derivative curves for PMAA samples (a) MAA1 (20 Hz, 300 pulses), (b) MAA2 (20 Hz, 200 pulses), and (c) MAA3 (10 Hz, 300 pulses). Comparison of aqueous-phase SEC analyses carried out at PI SAS (solid), PSS (dash) and KCPC (dotted).

Table 3. Primary, M_1, and secondary, M_2, points of inflection (in 10^{-3} g mol^{-1}) and k_p values for P(M)AA samples prepared by pulsed-laser polymerization. MMD has been characterized by aqueous-phase SEC and, after esterification, by THF-based SEC. The points of inflection are reported as obtained by (i) direct calibration via poly(sodium (meth)acrylate) standards, P(M)AANa, (ii) direct and universal calibration with poly(methyl methacrylate) and poly(methyl acrylate) analysis via the MHS parameter from ref. [48], and (iii) referred to (M)AANa repeat units.

Sample	Laboratory	SEC in aqueous phase[a)]					SEC in THF					$k_p \times 10^{-3}$ [L mol^{-1} s^{-1}]
		P(M)AANa calibration			Recalculated to P(M)AA		P(M)MA calibration			Recalculated to P(M)AA		
		M_1	M_2	M_1/M_2	M_1	M_2	M_1	M_2	M_1/M_2	M_1	M_2	
MAA1[b)]	PI SAS	31.2	62.1	0.50	24.8	49.5	–	–	–	–	–	3.41
		33.7	62.4	0.54	26.8	49.7	–	–	–	–	–	3.69
	PSS	32.1	62.2	0.52	25.6	49.5	–	–	–	–	–	3.50
		32.2	62.2	0.52	26.6	49.5	–	–	–	–	–	3.52
	KCPC	35.4	69.2	0.51	28.2	55.1	–	–	–	–	–	3.86
		35.4	69.2	0.51	28.2	55.1	–	–	–	–	–	3.86
MAA2[c)]	PI SAS	33.0	63.8	0.52	26.3	50.8	–	–	–	–	–	3.60
		32.2	64.7	0.50	25.6	51.5	–	–	–	–	–	3.53
	PSS	30.9	60.4	0.51	24.6	48.1	–	–	–	–	–	3.37
		31.2	61.1	0.51	24.8	48.7	–	–	–	–	–	3.41

Sample	Laboratory	SEC in aqueous phase[a)]					SEC in THF					$k_p \times 10^{-3}$ [L mol^{-1} s^{-1}]
		P(M)AANa calibration			Recalculated to P(M)AA		P(M)MA calibration			Recalculated to P(M)AA		
		M_1	M_2	M_1/M_2	M_1	M_2	M_1	M_2	M_1/M_2	M_1	M_2	
	UPMC	–	–	–	–	–	28.4	49.0	0.58	24.4	42.1	3.35
MAA3[d)]	PI SAS	52.5	117.2	0.45	41.8	93.3	–	–	–	–	–	2.87
		57.3	129.7	0.44	45.6	103.3	–	–	–	–	–	3.13
	PSS	53.7	114.8	0.47	42.8	91.4	–	–	–	–	–	2.94
		54.5	116.4	0.47	43.4	92.7	–	–	–	–	–	2.98
	KCPC	55.8	–	–	44.4	–	–	–	–	–	–	3.05
	UPMC	–	–	–	–	–	47.3	88.3	0.54	40.7	76.0	2.80
AA1[e)]	PI SAS	89.1	194.5	0.46	68.2	149.0	–	–	–	–	–	69.1
		90.6	225.9	0.40	69.4	173.0	–	–	–	–	–	70.3
	PSS	97.1	239.3	0.41	74.4	183.3	–	–	–	–	–	75.3
		97.7	239.9	0.41	74.8	183.8	–	–	–	–	–	75.8
	UPMC	–	–	–	–	–	64.4	140.6	0.46	53.9	117.7	54.6

Sample	Laboratory	SEC in aqueous phase[a)]					SEC in THF					$k_p \times 10^{-3}$ [L mol^{-1} s^{-1}]
		P(M)AANa calibration			Recalculated to P(M)AA		P(M)MA calibration			Recalculated to P(M)AA		
		M_1	M_2	M_1/M_2	M_1	M_2	M_1	M_2	M_1/M_2	M_1	M_2	
AA2[f)]	PI SAS	41.3	83.8	0.49	31.6	64.2	–	–	–	–	–	81.5
		40.1	82.2	0.49	30.7	63.0	–	–	–	–	–	79.1
		40.4	82.8	0.49	30.9	63.4	–	–	–	–	–	79.7
		40.3	82.4	0.49	30.8	63.1	–	–	–	–	–	79.5
		–	–	–	–	–	29.3	56.1	0.52	24.5	47.0	63.1
		–	–	–	–	–	29.6	56.5	0.52	24.8	47.3	63.7
		–	–	–	–	–	30.6	57.9	0.53	25.6	48.5	64.9
			–	–	–	–	30.6	57.8	0.53	25.6	48.4	64.9

[a)] The two values provided by most of the partners are from two injections of the same sample

[b)] MAA1 polymerization conditions: 15 wt% MAA, 20 °C, 1 x 10^{-3} mol L^{-1} DMPA, 20 Hz, 300 pulses

[c)] MAA2 polymerization conditions: 15 wt% MAA, 20 °C, 1 x 10^{-3} mol L^{-1} DMPA, 20 Hz, 200 pulses

[d)] MAA3 polymerization conditions: 15 wt% MAA, 20 °C, 1 x 10^{-3} mol L^{-1} DMPA, 10 Hz, 300 pulses

[e)] AA1 polymerization conditions: 10 wt% AA, 2 °C, 0.5 x 10^{-3} mol L^{-1} DMPA, 100 Hz, 30 pulses

[f)] AA2 polymerization conditions: 20 wt% AA, 6 °C, 2 x 10^{-3} mol L^{-1} DMPA, 500 Hz, 150 pulses (4 individual samples were prepared under the same conditions and analyzed by SEC in aqueous solutions in single injection; 2 samples were esterified separately and injected, two injections, on THF-based SEC)

in three laboratories. As described in detail elsewhere,[7] the degree of polymerization at the inflection points of the SEC trace (i.e., at the maxima of the first-derivative of the SEC curve) yields k_p with only monomer concentration and the selected pulse repetition rate being additionally required. The first-derivative curves in Figures 2a and 2b exhibit clear maxima, each of which allows for estimating k_p. The second maximum is less pronounced in Figure 2c, where the pulse repetition rate was only 10 Hz. Listed in **Table 3** are the molar masses of the first and second inflection points, M_1 and M_2, the ratio M_1/M_2, and the resulting k_p values for MAA (15 wt% in aqueous solution) at 20 °C. It should be noted that the molar masses and k_p values in Table 3 are the actual quantities divided by a factor of 1000.

The MMDs for MAA1 and MAA2 samples prepared at 20 Hz under identical polymerization conditions, apart from the number of laser pulses, show close agreement and therefore underline the high level of reproducibility in sample preparation and SEC characterization. The MAA3 sample has been prepared at 10 Hz, which shifts the primary point of inflection to a molar mass which is by about a factor of 2 greater than the corresponding masses of the MAA1 and MAA2 samples. The MMDs exhibit a PLP structure, which originates from initiation and termination being controlled by laser pulsing. The ratio of the first and second peak maximum of the derivative curve, M_1/M_2, is close to the value of 0.5, which demonstrates that an important consistency criterion of the PLP−SEC method is fulfilled.[74] The pulse repetition rate of 10 Hz selected for preparation of sample MAA3 is obviously less suitable than 20 Hz, as can be seen from the fact that the secondary point of inflection occurs as a shoulder rather than a maximum in the first-derivative curve. The samples MAA2 and MAA3 were methylated. The resulting MMDs and associated first-derivative curves of PMMA are depicted in **Figure 3**. The MMDs determined by aqueous-phase SEC, already presented in Figure 2, are included as grey lines for comparison. The resolution of inflection points after esterification is clearly enhanced for both

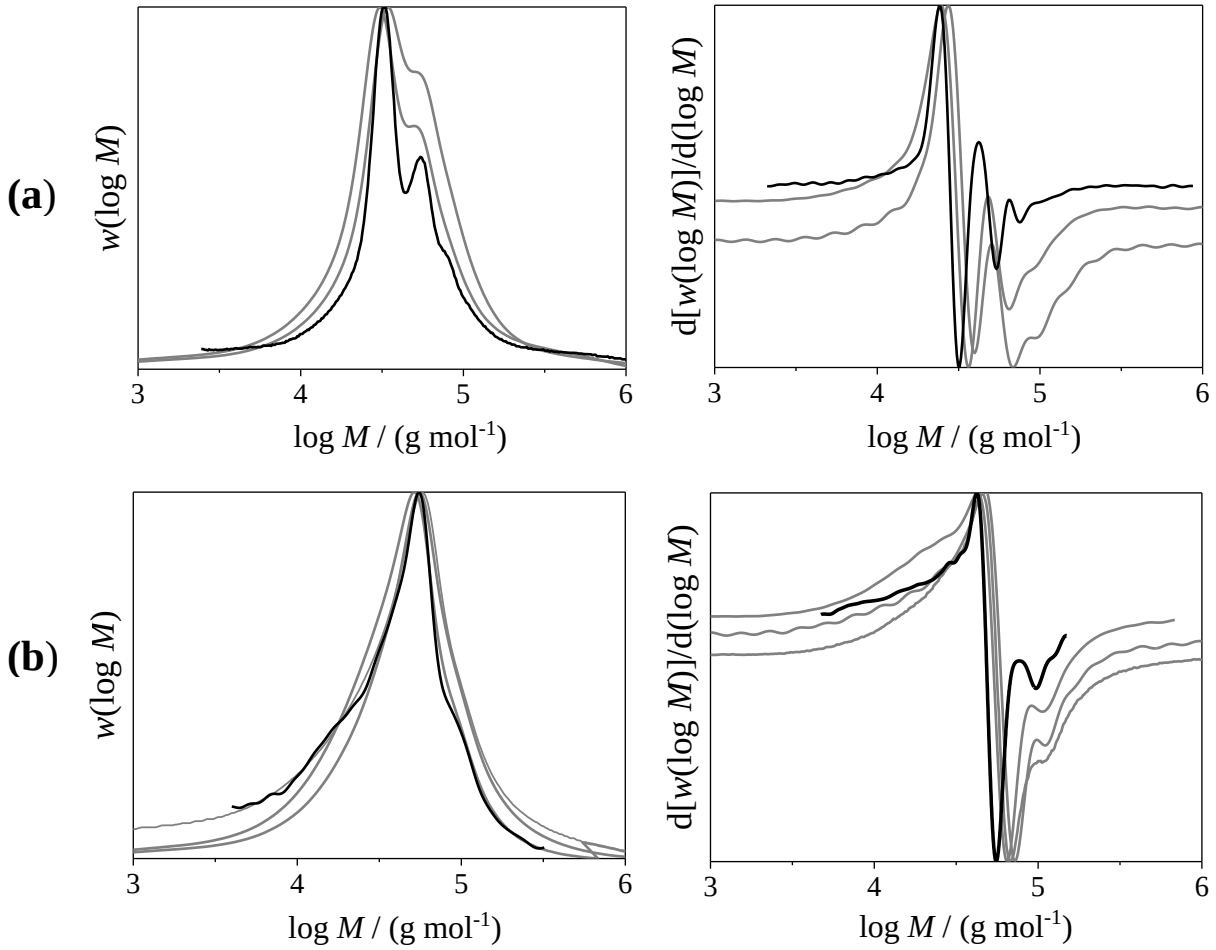

Figure 3. Molar mass distributions and associated first-derivative curves for the PMAA samples (a) MAA2 and (b) MAA3. Grey lines: aqueous-phase SEC analyses from Figure 2. Black line: THF-based SEC after esterification. Molar mass values refer to methacrylic acid repeat unit.

samples, thus even allowing for the identification of a tertiary point of inflection for MAA2 and a well-resolved secondary point of inflection for MAA3. This improvement results from the higher number of theoretical plates of THF-based SEC, which is of the order of 20 000 m^{-1} compared to 10 000 m^{-1} for aqueous-phase SEC, as determined at PI SAS.

The masses at the first inflection points of the esterified MAA2 and MAA3 samples, 24 400 g mol^{-1} and 40 700 g mol^{-1}, respectively, are in satisfactory agreement with the associated averaged values from aqueous-phase SEC, 25 300 g mol^{-1} and 43 600 g mol^{-1}, respectively, with

these numbers referring to MAA repeat units. The k_p value deduced from MAA2 is approximately 10 % greater than the one for MAA3, which remains within the typical limits of ±15 % accuracy of PLP–SEC experiments. The M_1/M_2 ratios do not perfectly match between the parent and the esterified samples but are sufficiently close to 0.5, thus indicating reliable PLP–SEC measurements. Beyond this proof of internal consistency, it is worth mentioning that the average k_p value of 3 300 ± 400 L mol^{-1} s^{-1} determined from the entire set of k_p data listed in Table 3 for MAA polymerization at 20 °C in aqueous solution (15 wt% MAA) is in agreement with the benchmark k_p value of 3 270 L mol^{-1} s^{-1}.[13] This demonstrates the reliability of the IUPAC benchmark paper on k_p of MAA in aqueous solution as well as the adequacy of both SEC strategies towards PMAA analysis.

The PLP-prepared sample AA1 from polymerization of 10 wt% AA in aqueous solution at 2 °C was also analyzed by both aqueous-phase SEC (**Figure 4**) and THF-based SEC after esterification to PMA (**Figure 5**). Satisfactory agreement is seen between the results of aqueous-phase SEC analysis in the two laboratories. Both MMDs exhibit a PLP structure and allow for k_p determination via the first-derivative SEC curves. The k_p values resulting from analysis at PI SAS and PSS are 69 700 and 75 600 L mol^{-1} s^{-1}, respectively (Table 3). These numbers are close to those reported for k_p at identical PLP conditions and aqueous-phase SEC analysis, which are between 77 000 and 84 000 L mol^{-1} s^{-1}.[9] On the other hand, these k_p values are by approximately 25 % above the value (k_p = 54 600 L mol^{-1} s^{-1}) obtained from THF-based SEC analysis of PMA (Figure 5) produced by esterification of the PAA sample. This discrepancy reflects the mismatch observed between the results obtained from the two types of SEC analysis performed on high-molar-mass PAANa standards (see above) and in earlier studies.[30] It should be noted that the PLP conditions used for producing sample AA1 are within a “suitable” range, as is indicated by the occurrence of a PLP structure on the SEC.

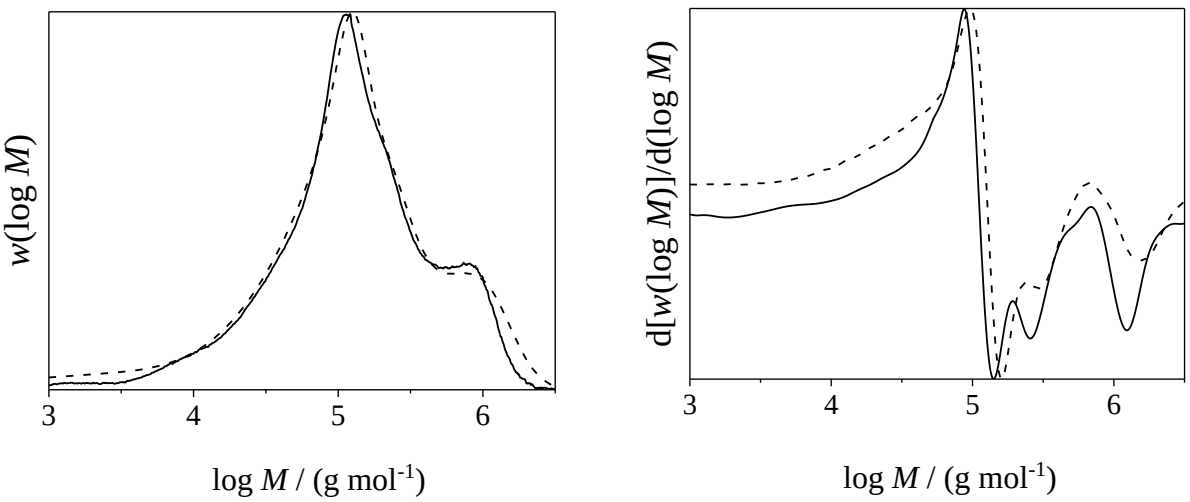

Figure 4. Molar mass distribution and associated first-derivative curves for the AA1 sample determined via aqueous-phase SEC at the PI SAS (solid) and PSS (dash) laboratories.

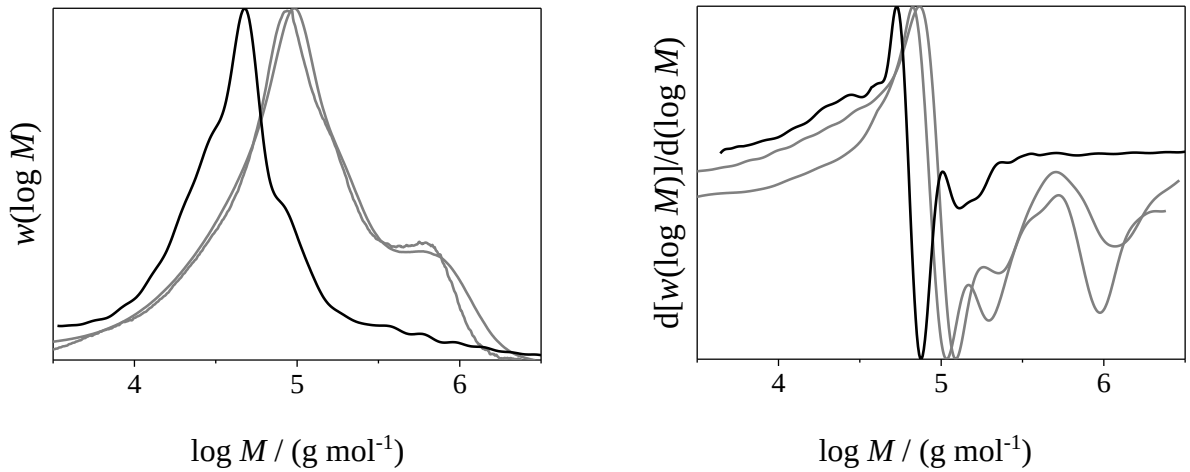

Figure 5. Molar mass distributions and associated first-derivative curves for sample AA1. Grey lines: aqueous-phase SEC from Figure 4. Black line: THF-based SEC after esterification. Molar mass values refer to acrylic acid repeat unit. The MMD of the PMA sample was evaluated via universal calibration using the MHS parameters from ref.[48]

Presented in Table 3 and in **Figure 6** are data of a second PLP sample, AA2, which has been prepared from an aqueous solution containing 20 wt% AA at 6 °C with a pulse-repetition rate of 500 Hz. The SEC traces obtained from both aqueous-phase and THF-based SECs are well resolved and exhibit three clean inflection points as evidenced by the clear maxima of the first-

derivative SEC curve. This is in line with the reduced branching density expected by increasing the pulse-repetition rate. Indeed, the characteristic time required for backbiting becomes larger than the time interval between two successive laser pulses, as reported for the PLP of *n*-butyl acrylate.[79] However, as observed for AA1 (Figure 1), the MMDs obtained by SEC-THF after methylation are again shifted towards lower molar masses in comparison to the MMDs obtained

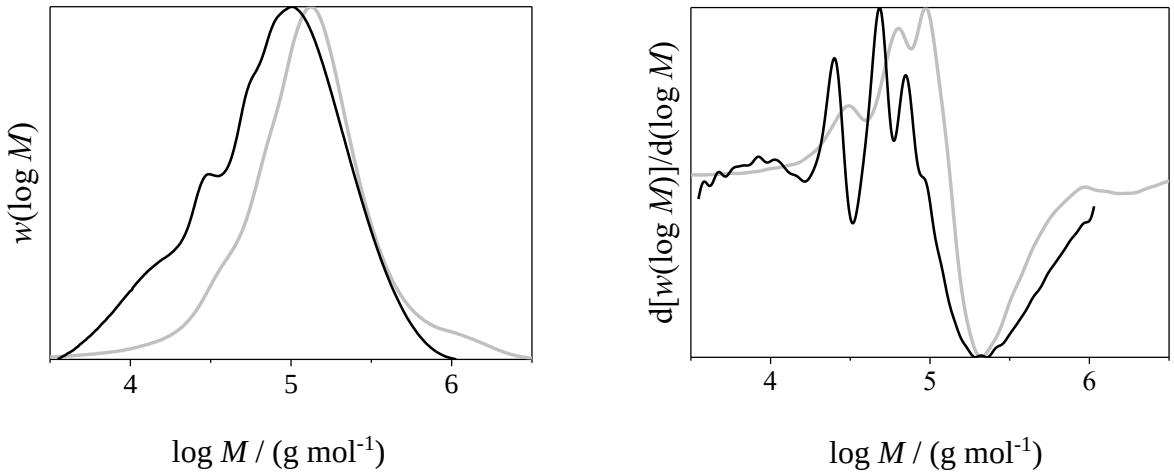

Figure 6. Molar mass distributions and associated first-derivative SEC curves for the AA2 sample; grey line: aqueous-phase SEC, black line: THF-based SEC after esterification. Molar mass values refer to acrylic acid repeat unit. The molar mass distribution of the PMA sample was determined via universal calibration with the MHS parameters taken from ref.[48]

by aqueous-phase SEC. The k_p value deduced from the primary point of inflection from aqueous-phase SEC is 80 000 ± 1000 L mol^{-1} s^{-1}. This value is approximately 15 % lower than the ones determined previously using a pulse-repetition rate of 100 Hz (91 200 and 95 900 L mol^{-1} s^{-1}),[30] which is considered as an acceptable difference. On the other hand, the k_p value obtained from the THF-based SEC after methylation of the AA2 sample is 64 100 ± 900 L mol^{-1} s^{-1}, i.e., is by about 20 % below the value determined from aqueous-phase SEC. This implies that branching is still occurring at these PLP conditions. The discrepancy between the values obtained from the two SEC modes for AA2 is somewhat weaker than for AA1 (prepared with 100 Hz pulsed-repetition rate), which indicates a lower level of branching for AA2. As foreseen during the

analysis of PAA standards (Figure 1), a higher discrepancy between aqueous-phase and THF-based SEC modes should be expected for PAA of higher molar mass. This is indeed reflected in the positions of the primary and secondary points of inflection for both AA1 and AA2 samples (Table 3). For AA1, the discrepancy between the positions of the points of inflection increases from ~25 % for the primary one to ~30 % for the secondary one, while for sample AA2, it increases from ~20 % to ~25 %.

The results reported above suggest that the MMD of PAA should be analyzed by direct aqueous-phase SEC and that polymer modification should therefore be avoided. It appears advisable to further check the reproducibility of PLP–aqueous-phase SEC measurement. A set of such experiments has been performed for 10 wt % AA at temperatures between 2 and 25 °C using a pulse repetition rate of 100 Hz. Only the PAA sample from PLP at 2 °C showed a characteristic PLP structure, from which k_p = 67 000 L mol^{-1} s^{-1} was obtained. This value is in close agreement with the one deduced from sample AA1 (Table 3), providing further support for using the PLP–aqueous-phase SEC strategy as the method of choice for reliable measurement of k_p for AA.

3.3. SEC characterization of RAFT-prepared PAA samples

The hypothesis of some degradation at branching points during methylation may be examined via PAA samples from RDRP. It is known that RDRP of acrylate monomers produces polymers with reduced branching density, as has been demonstrated for *n*-butyl acrylate polymerized by conventional and reversible-deactivation radical polymerizations.[80] It was recently demonstrated that the RAFT polymerization of AA at 65 °C yields highly linear polymers and that chain transfer to polymer is restricted with these samples.[19] Hence, the PAA samples obtained in this way should not exhibit major differences upon using the two different SEC

Table 4. SEC evaluation of AA-RAFT samples prepared at C2P2 using THF-based SEC after their methyl esterification (C2P2) to PMA and compared to direct aqueous-phase SEC analysis (multiplied entries are from repeated injections). $\overline{M}_n$ values are in 10^{-3} g mol^{-1} and are shown as experimentally obtained values from both modes of SEC and as values recalculated to AA repeat unit.

C2P2					PISAS		
conv. [%]	Time [min]	$\overline{M}_{n,exp}$ [a)] PMA	$\overline{M}_{n,exp}$ Recalculated to PAA	$Đ$	$\overline{M}_{n,exp}$ PAANa	$\overline{M}_{n,exp}$ PAA	$Đ$
45	50	65.7	56.3	1.06	76.5	58.6	1.08
					77.5	59.4	1.07
60	61	79.3	68.0	1.06	89.8	68.8	1.07
					89.6	68.6	1.07
71	97	99.3	85.1	1.09	106.2	81.3	1.06
					105.6	80.9	1.07
85	180	114.5	98.2	1.08	120.5	92.3	1.07
					120.9	92.6	1.07
94	420	125.6	107.7	1.12	131.1	100.4	1.11
					129.2	99.0	1.12

[a)] K = 1.95 x 10^{-4} dL g^{-1} and a = 0.660 from ref.[48]

procedures for high molar mass material. PAA samples have therefore been prepared at C2P2 and subsequently characterized by THF-based SEC at C2P2 and aqueous-phase SEC at PI SAS (**Table 4**). The $\overline{M}_n$ values for AA-RAFT samples at conversions from 45 to 94 % vary between 70 000 and 130 000 g mol^{-1} with respect to an AANa monomer unit. This molar mass range largely exceeds the value of ~ 20 000 g mol^{-1}, which is well above the limit where the discrepancy between both modes of SEC turned out to be significant for PAANa standards (Figure 1). Similarly, as shown by Ji et al.[19], the ^{13}C NMR analysis on AA-RAFT samples did not reveal the characteristic peak of quaternary carbon, which is indicative of acrylate branching (**Figure SI2**). The agreement between the $\overline{M}_n$ and dispersity values obtained using both aqueous-phase and THF-based SECs for AA-RAFT samples implies that the level of branching of PAA is responsible for discrepancies between these two modes of SEC seen with other PAA samples. This conclusion based on SEC analysis of PAA samples prepared by conventional

polymerization (the case of PAANa standards), by PLP, and by RAFT polymerizations suggests that either long-chain branching in PAA leads to incomplete SEC separation, or the methylation with diazomethane or trimethylsilyldiazomethane is accompanied by a side reaction, which leads to some scission of the polymer backbone by a mechanism which remains to be elucidated. It is beyond the scope of this contribution to resolve, which of the two effects that are both related to branching, plays the major role. The clear message is that aqueous-phase SEC should definitely be preferred for analysis of PAA samples.

4. Conclusions

The molar mass distribution of poly(methacrylic acid) may be reliably characterized by either aqueous-phase SEC or, after esterification to poly(methyl methacrylate), by THF-based SEC. Both methods may be applied in conjunction with pulsed-laser polymerization for k_p measurement. With poly(acrylic acid), however, significant differences may occur between molar masses deduced from aqueous-phase SEC and from THF-based analysis after methylation. These differences are assigned to transfer reactions in case of AA polymerization. The resulting branched structure appears either to suffer from incomplete SEC separation according to molar mass or to be vulnerable to side reactions which lower the degree of polymerization during methylation with diazomethane or trimethylsilyldiazomethane. Thus, methylation and THF-based analysis of poly(acrylic acid) samples disfavor k_p measurements, which require an accurate determination of absolute molar masses at characteristic points of inflection of the molar mass distribution. Aqueous-phase SEC is recommended as the method of choice for reliably measuring k_p of acrylic acid. Aqueous-phase SEC is also recommended for molar mass analysis of poly(acrylic acid) produced by conventional radical polymerization. THF-based analysis of methylated poly(acrylic acid) (at least employing (trimethylsilyl)diazomethane) should only be

used for PAA samples without significant branching, such as the ones prepared by reversible addition-fragmentation chain transfer polymerization in this study.

Acknowledgements

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Supporting Information

SEC Analysis of Poly(Acrylic Acid) and Poly(Methacrylic Acid)

Igor Lacík,* Marek Stach, Peter Kasák, Vladislav Semak, Lucia Uhelská, Anna Chovancová, Günter Reinhold, Peter Kilz, Guillaume Delaittre, Bernadette Charleux, Isabelle Chaduc, Franck D'Agosto, Muriel Lansalot, Marianne Gaborieau, Patrice Castignolles, Robert G. Gilbert, Zachary Szablan, Christopher Barner-Kowollik, Pascal Hesse, Michael Buback

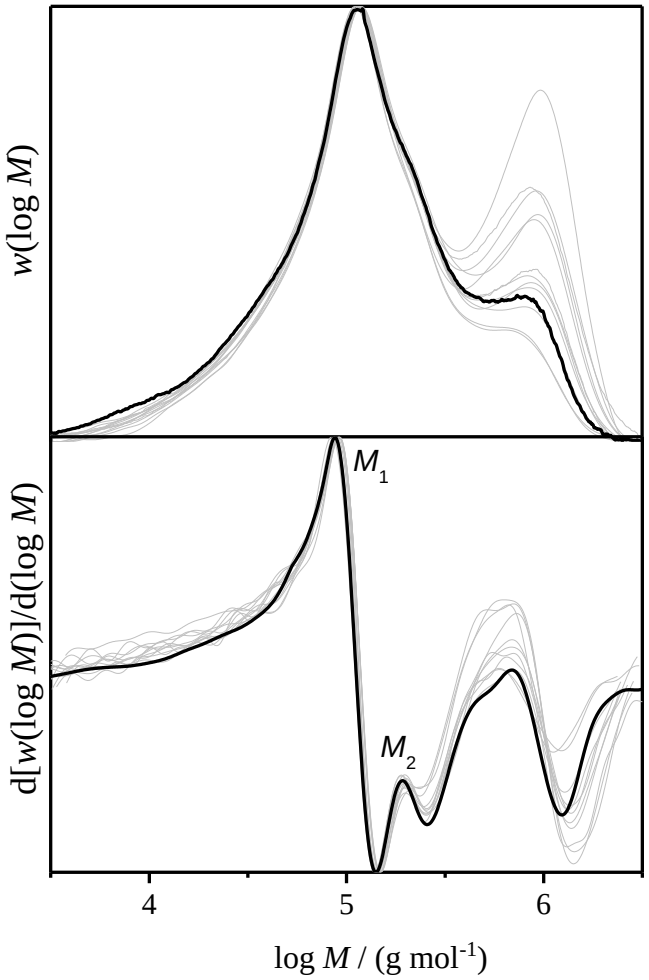


Figure SI1: Molar mass distributions and their associated first derivatives for AA1 sample. Individual 12 polymerizations (grey lines) and pooled sample (black line). Average positions of M_1 and M_2 are 89 700 ± 2 600 L mol^{-1} s^{-1} and 201 500 ± 9 700 L mol^{-1} s^{-1}.

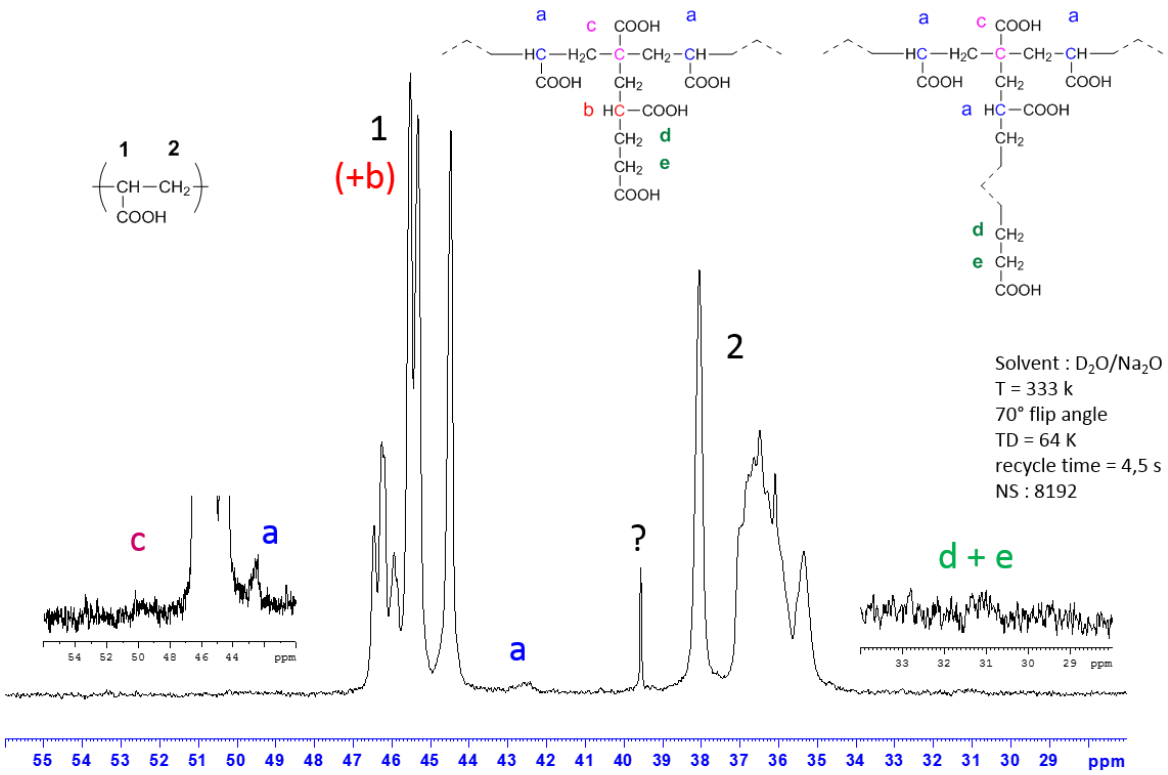


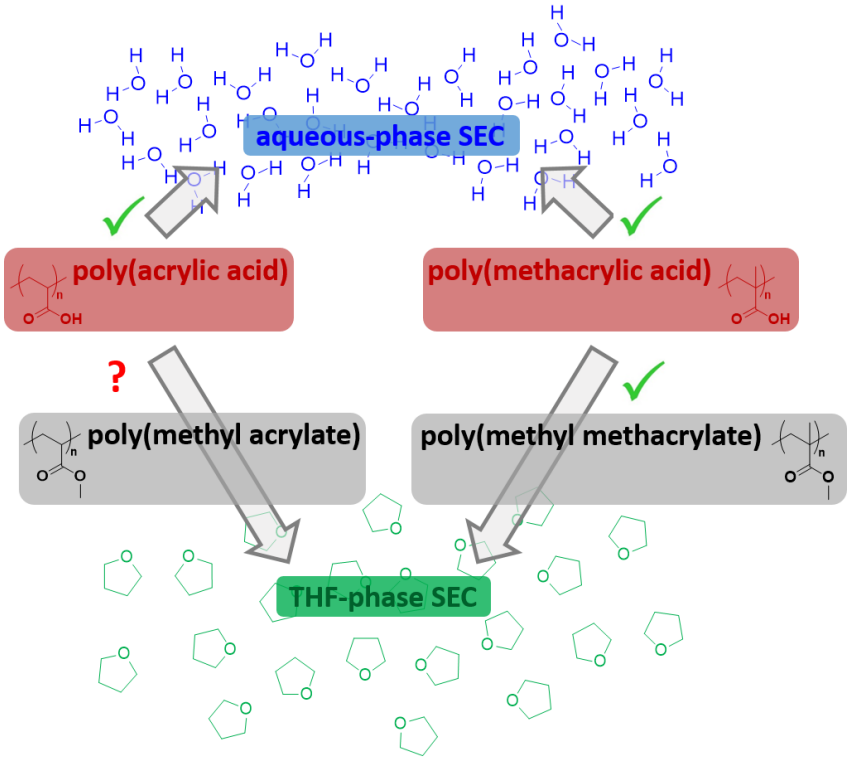
Figure SI2: ^{13}C NMR (100.6 MHz) spectrum of PAA-RAFT (C2P2, conv = 94%, $\overline{M_n}$ = 107.7 10^3 g mol^{-1}) in D_2O/Na_2O.

TOF file

SEC Analysis of Poly(Acrylic Acid) and Poly(Methacrylic Acid)

Igor Lacík,* Marek Stach, Peter Kasák, Vladislav Semak, Lucia Uhelská, Anna Chovancová, Günter Reinhold, Peter Kilz, Guillaume Delaittre, Bernadette Charleux, Isabelle Chaduc, Franck D'Agosto, Muriel Lansalot, Marianne Gaborieau, Patrice Castignolles, Robert G. Gilbert, Zachary Szablan, Christopher Barner-Kowollik, Pascal Hesse, Michael Buback

Molar mass distributions of poly(acrylic acid) and poly(methacrylic acid) were characterized by size-exclusion chromatography (SEC) employing both aqueous-phase SEC and THF-based SEC after methylation of parent samples. Both SEC methods are recommended for characterization of poly(methacrylic acid), while aqueous-phase SEC is recommended for characterization of poly(acrylic acid) unless it is devoid of branched structure.



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Supporting Information

SEC Analysis of Poly(Acrylic Acid) and Poly(Methacrylic Acid)

Igor Lacík,* Marek Stach, Peter Kasák, Vladislav Semak, Lucia Uhelská, Anna Chovancová, Günter Reinhold, Peter Kilz, Guillaume Delaittre, Bernadette Charleux, Isabelle Chaduc, Franck D'Agosto, Muriel Lansalot, Marianne Gaborieau, Patrice Castignolles, Robert G. Gilbert, Zachary Szablan, Christopher Barner-Kowollik, Pascal Hesse, Michael Buback

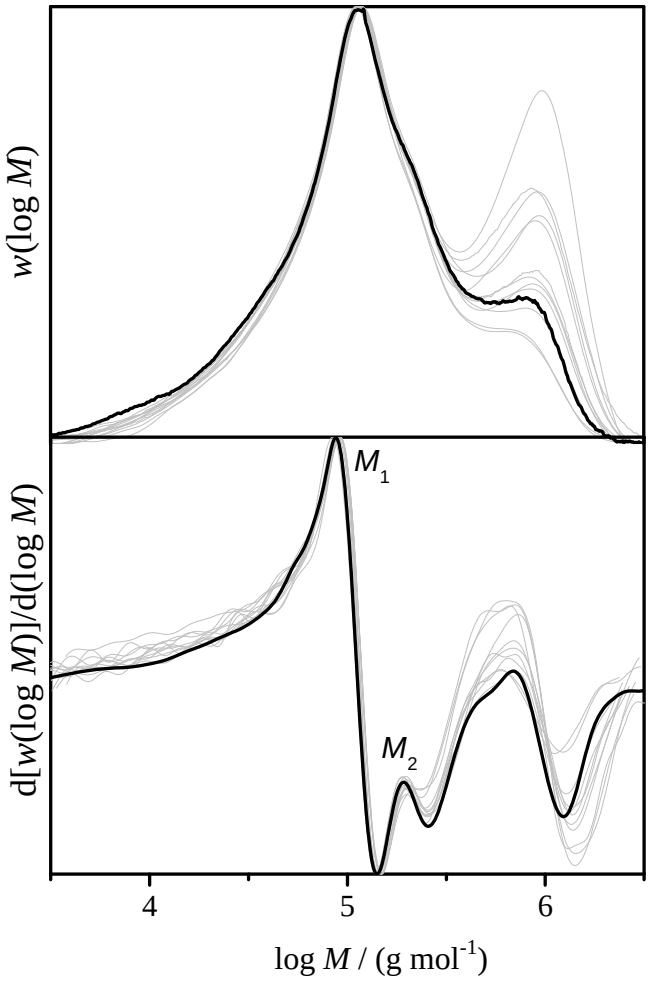

Figure SI1: Molar mass distributions and their associated first derivatives for AA1 sample. Individual 12 polymerizations (grey lines) and pooled sample (black line). Average positions of M_1 and M_2 are 89 700 ± 2 600 L mol^{-1} s^{-1} and 201 500 ± 9 700 L mol^{-1} s^{-1}.

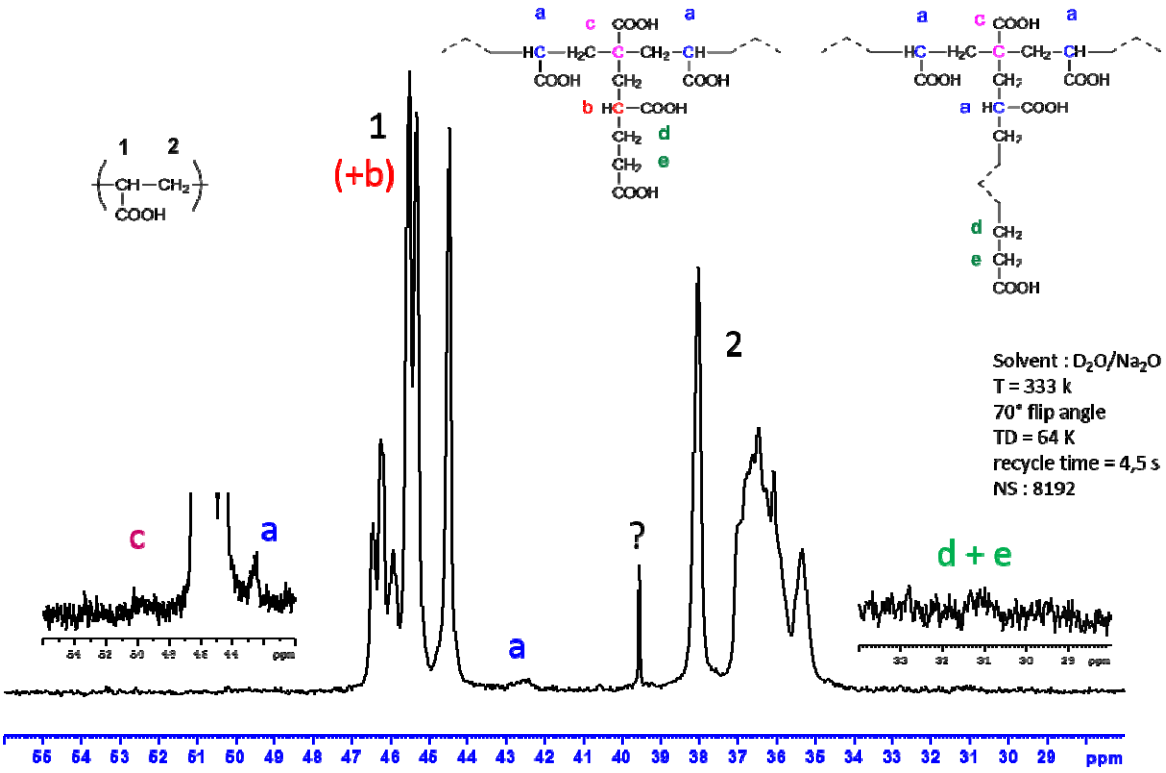

Figure SI2: ^{13}C NMR (100.6 MHz) spectrum of PAA-RAFT (C2P2, conv = 94%, $\overline{M_n}$ = 107.7 10^3 g mol^{-1}) in D_2O/Na_2O.