

# Dual hydrophilic polymers based on (meth)acrylic acid and poly(ethylene glycol) – synthesis and water uptake behavior†

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Synthesis and characterization of dual hydrophilic random and block copolymers of acrylic acid (AA) or methacrylic acid (MAA) with poly(ethylene glycol) (PEG) *via* different controlled radical polymerization techniques are discussed. Initially, reversible addition fragmentation chain transfer (RAFT) polymerization was employed to synthesize homo, random and block copolymers of AA and MAA in ethanol. The polymers were characterized in detail by means of size exclusion chromatography (SEC), <sup>1</sup>H NMR spectroscopy, matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry as well as MALDI-TOF MS coupled with collision induced dissociation (CID) to identify the end groups and the repeating units. Following that, atom transfer radical polymerization (ATRP) and RAFT polymerization were employed for the preparation of block copolymers using a PEG macroinitiator and a PEG macro chain transfer agent. Moreover, graft copolymers that contain oligo(ethyleneglycol) pendant groups and AA or MAA have been prepared using the RAFT polymerization process. Additionally, selected homo or block copolymers were tested for their water-uptake properties using a thermal gravimetric analyzer with a controlled humidity chamber. An advantageous behavior of the copolymers compared to the related homopolymers was reached with the obtained ability to absorb moisture over the complete humidity range as well as to a very high absolute water uptake.

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## Introduction

Water-soluble polymers with various architectures are of great interest in the field of polymer science due to their wide range of possible applications, *i.e.* in drug-delivery systems, dispersing agents and absorbent materials.<sup>1–4</sup> The most widely used structures to construct dual hydrophilic polymers are based on acrylic acid (AA), methacrylic acid (MAA) and poly(ethylene glycol) (PEG). AA and MAA can be polymerized by controlled radical polymerization techniques whereas PEG can be obtained by ionic polymerization.<sup>5–7</sup> Various polymeric architectures can be constructed using these monomers or polymers. However, the synthesis and characterization of well-defined water soluble polymers requires not only dedicated reaction conditions and catalysts but also suitable analytical instruments to precisely assign their structures.

There are two main approaches which are possible for obtaining polymers of desired architectures. The first possibility is the reaction of end group or side group functionalized polymers with the second block or functional side group to form

block or graft copolymers, respectively. The reactions which are nowadays employed in this route are mainly found among the so called “click” reactions.<sup>8–10</sup> The other possibility is the construction of the desired compositions and architectures directly by the polymerization process itself. Therefore, macroinitiators, macromonomers or macro chain transfer agents (macro-CTA) have to be prepared according to the targeted polymeric structures.<sup>11</sup> In the present study, the latter approach was applied to obtain linear as well as graft block and random copolymers.

Controlled radical polymerization (CRP) techniques provide enormous possibilities for synthesizing well-defined polymers with controlled architectures and molar masses. For instance, reversible addition fragmentation chain transfer (RAFT) polymerization allows the use of acidic monomers and also the use of polar solvents like ethanol. Therefore, this technique is the most widely employed method to prepare water soluble polymers.<sup>12</sup> However, the CTA has to be carefully selected depending on the nature of the monomer.<sup>13–15</sup>

Alternatively, transition metal-catalyzed controlled radical polymerization techniques provide good control over the polymerization of several monomers.<sup>16</sup> Unfortunately, these techniques, namely atom transfer radical polymerization (ATRP) and single electron transfer controlled radical polymerization (SET-LRP), are based on the oxidation reduction equilibrium of the transition metal and ligand complex which can be disturbed in the presence of acidic monomers.<sup>17–19</sup> As a consequence, protected monomers have to be used during the polymerization.

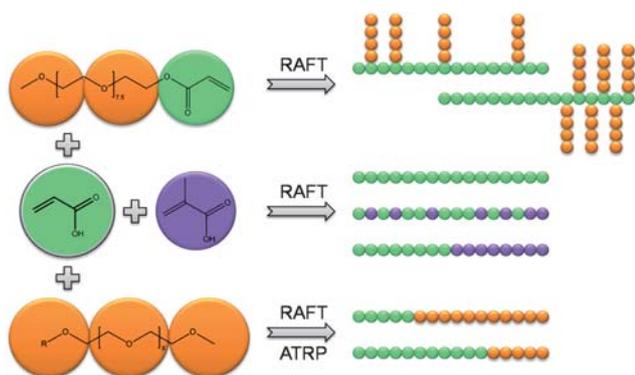
While actual studies are, for example, investigating the morphology of dual hydrophilic copolymers, *e.g.* P(AA-*co*-EG)

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**Scheme 1** A schematic representation of the monomers used and the block and random copolymer architectures obtained by different synthetic approaches.

nanofibers, like recently reported by Charleux *et al.*,<sup>20</sup> the present contribution focuses on structural investigation and the study of the water uptake behavior.

Water uptake properties of polymers are relatively rarely investigated, but represent a very important polymer characteristic and play a crucial role in several applications of polymers such as personal care products,<sup>21–23</sup> coatings, composite materials, cement,<sup>24</sup> membranes and sensors,<sup>25</sup> agriculture products,<sup>26–30</sup> biomedical materials,<sup>31–33</sup> insulation of underwater cables<sup>34</sup> or recreational activities (*e.g.* artificial snow). Researchers have focused on the modification and optimization of polymers in terms of water absorbency, absorption–desorption rates and gel strength (in cross-linked systems).<sup>35</sup> Moisture uptake can be measured directly from water or from a humid atmosphere. However, most of the reported research has focused on the investigation of cross-linked polymer systems (super absorbent polymers) in direct contact with water. Other measurements require the use of conditioned desiccators and several days to weeks of measurement time until the samples are saturated with water molecules. Alternatively, water uptake properties of polymeric materials can be measured by a thermal gravimetric analyzer with a controlled humidity chamber. This technique requires a very small amount of sample (a few milligrams) and the measurement can be performed in any form, such as in powder, liquid or crosslinked gel.

Different strategies to synthesize dual hydrophilic polymers in various architectures were studied, as illustrated in Scheme 1. Homopolymers, block and random copolymers of AA and MAA have been prepared using RAFT polymerization. Moreover, graft copolymers were prepared using oligo(ethylene glycol) acrylate (OEGA) and AA or MAA. Furthermore, macroinitiator and macro chain transfer agents were synthesized in order to use those in the block copolymerization. ATRP and RAFT polymerization were employed to synthesize PEG-*b*-AA and PEG-*b*-MAA block copolymers. Finally, these polymers are tested for their water uptake properties.

## Experimental section

### Materials

Poly(ethylene glycol) monomethyl ether (mPEG<sub>1k</sub>: CH<sub>3</sub>-PEG<sub>22</sub>-OH,  $M_n = 1000 \text{ g mol}^{-1}$ , PDI = 1.07 and mPEG<sub>2k</sub>: CH<sub>3</sub>-PEG<sub>44</sub>-

OH,  $M_n = 2000 \text{ g mol}^{-1}$ , PDI = 1.08) were purchased from Sigma-Aldrich. The monomers acrylic acid (AA), methacrylic acid (MAA), *tert*-butyl acrylate (*t*BuA) and oligo(ethylene glycol) acrylate ( $M_n = 480 \text{ g mol}^{-1}$ ) (OEGA<sub>480</sub>) were purchased from Sigma-Aldrich and passed through a column with inhibitor remover by Sigma-Aldrich before using. CuBr, *N,N',N'',N''',N''''*-pentamethyl diethylene triamine (PMDETA) and ethyl 2-bromo-isobutyrate (EtBriB) were purchased from Sigma-Aldrich and used as received without further purification. 2-(Butylthiocarbonothioylthio) propanoic acid (BPTC) and 2-cyano-2-butylidithiobenzoate (CBDB) were synthesized according to the literature and used without further purification.<sup>36,37</sup> Azobis(isobutyronitrile) (AIBN) was received from Sigma-Aldrich and recrystallized from methanol before using. Other solvents and reagents were used as received without further purification.

### Instrumentation

<sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> on a Bruker AC 300 MHz using the residual solvent resonance as an internal standard. Size exclusion chromatography (SEC) was performed on a Shimadzu system equipped with a SCL-10A system controller, a LC-10AD pump, a RID-10A refractive index detector and both a PSS Gram30 and a PSS Gram1000 column in series, whereby *N,N*-dimethylacetamide (DMAc) with 5 mmol lithium chloride (LiCl) was used as an eluent at 1 mL min<sup>-1</sup> flow rate and the column oven was set to 60 °C. The system was calibrated with polystyrene (370 g mol<sup>-1</sup>–67 500 g mol<sup>-1</sup>) and poly(methyl methacrylate) (2000 g mol<sup>-1</sup>–88 000 g mol<sup>-1</sup>) standards, respectively. For the measurement of the matrix assisted laser desorption/ionization (MALDI) spectra an Ultraflex III TOF/TOF (Bruker Daltonics, Bremen, Germany) instrument was used. The instrument was equipped with a Nd:YAG laser and a collision cell. All spectra were measured in the positive reflector or linear mode. The instrument was calibrated prior to each measurement with an external PMMA standard from PSS Polymer Standards Services GmbH (Mainz, Germany). Monomer conversions were determined by gas chromatography (GC) using anisole as internal standard. The number-average molar mass ( $M_n$ ) and the polydispersity index (PDI) were determined by size-exclusion chromatography (SEC) using chloroform or *N,N*-dimethyl acetamide (DMAc) as solvents depending on the solubility behavior of the samples. The water-uptake measurements of the polymers were investigated on a Q5000 SA thermogravimetric analyzer from TA Instruments containing a microbalance in which the sample and reference pans were enclosed in a humidity and temperature controlled chamber. The temperature in the Q5000 SA was controlled by Peltier elements. Dried N<sub>2</sub> gas flow (200 mL min<sup>-1</sup>) was split into two parts, of which one part was wetted by passing it through a water-saturated chamber. The desired relative humidity (RH) for the measurements could subsequently be obtained by mixing proper proportions (regulated by mass-flow controllers) of dry and wet stream.

### Synthesis

**Homopolymerization of AA and MAA via RAFT.** AA and MAA were homopolymerized separately by RAFT

polymerization. The general procedure was introduced as follows. A mixture 288 mg AA or 344 mg MAA (4 mmol) with 6.6 mg AIBN (0.04 mmol) and 38 mg CTA (0.16 mmol BPTC for PAA or 0.16 mmol CBDB for PMAA) was dissolved in 1.5 mL absolute ethanol and 0.2 mL anisole in a capped vial leading to a final monomer concentration of 2 mol L<sup>-1</sup>. The reaction mixture was bubbled with argon for half an hour and the  $t_0$ -sample was withdrawn for the subsequent GC measurements. The reaction solution was placed in a preheated oil bath at 70 °C. After the desired period of time the mixture was cooled to ambient temperature and a  $t_{\text{end}}$ -sample for GC was taken. The solution was diluted by adding 2 mL ethanol and precipitated into 75 mL ethyl acetate. The solid polymer obtained was dried, washed with diethyl ether and dried again until the mass of the polymer was constant.

**Block copolymerization of MAA and AA via RAFT.** The PMAA homopolymer was synthesized by RAFT polymerization as described above. To 0.288 mg AA (4 mmol) the prepared PMAA macro-CTA was added to such an extent that the desired monomer/CTA ratio was reached. Furthermore, 0.25 eq. AIBN relative to the PMAA macro-CTA (1 eq.) were added, and the whole mixture was diluted in 3.3 mL ethanol and 0.4 mL anisole leading to a final AA concentration of 1 mol L<sup>-1</sup>. The reaction mixture was bubbled with argon for half an hour, and the  $t_0$ -sample was withdrawn for the subsequent GC measurements. The reaction solution was placed in a preheated oil bath at 70 °C. After the desired period of time, the mixture was cooled to ambient temperature and a  $t_{\text{end}}$ -sample for GC was taken. The solution was precipitated into 75 mL ethyl acetate. The solid polymer obtained was dried, washed with diethyl ether and dried again until the mass of the polymer was constant.

**Random copolymerization of MAA and AA via RAFT.** The P(MAA-*r*-AA) random copolymers were prepared by RAFT polymerization according to the general procedure as follows. AA and MAA were mixed in a desired ratio leading to a final total amount of monomer of 4 mmol. With 3.3 mg AIBN (0.02 mmol) and 16 mg CBDB (0.08 mmol), the monomers were dissolved in 1.5 mL absolute ethanol and 0.2 mL anisole in a capped vial leading to a final total monomer concentration of 2 mol L<sup>-1</sup>. The reaction mixture was bubbled with argon for half an hour and the  $t_0$ -sample was withdrawn for the subsequent GC measurements. The reaction solution was placed in a preheated oil bath at 70 °C. After the desired period of time, the mixture was cooled to ambient temperature, and a  $t_{\text{end}}$ -sample for GC was taken. The solution was diluted by adding 2 mL ethanol and precipitated into 75 mL ethyl acetate. The solid polymer obtained was dried, washed with diethyl ether and dried again until the mass of the polymer was constant.

**Homopolymerization of OEGA<sub>480</sub> via RAFT.** OEGA was polymerized by RAFT polymerization. A mixture of 480 mg OEGA<sub>480</sub> (1 mmol), 29.8 mg BPTC (0.125 mmol) and 2 mg AIBN (0.013 mmol) were dissolved in 2 mL absolute ethanol in a capped vial leading to a final monomer concentration of 0.5 mol L<sup>-1</sup>. The reaction mixture was bubbled with argon for half an hour and the  $t_0$ -sample was withdrawn for the subsequent SEC measurements. The reaction solution was placed in

a preheated oil bath at 70 °C. After 5 h, the mixture was cooled to ambient temperature and a  $t_{\text{end}}$ -sample for GPC was taken. The solution was precipitated into cold diethyl ether.

**Random copolymerization of AA and OEGA<sub>480</sub> via RAFT.** A mixture of AA (35 or 70 eq.), OEGA<sub>480</sub> (5 eq.), BPTC (1 eq.) and AIBN (0.25 eq.) was dissolved in absolute ethanol with a total monomer concentration of 4 mol L<sup>-1</sup>. The reaction solution was purged with argon for 60 min and placed in a preheated oil bath (70 °C). After 6 h the reaction was stopped and the solution was precipitated into cold ethyl acetate. The final polymer was obtained after washing with cold diethyl ether to remove ethyl acetate residues. It was dried until the mass of the polymer was constant. The determination of the conversion were done by GC using anisole as internal standard.

**Block copolymerization of AA and OEGA<sub>480</sub> via RAFT.** These block copolymers were prepared in a sequential monomer addition process using the RAFT method, whereby AA was polymerized at first resulting in a macro chain transfer agent. To a mixture of BPTC (1 eq.) and AIBN (0.25 eq.) AA (35 or 70 eq.) was added and the mixture was dissolved in absolute ethanol in a capped vial with a total monomer concentration of 3.5 mol L<sup>-1</sup>. The reaction solution was purged with argon for 60 min and placed in a preheated oil bath (70 °C). After 5 h OEGA<sub>480</sub> ([OEGA<sub>480</sub>]<sub>0</sub> = 0.5 mol L<sup>-1</sup>) was added *via* a syringe to this capped vial (OEGA<sub>480</sub> : PAA : AIBN = 5 : 1 : 0.25) and the solution was further heated for 6 h. The polymer was isolated by precipitation into cold ethyl acetate and washed with diethyl ether to remove the residual monomer and solvent. The polymer was dried until the mass of the sample was constant.

**Synthesis of PEG macroinitiator for ATRP (PEG-EBr<sub>i</sub>B).** 2-Bromo-2-methyl-propionate end-functionalized mPEG<sub>1k</sub> was synthesized by reacting 2-bromo-2-methyl-propionyl bromide and mPEG<sub>1k</sub> in the presence of triethylamine at room temperature in dry THF.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 4.31 (*m*, CH<sub>2</sub>-OCO), 3.63 (*m*, O-CH<sub>2</sub>), 3.36 (*m*, CH<sub>3</sub>-O), 1.92 (*s*, (CH<sub>3</sub>)<sub>2</sub>CBr) ppm.

**Synthesis of PEG macro chain transfer agent for RAFT (PEG-BPTC).** mPEG<sub>2k</sub> end-functionalized with BPTC was synthesized by reacting 2-(butylthiocarbonothioylthio) propanoyl benzotriazolid and mPEG<sub>2k</sub> in the presence of triethylamine in dry THF.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 4.73 (CH-SCS<sub>2</sub>), 4.20 (CH<sub>2</sub>-OCO), 3.55 (CH<sub>2</sub>-O), 3.28 (CH<sub>3</sub>-O), 3.26 (CH<sub>2</sub>-SCS<sub>2</sub>), 1.59 (CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.50 (CH<sub>3</sub>-CH), 1.33 (CH<sub>2</sub>-CH<sub>3</sub>), 0.84 (CH<sub>2</sub>-CH<sub>3</sub>) ppm.

**Synthesis of PEG-*b*-AA via ATRP.** Poly(ethylene glycol-*block-tert*-butyl acrylate) (P(EG-*b*-tBA)) was synthesized by ATRP. 0.058 mL PMDETA (48 mg, 0.28 mmol) and 40 mg CuBr (0.28 mmol) were dissolved in 2.5 mL anisole and flushed with argon. After the formation of the complex 200 mg (0.2 mmol) PEG<sub>1k</sub>-EBr<sub>i</sub>B ( $M_n$  = 1040 g mol<sup>-1</sup> according to MALDI-TOF MS) and 1.45 mL *t*BuA (1.28 g, 10 mmol) were added. The reaction mixture was further degassed with argon, and a  $t_0$ -sample for GC was taken *via* syringe. The closed vial was placed in

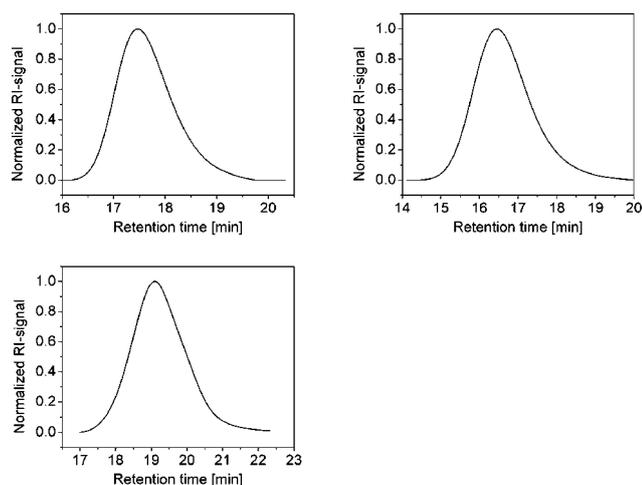
a preheated oil bath at 90 °C and reacted for 4 h. Afterwards, a  $t_{\text{end}}$ -sample for GC was withdrawn and the mixture was passed over a short  $\text{Al}_2\text{O}_3$  column to remove the copper catalyst and precipitated into a methanol–water mixture. The dried polymer was stirred with 5 equivalence of trifluoroacetic acid relative to the *tert*-butyl functionalities for 24 h to cleave the *tert*-butyl groups that will finally yield P(EG-*b*-AA).

**Synthesis of P(EG-*b*-AA) via RAFT.** Poly(ethylene glycol-*block*-acrylic acid) (P(EG-*b*-AA)) was synthesized by RAFT polymerization. In a capped vial, a mixture of 200 mg PEG<sub>2k</sub>-CTA (0.1 mmol) ( $M_n = 2000 \text{ g mol}^{-1}$  according to MALDI-TOF MS), 343  $\mu\text{L}$  AA (360 mg, 5 mmol) and 3.3 mg AIBN (0.02 mmol) was dissolved in 0.250 mL anisole and 1.9 mL ethanol. After flushing the solution with argon for 30 min, a  $t_0$ -sample for GC was taken and the mixture was placed in a preheated oil bath at 70 °C and reacted for 5 h. The reaction solution was cooled to ambient temperature, and a  $t_{\text{end}}$ -sample for GC was withdrawn. Subsequently, 2.5 mL ethanol were added and the solution was precipitated into cold diethyl ether.

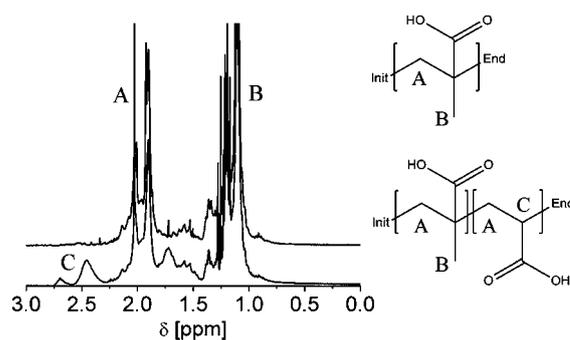
## Results and discussion

The synthesis of polymers based on AA or MAA *via* CRP techniques can be challenging due to the acidic nature, as described previously. Therefore, the RAFT polymerization was preferred over ATRP to obtain the desired polymers. However, a dedicated CTA is necessary to successfully polymerize both acrylic and also methacrylic monomers. CBDB is an adequate CTA to reach control in the present case and allowed the preparation of the desired random and block copolymers of AA and MAA. The obtained SEC results of homopolymers, random- and block copolymers of AA and MAA are shown in Fig. 1.

The relatively similar structures of AA and MAA raise the question about the possibilities to determine the compositions of the obtained polymers. An indirect approach is the calculation of molar mass and polymer composition in correlation to the monomer conversion during the polymerization which can be determined by GC. On the other hand,  $^1\text{H}$  NMR spectroscopy



**Fig. 1** SEC traces of PAA (top left), P(MAA-*r*-AA) (top right) and P(MAA-*b*-AA) (bottom left).



**Fig. 2**  $^1\text{H}$  NMR spectra (300 MHz,  $\text{CDCl}_3$ ) of P(MAA) (top) and P(MAA-*co*-AA) (bottom) with the corresponding schematic representation of the polymer structures.

allows to distinguish between both compounds in the final polymer; thereby a selective and quantitative analysis of the real polymer composition can be performed (Fig. 2).

The conversion of the monomers were calculated using both GC and  $^1\text{H}$  NMR spectroscopy. This allows the direct calculation of the polymer composition. The comparison of the obtained values using both approaches shows a rather good agreement in most cases. It has to be considered that possible solvent residues, in particular those with alkyl functionalities, can lead to an overestimation of the MAA content using the  $^1\text{H}$  NMR technique.

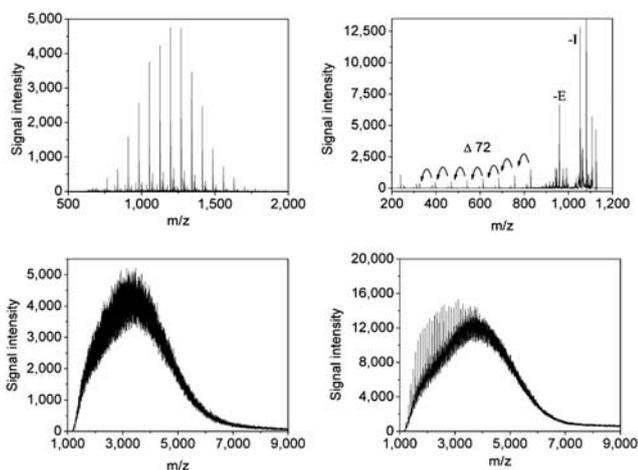
The versatility of the RAFT technique allowed the synthesis of various polymers with different compositions. A comparison of the prepared polymers including their characteristic data obtained by several analytical techniques, *i.e.* GC, SEC, and  $^1\text{H}$  NMR spectroscopy, is provided in Table 1.

SEC is a widely used technique in polymer analysis. The obvious discrepancy between the theoretical molar masses and the experimental values in the current case is caused by the significantly larger hydrodynamic volume of the polymers prepared in comparison to the polymer standards used for the calibration of the SEC (PS calibration). A route to circumvent this problem is the use of a direct molar mass determination technique, *i.e.* MALDI-TOF mass spectrometry. Since the exact determination of polymeric structures is one of the most important goals in polymer research, this technique represents a very powerful tool. The combination of a mass spectrometric analysis of a polymer, providing a molar mass distribution, with the subsequent fragmentation of single and distinct macromolecules offers a great possibility to analyze polymers down to their precise structure and composition. The prerequisite for such a tandem mass spectrometric analysis is the selective admittance of already desorbed and ionized molecules into a gas filled collision cell. Further fragmentation occurs inside, which is kinetically induced by the collision gas (argon or nitrogen). Fig. 3 shows the analysis of the selected polymers by MALDI-TOF MS and tandem-MS technique. However, besides the stated advantages, one should be aware of potential disadvantages of the MALDI-TOF MS technique. Due to its rather harsh ionization method, fragmentations can occur during the measurement process itself leading to fragments not representing the real polymer structure. Furthermore, possible ionization biases can make an accurate molar mass determination difficult. MS

**Table 1** Representative data of homopolymers (H), random (R) and block (B) copolymers of AA and MAA synthesized *via* RAFT polymerization

Run	MAA (feed)	AA (feed)	MAA <sup>a</sup> (conv.)	AA <sup>a</sup> (conv.)	$M_{n,theo}^b$ /g mol <sup>-1</sup>	$M_{n,SEC}^c$ /g mol <sup>-1</sup>	PDI <sup>c</sup>	MAA : AA (GC)	MAA : AA <sup>d</sup> ( <sup>1</sup> H NMR)
H1	—	30	—	0.84	2053	4300	1.19	0 : 1	0 : 1
H2	25	—	0.54	—	1396	3600	1.31	1 : 0	1 : 0
R <sub>1</sub>	20	48	0.96	0.60	3960	7900	1.26	0.39 : 0.61	0.40 : 0.60
R <sub>2</sub>	25	25	0.87	0.55	3099	6400	1.25	0.61 : 0.39	0.60 : 0.40
R <sub>3</sub>	11	67	0.88	0.43	3146	6900	1.21	0.26 : 0.74	0.33 : 0.67
B <sub>1</sub>	18	35	0.99	0.50	3027	6000	1.34	0.50 : 0.50	0.71 : 0.29
B <sub>2</sub>	20	25	0.95	0.45	2679	4300	1.39	0.63 : 0.37	0.67 : 0.33
B <sub>3</sub>	20	60	0.96	0.3	3182	7300	1.28	0.53 : 0.47	0.55 : 0.44

<sup>a</sup> Conversion values were determined by GC. <sup>b</sup> Calculated according to formula ( $M_n(theo.) = ([M]/[CTA]) \times conv. \times M_{Monomer} + M_{CTA}$ ). <sup>c</sup> Calculated according to PS standards. <sup>d</sup> The ratios were calculated from the corresponding peaks shown in Fig. 2.



**Fig. 3** Representative MALDI-TOF mass spectra of PAA (H1) (top left), P(MAA-*r*-AA) (R3) (bottom left) and P(MAA-*b*-AA) (B3) (bottom right). Tandem MS spectrum of PAA (top right).

techniques applying softer ionization methods, *e.g.* electron spray ionization (ESI), can add further insights.<sup>38</sup>

The MALDI-TOF mass spectrum of the homopolymer allows the assignment of molecular structures corresponding to the obtained distributions. The distance between the signals of each distribution corresponds to the molar mass of the monomer unit. The main distribution represents the expected structure plus the charge carrying sodium ion. The three minor signal distributions are probably caused by fragmentations during the MALDI measurement itself. One of these fractions can for example be assigned to the expected structure after the loss of the *n*-butyl substituent from the end-group.

Furthermore, tandem mass spectrometry is possible providing an even deeper insight into the polymeric structure. The major signals in the high molar mass region can be assigned to the desired structure after losing H<sub>2</sub>O (−18) and CO<sub>2</sub> (−44) due to anhydrite formation, decarboxylation reactions and combinations of both.<sup>39</sup> The two important signals marked as −I and −E represent the polymer after loss of the initiator group (−I) or the chain transfer agent end group (−E). The Δ72 distribution in the middle mass region represents the different chain lengths, which can be formed by fragmentation of different amounts of repeating units of AA.

The clear structure of the homopolymer mass spectra is lost in the case of the random and block copolymers. The large amount of possible monomer combinations and, thereby, the wide range of resulting molar masses leads to complex spectra. Single signal assignments are no longer possible.

The resulting  $M_n$  values correspond to the expected molar masses calculated from the monomer. In case of the block copolymer, residual homopolymer of the unconverted first block is visible on the low molar mass shoulder of the distribution. However, it is not possible to draw any quantitative conclusions concerning the amount of remaining homopolymer from the MALDI-TOF mass spectra.

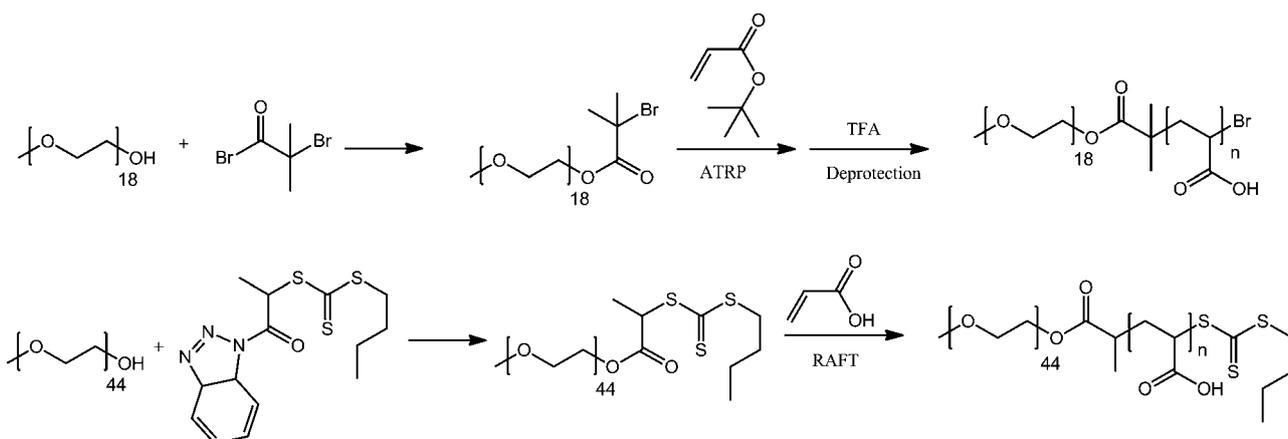
Dual hydrophilic block copolymers composed of EG and AA are a versatile polymer class suitable for many applications, *e.g.* to control structure and size of mineral particles.<sup>40</sup> The synthetic approach mainly utilized towards these polymers up to now is the synthesis of a macro-initiator suitable for ATRP by an esterification reaction. Subsequently a protected acrylic monomer, *e.g.* *t*-butyl acrylate (*t*-BuA), is polymerized onto this macroinitiator, providing the desired poly(EG-*b*-AA) after a deprotection step.

A second possibility, with the advantage of avoiding the deprotection step, is the synthesis of a macro chain transfer agent applicable for a RAFT polymerization of acrylic acid. A visualization of both synthetic approaches is provided in Scheme 2. In the present study, both methods were applied to obtain P(EO-*b*-AA) block copolymers. In Table 2, the characteristic data for all polymers prepared using both approaches are summarized.

The macroinitiator synthesis as well as the polymerization and deprotection steps could be followed *via* MALDI-TOF mass spectrometry. The resulting spectra including the assigned structures are provided exemplarily for the ATRP approach in Fig. 4.

The main distribution could be assigned to the desired product plus a sodium ion. Also the second largest distribution represents an acceptable product with the only difference being a hydroxyl end-group at the second chain-end of the macroinitiator. Only a very small educt specific distribution is observed. An overlay of the MALDI-TOF mass spectra of the macroinitiator and its block copolymer with *t*BuA before and AA after deprotection illustrates the controlled synthesis of the block copolymer as well as its subsequent deprotection.

The approach *via* the RAFT-polymerization enabled the synthesis of comparably well-defined polymers. The

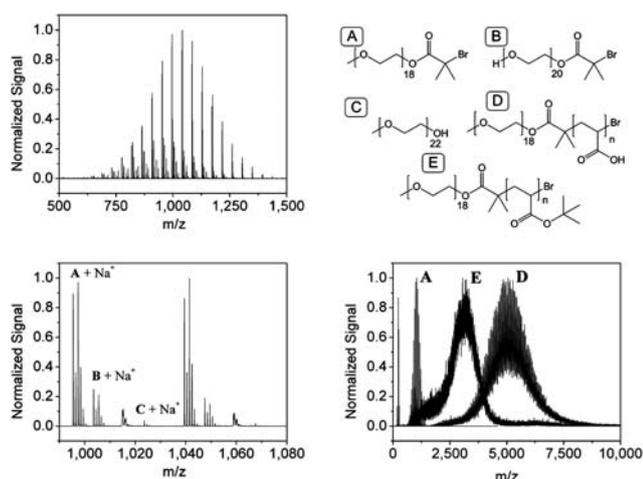


**Scheme 2** A schematic representation of the ATRP macroinitiator approach (top) and the RAFT macro chain transfer agent approach (bottom) towards P(EG-*b*-AA) block copolymers.

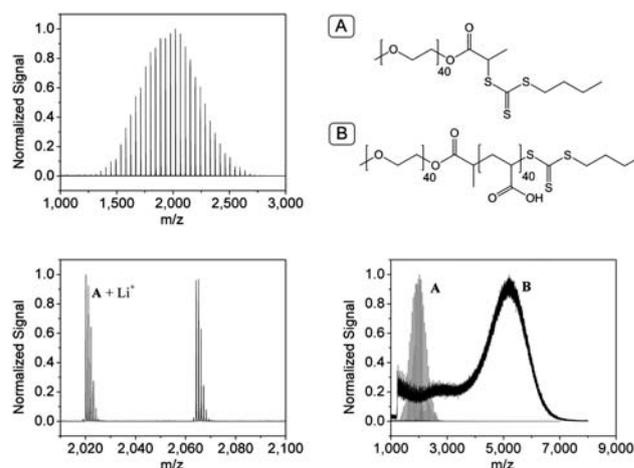
**Table 2** Characteristic data of the polymers which were included in the synthesis of P(EG-*b*-AA) via the ATRP or the RAFT route, respectively

Type	$M_n^a$ /g mol <sup>-1</sup>	PDI <sup>a</sup>	$M_p^b$ /g mol <sup>-1</sup>	$M_n^c$ /g mol <sup>-1</sup>	Comp. <sup>d</sup> EG : A.
mPEG <sub>1k</sub>	1700	1.06	1000	—	—
mPEG-Br	2100	1.07	1040	—	1 : 0
P(EG- <i>b</i> - <i>t</i> BuA)	4100	1.09	5050	5250	0.32 : 0.68
P(EG- <i>b</i> -AA)	8500	1.22	3100	3390	0.33 : 0.67
mPEG <sub>2k</sub>	—	—	—	1950	1 : 0
mPEG-CTA	2900	1.08	2000	2130	1 : 0
P(EG- <i>b</i> -AA)	12 000	1.27	5300	5480	0.49 : 0.51

<sup>a</sup> Determined by SEC analysis according to PS standards. <sup>b</sup> Determined by MALDI-TOF/MS analysis. <sup>c</sup> Determined by <sup>1</sup>H NMR measurements. <sup>d</sup> The ratios were calculated from the corresponding peaks.



**Fig. 4** MALDI-TOF mass spectrum of the PEG macroinitiator (top left), its magnification (bottom left) and an overlay of the MALDI-TOF mass spectra of macro-initiator, P(EG-*b*-*t*BuA) and P(EG-*b*-AA) (bottom right) with a schematic representation of the assigned structures (top right).

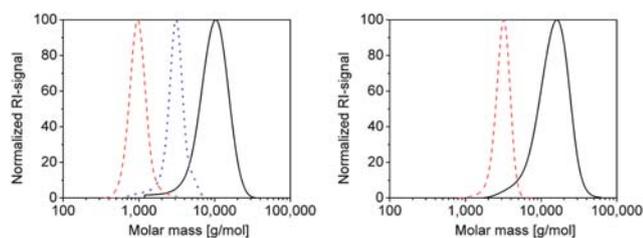


**Fig. 5** MALDI-TOF mass spectrum of the mPEG macro-CTA (top left), magnification of the main distribution (bottom left) and an overlay of the MALDI-TOF mass spectra of the macro chain transfer agent and the prepared P(EG-*b*-AA) (bottom right) with a schematic representation of the assigned structures (top right).

MALDI-TOF mass spectra are provided in Fig. 5. The starting material and product resulted in the same molar mass and are thereby not distinguishable by MALDI-TOF/MS. Nevertheless, the desired structure could be proven by tandem MS analysis leading to a MS spectrum of the product which is different to mPEG-OH.

The SEC analysis revealed once more the difference in hydrodynamic volume between polymers containing acrylic acid and the usual standard polymers used to calibrate the SEC. Fig. 6 visualizes the SEC results obtained for the P(EG-*b*-AA) polymers in comparison to their precursors prepared by the ATRP and the RAFT approach. To obtain comparable results PS-calibrations were used to calculate molar masses and PDI values. Nevertheless nearly quantitative conversions between different states of the block copolymer synthesis could be observed using SEC analysis.

The routes described led to linear block copolymers P(EG-*b*-AA). The copolymerization of AA and oligo(ethylene glycol)



**Fig. 6** Overlay of SEC traces of polymers obtained from the ATRP approach (P(EG-*b*-AA) (—), P(EG-*b*-tBuA) (....), mPEG macroinitiator (---)) (left) and the ones obtained during the RAFT approach (P(EG-*b*-AA) (—) and mPEG macro-CTA (---)) (right).

acrylate ( $M_n = 480 \text{ g mol}^{-1}$ ) (OEGA<sub>480</sub>) will lead to graft block and random copolymers. The chosen technique to obtain these polymers was the RAFT polymerization using BPTC as CTA and AIBN as radical source.

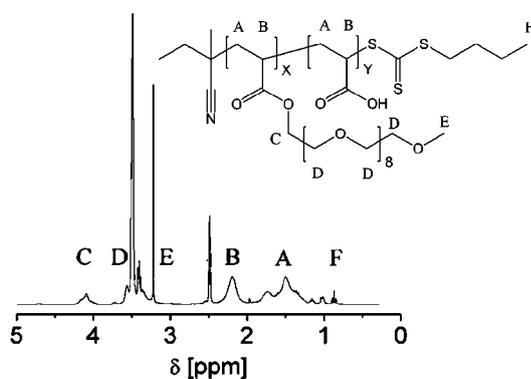
The resulting polymers including characterizing data obtained by SEC and <sup>1</sup>H NMR measurements are summarized in Table 3.

The specific separated signals obtained by <sup>1</sup>H NMR spectroscopy enabled the determination of the relative and even the absolute polymer composition as seen in Fig. 7. The accuracy of the determination of the absolute composition is of course dependent on a quantitative end-group functionalization. Analysis *via* SEC revealed narrow molar mass distributions

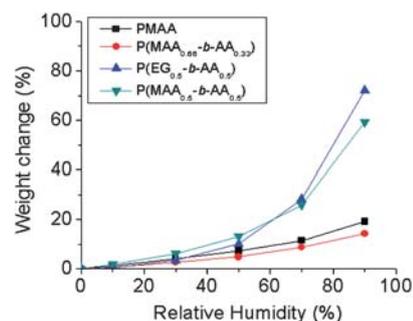
**Table 3** Characteristic data of the block (B) and random (R) copolymers of AA and OEGA<sub>480</sub>

Sample	Feed	$M_n$ (theor.) <sup>a</sup> /g mol <sup>-1</sup>	$M_n$ <sup>b</sup> (SEC) /g mol <sup>-1</sup>	PDI <sup>b</sup> (SEC)	Comp. <sup>c</sup> ( <sup>1</sup> H NMR)
POEGA <sub>480</sub>	0/8	3800	3000	1.15	—
R4	35/5	4800	6400	1.28	0.81 : 0.19
R5	45/5	5700	7100	1.21	—
R6	70/5	7700	8100	1.38	0.91 : 0.09
B4	35/5	4800	6000	1.20	0.87 : 0.13
B5	45/5	5700	6600	1.25	—
B6	70/5	7700	11 000	1.20	0.93 : 0.07

<sup>a</sup> Calculated according to formula ( $M_n(\text{theor.}) = ([M]/[CTA] \times \text{conv.} \times M_{\text{Monomer}}) + M_{\text{CTA}}$ ). <sup>b</sup> Calculated according to PS standards. <sup>c</sup> The ratios were calculated from the corresponding peaks shown in Fig. 7.



**Fig. 7** <sup>1</sup>H NMR spectrum for P(AA-*co*-OEGA<sub>480</sub>) with the corresponding schematic representation of the structure and the signal assignments (300 MHz, DMSO-*d*<sub>6</sub>).



**Fig. 8** Water uptake measurements of P(MAA-*b*-AA) with varying composition and P(EG-*b*-AA).

which led to different molar mass values due to the discrepancy in the hydrodynamic volume relative to the polystyrene standards used for calibration.

To investigate the water uptake behavior of the prepared polymers, thermogravimetric analysis of dried polymer samples were performed under changing humidity. In previous studies the water uptake of several linear polymers including PEG, PAA and poly(sodium acrylate) was investigated and reported.<sup>4</sup> These measurements showed the remarkable difference of the absorption behavior of pure PAA and the sodium salt of PAA as well as PEG. The highest water uptake at 90% relative humidity was observed for the PAA sodium salt (88%) and PEG (73%) whereas pure PAA could take up only 33%. In difference to the other two polymers, PAA absorbs water during the whole range of air humidity (10 to 90%) while PEG and PAA sodium salt do not absorb relevant amounts of water before a humidity level of at least 40% (PAA sodium salt) or even 70% (PEG) is reached.

In the present work the water uptake of P(MAA-*b*-AA) copolymers and P(EG-*b*-AA) was investigated. The results are shown in Fig. 8. While the ratio of MAA and AA in the corresponding block copolymers seems to have only a small influence, the total water uptake is surprisingly high in particular for **B3** (59% at 90% humidity).

An interesting result was observed in case of the P(EG<sub>40</sub>-*b*-AA<sub>42</sub>) block copolymer. The high water uptake of PEG at high humidity levels could be combined with the early starting uptake of water of PAA at lower humidity levels. Therefore, the resulting combined water uptake behavior could overcome the disadvantages of each homopolymer leading to the ability to absorb moisture over the complete humidity range as well as to a very high absolute water uptake level.

## Conclusions

Dual hydrophilic copolymers consisting of acrylic acid and methacrylic acid could be synthesized successfully. Random as well as block copolymers were prepared by controlled radical polymerization, *i.e.* the RAFT technique. The materials obtained were characterized by multiple analytical techniques like SEC, MALDI-TOF mass spectrometry, <sup>1</sup>H NMR spectroscopy, and water uptake measurements.

Well-defined dual hydrophilic linear and graft block copolymers based on acrylic acid and poly(ethylene glycol) could be prepared by RAFT and ATRP. The synthesized precursors, *i.e.*

macroinitiator and macro chain transfer agent, and the final block copolymers were characterized by SEC analysis,  $^1\text{H}$  NMR spectroscopy, and MALDI-TOF mass spectrometry. Additionally, the successful synthesis of well-defined block and random copolymers consisting of acrylic acid and oligo(ethylene glycol) acrylate led to dual hydrophilic copolymers of branched architecture. The synthesized polymers were characterized by  $^1\text{H}$  NMR spectroscopy and size exclusion chromatography (SEC).

During further investigations of the water uptake behavior of several selected polymers, an interesting water absorbing hybrid behavior could be observed for the P(EG-*b*-AA) block copolymer. The disadvantage of PEG, which is not able to absorb moisture below 70% humidity in a larger amount, could be overcome while keeping the final absolute water uptake at a high level of above 70%.

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