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## Characterization of Diblock Copolymers by Capillary Electrophoresis: From Electrophoretic Mobility Distribution to Distribution of Composition

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1 **Characterization of diblock copolymers by capillary electrophoresis: From**  
2 **electrophoretic mobility distribution to distribution of composition**

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10 **Abstract**

11 Free solution capillary-electrophoresis (CE) is a powerful separation technique for the  
12 characterization of diblock copolymers. In this work, four series of double-hydrophilic anionic and  
13 cationic block copolymers, namely, poly(acrylamide)-*block*-poly(acrylic acid) (PAM-*b*-PAA),  
14 poly(acrylamide)-*block*- poly((3-acrylamidopropyl)trimethylammonium chloride) (PAM-*b*-PAPTAC),  
15 poly(ethylene oxide)-*block*-poly(acrylic acid) (PEO-*b*-PAA) and poly(poly(ethylene glycol) methyl  
16 ether acrylate)-*block*-poly(acrylic acid) (P(PEGA)-*b*-PAA), were synthesized by reversible addition-  
17 fragmentation chain transfer (RAFT) polymerization and characterized by CE. The electrophoretic  
18 mobility distributions of the copolymers were transformed into distributions of composition ratio by  
19 introducing a retardation parameter,  $X_{exp}$ , that represents the hydrodynamic drag retardation due to the  
20 neutral block of the copolymer. A linear correlation between  $X_{exp}$  and the ratio of the degrees of  
21 polymerization of each blocks was experimentally established and was consistent with the model of  
22 electrophoretic mobility of composite macromolecules with hydrodynamic coupling. Finally, the  
23 comparison of the distributions between the different copolymer families was significantly improved by  
24 considering the distributions in composition ratio compared to the electrophoretic mobility distributions,  
25 since it takes into account the differences in solvation, expansion and drag force according to the  
26 chemical nature of the blocks.

## 27 1 Introduction

28 The characterization of diblock copolymers by separation techniques is challenging but of  
29 primary importance to check their purity and to characterize their distributions in size and in chemical  
30 composition.<sup>1</sup> Block copolymers prepared by reversible deactivation radical polymerization frequently  
31 contain homopolymer impurities.<sup>2, 3</sup> These include dead chains from termination reactions during  
32 polymerization of the first block, as well as the products of side-reactions such as chain transfer to  
33 solvent or monomer during polymerization of the second block. The growth of the second block in  
34 copolymer synthesis is often evidenced by a decrease of the elution time in size-exclusion  
35 chromatography (SEC) as a result of the increased hydrodynamic radius<sup>4, 5</sup>. However, this only holds if  
36 the second block contributes significantly to the hydrodynamic radius of the diblock copolymer. Getting  
37 more quantitative information can be challenging especially in aqueous SEC. Different solvation  
38 properties between the blocks of a block copolymer can lead to coelution of polymers of different mass  
39 in SEC, resulting in inaccuracy in the obtained molar masses.<sup>6</sup> Additionally, interactions with the  
40 stationary phase<sup>3</sup> may lead to HPLC-type elution which is dependent on the chemical composition of  
41 the polymer as well as its size. For diblock copolymer SEC, particular elution conditions are generally  
42 required and size distributions should be expressed in terms of hydrodynamic radius (and not molar  
43 mass) due to the difference in chemical composition / solvation of the two blocks<sup>6</sup>. The proportion of  
44 each monomer in a copolymer can be obtained by liquid chromatography under critical conditions  
45 LCCC, also known as LC-PEAT, for the point of exclusion-adsorption transition for neutral blocks<sup>7, 8</sup>.  
46 The critical conditions for LCCC (or LC-PEAT) are usually difficult to find and are very sensitive to  
47 small changes in mobile phase composition and/or temperature.

48 An alternative separation technique for charged copolymers is free solution capillary  
49 electrophoresis (CE)<sup>2, 3, 7-9</sup>. The electrophoretic separation of charged homopolymers from diblock  
50 copolymers is generally easily obtained in free solution CE. Moreover, for self-assembling diblock  
51 copolymers, CE can also separate micelles from unimers<sup>2, 7, 8</sup> and allows studying the impact of added  
52 surfactant on the copolymer micelles<sup>2, 7</sup>. In the presence of cationic blocks, experimental difficulties

53 arise from polymer adsorption onto the wall of silica based capillaries. The characterization of cationic  
54 diblock copolymers requires the use of a neutrally coated<sup>3</sup>, or positively charged capillary<sup>10</sup>.  
55 Another challenging issue in the characterization of diblock copolymers by CE is to extract the  
56 distribution in composition of the copolymers from the electropherogram. Raw electropherograms can  
57 be transformed into distributions of effective mobility, or of any other related parameter, provided that  
58 the relationship between effective mobility and the considered parameter is known<sup>11</sup>. The determination  
59 of polymer dispersity via the variance of the chemical composition distribution<sup>11</sup> or via the calculation  
60 of the ratio of moments of the distribution has also been studied<sup>1</sup>. A key point to achieve such  
61 electropherogram transformation is to have a reliable relation between the effective mobility of the  
62 diblock copolymer and the degrees of polymerization of each block and thus, to the chemical  
63 composition of the copolymer<sup>3</sup>. The electrophoretic mobility of a diblock copolymer is generally  
64 expressed as a weighted average of the mobilities of different subunits constituting the copolymer<sup>12</sup>. The  
65 choice of the subunits and the corresponding weights have been described in the literature as depending  
66 on the conformations of each block and on the hydrodynamic coupling regime between the two blocks  
67 <sup>12-15</sup>. More recently, Chubynsky and Slater studied in more detail the “end-effect” (i.e. the fact that the  
68 ends of the copolymer chain are more hydrodynamically exposed to the solvent)<sup>16</sup> and the effect of  
69 polymer stiffness on the electrophoretic modeling<sup>17</sup>. The electrophoretic models of composite objects<sup>12-</sup>  
70 <sup>13</sup> which are relevant for diblock copolymers, were also applied to end-labeled free solution  
71 electrophoresis (ELFSE)<sup>14, 15</sup>, which consists in attaching a monodisperse neutral block (drag-tag) to a  
72 polydisperse biopolyelectrolyte (for instance, for DNA sequencing in free solution<sup>15, 18</sup>), or conversely,  
73 in attaching a monodisperse polyelectrolyte to a polydisperse neutral polymer (for instance, for size-  
74 based neutral polymer characterization<sup>14</sup>). In this way, the dependence of electrophoretic mobility with  
75 the molar mass of the end-labelled composite object is obtained in free solution due to the variation of  
76 the charge-to-friction ratio.

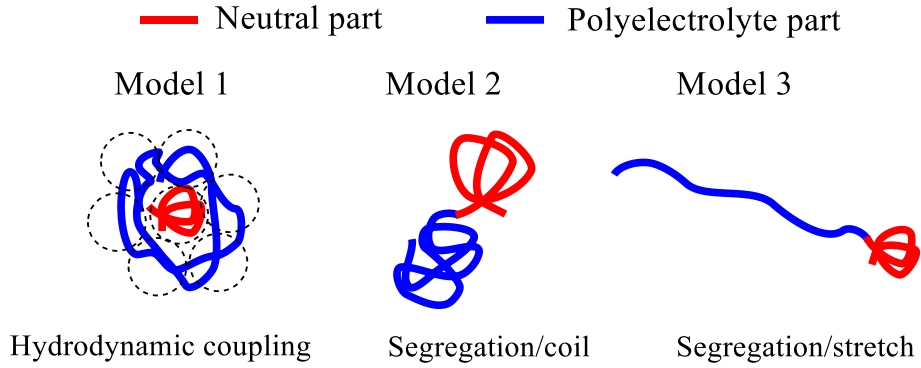
77 Double-hydrophilic block copolymers (DHBC) are block copolymers containing two hydrophilic  
78 segments. DHBCs on their own are completely soluble in water and do not self-assemble in dilute  
79 conditions. DHBCs can still retain an amphiphilic character and this can lead to self-organization at the  
80 meso-scale in concentrated conditions<sup>19</sup>. They can undergo morphological transitions induced by

81 external stimuli<sup>20</sup> in dilute solution. The great development of reversible deactivation radical  
82 polymerization<sup>21-24</sup> in the last two decades allows tailoring the stimuli-responsiveness (e.g. to changes  
83 in pH, temperature, ionic strength, or light) of these polymers by controlling both the nature of  
84 monomers and the degree of polymerization of the blocks. When one block is a polyelectrolyte, DHBCs  
85 can undergo micellization by electrostatic complexation in the presence of an oppositely charged  
86 polyelectrolyte. These properties lead to a wide range of applications such as control of crystallization  
87 of inorganic compounds<sup>25</sup>, drug delivery<sup>26</sup> or template for ordered mesoporous materials<sup>27</sup>. For this last  
88 application of DHBC, the asymmetry ratio, defined as the ratio of degrees of polymerization of both  
89 blocks, is of crucial interest since it determines the structure of the DHBC-templated mesoporous  
90 materials.

91 It is the aim of the present work to characterize the composition of DHBC by CE, with particular  
92 attention to the asymmetry ratio. The approach has been applied to series of anionic and cationic  
93 DHBCs, namely, poly(acrylamide)-*block*-poly(acrylic acid) (PAM-*b*-PAA), poly(acrylamide)-*block*-  
94 poly((3-acrylamidopropyl)trimethylammonium chloride) (PAM-*b*-PAPTAC), poly(ethylene oxide)-  
95 *block*-poly(acrylic acid) (PEO-*b*-PAA) and poly(poly(ethylene glycol) methyl ether acrylate)-*block*-  
96 poly(acrylic acid) (P(PEGA)-*b*-PAA). These DHBC have been synthesized in aqueous medium by  
97 reversible addition-fragmentation transfer (RAFT) polymerization.

98 In the next section, different models for the electrophoretic mobility of composite objects such as block  
99 copolymers are briefly reviewed. In the third section, the synthesis of the copolymers and the  
100 experimental conditions of their characterization by CE are reported. The results of this work are  
101 presented in section 4, where we describe a method to transform the distribution of electrophoretic  
102 mobility into a distribution of the ratio of degree of polymerization of both blocks.

103 **2 Mobility of diblock copolymers constituted of a polyelectrolyte and a neutral block**



**Figure 1.** Representation of possible conformations of a double hydrophilic block copolymer composed of a neutral Gaussian coil (in red) linked to a polyelectrolyte block (in blue). In model 1, the polyelectrolyte chain is a coil in hydrodynamic interaction with the neutral Gaussian coil. In model 2, the polyelectrolyte and the neutral polymer separate into two coils. In model 3, the polyelectrolyte is fully stretched and has no hydrodynamic coupling with the neutral coil. Adapted from<sup>28</sup>

104 In this section, we present different possible electrophoretic mobility models that are relevant  
 105 for diblock copolymers composed of a polyelectrolyte part attached to a neutral polymer coil. These  
 106 theoretical models were developed by Desruisseaux et al<sup>28</sup>, building on previous work by Long et al.<sup>12</sup>.  
 107 <sup>13</sup> Figure 1 shows the different possible conformations that can be encountered for DHBC, corresponding  
 108 to the different models presented below.

109 **2.1 Model 1: hydrodynamic coupling**

110 In Model 1, hydrodynamic coupling between the polyelectrolyte part and the neutral coil is taken  
 111 into account. The polyelectrolyte block of the DHBC is composed of  $N_{blob}$  equivalent blobs of a size  
 112 equivalent to the hydrodynamic radius of the neutral coil  $R_h^{neutral}$ . If  $R_h^{neutral}$  is larger or equal to the  
 113 Debye length, Long et al.<sup>29</sup> demonstrated that the electrophoretic mobility of the DHBC composite  
 114 object composed of  $N_{blob} + 1$  subunits of equal size, is given by the number-average of the electrophoretic  
 115 mobilities calculated on all the equivalent blobs constituting the object. The electrophoretic mobility of  
 116 the DHBC,  $\mu_{ep,1}^{diblock}$ , is thus given by<sup>28</sup>:

$$\mu_{ep,1}^{diblock} = \frac{\sum_{i=0}^{N_{blob}} \mu_{ep}^i}{N_{blob} + 1} = \frac{N_{blob} \mu_{ep}^0 + \mu_{ep}^{neutral}}{N_{blob} + 1} = \frac{\mu_{ep}^0}{1 + \frac{\alpha}{DP_0}} \quad (1)$$

118 where  $\mu_{ep}^i$  is the effective mobility of the  $i^{\text{th}}$  entity (or blob) constituting the DHBC,  $DP_0$  is the degree  
 119 of polymerization of the polyelectrolyte block,  $\alpha$  is the number of charged monomers per blob,  $\mu_{ep}^0$  is  
 120 the effective electrophoretic mobility of the polyelectrolyte part (alone) and  $\mu_{ep}^{neutral}$  is the electrophoretic  
 121 mobility of the neutral part ( $\mu_{ep}^{neutral} = 0$ ). The number of equivalent blobs in the polyelectrolyte chain  
 122 is given by  $N_{blob} = \frac{DP_0}{\alpha}$ . Note that  $N_{blob}$  (and  $\mu_{ep,1}^{diblock}$ ) depends on the polyelectrolyte persistence  
 123 length, and thus, on the ionic strength. Equation (1) neglects the so-called end-effect<sup>16</sup>. Please note that  
 124 subscript and superscript 0 refer to the polyelectrolyte block, for consistency with ref 28.

## 125 2.2 Models without hydrodynamic coupling

### 126 2.2.1 Model 2: polyelectrolyte chain in coil conformation

127 Model 2 in Figure 1 corresponds to the segregation of the neutral polymer coil from the  
 128 polyelectrolyte coil. In the absence of hydrodynamic coupling between the two parts, and if the  
 129 polyelectrolyte chain does not stretch during electrophoresis (i.e. at sufficiently low electric field), the  
 130 electrophoretic mobility of the DHBC,  $\mu_{ep,2}^{diblock}$ , is given by the average electrophoretic mobility of the  
 131 two parts weighted by their hydrodynamic friction coefficient<sup>12</sup>. Using Stokes equation for spherical  
 132 objects,  $\mu_{ep,2}^{diblock}$  is expressed as<sup>13, 28</sup>:

$$\mu_{ep,2}^{diblock} = \frac{\sum_{i=0}^1 \gamma_i \mu_{ep}^i}{\sum_{i=0}^1 \gamma_i} = \frac{\mu_{ep}^0}{1 + \frac{R_h^{neutral}}{R_h^0}} \quad (2)$$

134 where  $\gamma_i$  is the friction coefficient of the  $i^{\text{th}}$  part constituting the DHBC,  $R_h^{neutral}$  is the hydrodynamic  
 135 radius of the neutral coil,  $R_h^0$  is the hydrodynamic radius of the polyelectrolyte block.

## 136 2.2.2 Model 3: polyelectrolyte chain in fully stretched conformation

137 When the polyelectrolyte coil is stretched under the concomitant influence of the electric field  
138 and the opposed drag force due to the presence of the neutral coil, it can reach a fully extended  
139 conformation as depicted in Figure 1 (Model 3). Stokes law is no longer appropriate for the frictional  
140 coefficient of the polyelectrolyte chain, and the electrophoretic mobility of the DHBC,  $\mu_{ep,3}^{diblock}$ , is given  
141 by<sup>27</sup> :

$$142 \mu_{ep,3}^{diblock} = \frac{\sum_{i=0}^1 \gamma_i \mu_{ep}^i}{\sum_{i=0}^1 \gamma_i} = \frac{\mu_{ep}^0}{1 + \frac{2R_h^{neutral}}{b_0 DP_0} \ln DP_0} \quad (3)$$

143 where  $b_0$  is the size of a charged monomer in the polyelectrolyte chain. Equation (3) assumes that the  
144 friction coefficient  $\gamma_{rod}$  of the stretched polyelectrolyte cylinder is averaged on all orientations relative  
145 to the flow direction, and is given by:

$$146 \gamma_{rod} = \frac{3\pi\eta b_0 DP_0}{\ln(DP_0)} \quad (4)$$

147 where  $\eta$  is the viscosity of the solvent.

148 Even if the electrical field is not strong enough to stretch the polyelectrolyte block (hydrodynamic  
149 segregation), the polyelectrolyte contour length may still be shorter than the persistence length of the  
150 polyelectrolyte. In this situation, the segregation between the neutral and the polyelectrolyte parts is  
151 sterically obtained, but the electrophoretic mobility is still described by equation (3)<sup>27</sup>.

## 152 3 Experimental

### 153 3.1 Chemicals

154 Ammonium persulfate (APS, 98%) and sodium formaldehyde sulfoxylate dehydrate (NaFS, 98%) were  
155 purchased from Acros organics. Poly(ethylene glycol) methyl ether acrylate ( $M_n = 480$  g/mol, 8.5 EO  
156 units on average) and (3-acrylamidopropyl)trimethylammonium chloride (APTAC) aqueous solution (75



157 wt.%) were purchased from Sigma Aldrich (Saint-Quentin-Fallavier, France) and used as received.  
158 Acrylic acid from the same suppliers was distilled under vacuum at room temperature. PEO  $M_n=5000$   
159  $\text{g}\cdot\text{mol}^{-1}$ ,  $D = 1.04$  was purchased from. 4,4'-azobiscyanopentanoic acid (ACPA, Aldrich, 98%) and 2,2-  
160 Azobis(isobutyramidine) dihydrochloride (AIBA, Sigma-Aldrich, 97%) were used as received.

161  
162 For EC experiments, background electrolytes were prepared in ultra-pure water purified on a Millipore  
163 system (Molsheim, France) from tris(hydroxymethyl)aminomethane (TRIS, 99,9%, Merck), 4-  
164 Morpholinoethanesulphonic acid (MES, >99%, Acros Organics), and 2-[Bis(2-hydroxyethyl)amino]-2-  
165 (hydroxymethyl)propane-1,3-diol (BIS-TRIS, >99%, Acros Organics). Anisic acid (99,5%), ammediol  
166 (99,5%) used as markers for detection were purchased from Sigma-Aldrich.

167

## 168 **3.2 Double-hydrophilic block copolymer synthesis**

169 This section describes the synthesis of the copolymers. The synthetic pathway, the size exclusion  
170 chromatograms and the  $^1\text{H}$  NMR spectra are given in SI as well as the temporal electropherograms.

### 171 **3.2.1 Synthesis of poly(acrylamide)-*b*-poly(acrylic acid)**

#### 172 **Aqueous RAFT/MADIX polymerization of AA**

173 Polyacrylamide macro RAFT/MADIX agent (PAM-Xa,  $M_n= 5000 \text{ g}\cdot\text{mol}^{-1}$ ) was synthesized according  
174 the procedure described by Layrac et al..<sup>30</sup> Synthesis of PAM<sub>70</sub>-*b*-PAA<sub>20</sub> was performed as follows<sup>31</sup>:  
175 PAM-based chain transfer agent (PAM-Xa<sub>1</sub>) (15.76 g, 3.029 mmol), acrylic acid (4.24 g; 58.77 mmol),  
176 AIBA (0.0821 g, 0,3 mmol) and water (42 g) (solids = 30.6%) were introduced in a round bottom flask.  
177 The mixture was degassed with argon at room temperature for 30 min and then placed in a thermostated  
178 oil bath at 65°C under argon for 2 hours. Conversion was quantitative, acrylic acid traces were  
179 eliminated by dialysis (MWCO 1000 Da) and pH-metric monitoring. The polymer solution was then  
180 freeze dried and a white powder was obtained. Four DHBC were synthesized according to this  
181 procedure: PAM<sub>70</sub>-*b*-PAA<sub>20</sub>, PAM<sub>140</sub>-*b*-PAA<sub>40</sub>, PAM<sub>140</sub>-*b*-PAA<sub>60</sub> and PAM<sub>140</sub>-*b*-PAA<sub>80</sub> (see Table 1).

### 182 **3.2.2 Synthesis of poly(acrylamide)-*b*-poly((3-acrylamidopropyl)trimethylammonium chloride)**

#### 183 **Aqueous redox RAFT/MADIX polymerization of APTAC**

184 Synthesis of PAM<sub>70</sub>-*b*-PAPTAC<sub>30</sub> was performed as follows: two aqueous solutions of NaFS (5% w)  
185 (1.23 g of solution, 0.4 mmol) and NaPS (5% w) (2.37 mg of solution, 0.5 mmol) were prepared. PAM-  
186 Xa macroxanthate (9.97 g, 1.99 mmol), APTAC monomer (13.3 g of solution, 0.057 mmol), and water  
187 (50 g) (solids = 25.4%) were introduced in a round bottom flask. The pH of the mixture was first adjusted  
188 at 2 with hydrochloric solution 1M. Then the mixture was degassed with argon at room temperature for  
189 30 min and placed in a thermostated oil bath at 25°C under argon. Both solution of NaFS and NaPS  
190 were introduced in the round bottom flask and the reaction mixture was stirred for 3 hours. Monomer  
191 traces were eliminated with dialysis (MWCO 1000 Da) and conductivity monitoring. The polymer  
192 solution was then lyophilized and a white powder was obtained. This redox process at 25°C was  
193 developed after the paper of Sutton et al.<sup>9</sup> to minimize the formation of dead chains. Four DHBC were  
194 synthesized according to this procedure: PAM<sub>70</sub>-*b*-PAPTAC<sub>30</sub>, PAM<sub>70</sub>-*b*-PAPTAC<sub>60</sub>, PAM<sub>140</sub>-*b*-  
195 PAPTAC<sub>60</sub> and PAM<sub>140</sub>-*b*-PAPTAC<sub>120</sub> (see Table 1).

### 196 **3.2.3 Synthesis of poly(ethylene oxide)-*b*-poly(acrylic acid)**

#### 197 **Aqueous RAFT polymerization of AA**

198 Synthesis of PEO<sub>105</sub>-*b*-PAA<sub>20</sub> was performed as follows: PEO<sub>105</sub>-CTA (poly(ethylene oxide)-chain  
199 transfer agent) macro RAFT agent was obtained following the procedure published by Bathfield et al<sup>32</sup>.  
200 PEO<sub>105</sub>-CTA, (10.53 g, 2.19 mmol), ACPA (0.123 mg, 0,439 mmol), acrylic acid (5.5 g, 76 mmol) and  
201 deionized water (29.5 mL) (solids=35.4%) were introduced in a Schlenk tube equipped with a magnetic  
202 stirrer. The mixture was degassed by five freeze-evacuate-thaw cycles and then heated for 42 hours at  
203 75°C under nitrogen in a thermostated oil bath. Final conversion = 72%. Monomer conversion was  
204 determined by <sup>1</sup>H NMR spectroscopy, using a Bruker 400MHZ spectrometer. Samples for analysis by  
205 NMR were prepared by adding 0.6 mL of D<sub>2</sub>O to 0.1 mL of polymerization medium. Once the reaction  
206 was complete, the solvent was evaporated, and then the DHBC was dissolved in a minimum amount of  
207 dichloromethane before being precipitated twice in a large volume of cold diethyl ether. It was then  
208 recovered by filtration, and finally dried under vacuum overnight before analysis by SEC and <sup>1</sup>H-NMR.  
209 SEC was performed in DMF-LiBr after methylation<sup>33</sup> with trimethylsilyldiazomethane. Four DHBC

210 were synthesized according to this procedure: PEO<sub>105</sub>-*b*-PAA<sub>20</sub>, PEO<sub>105</sub>-*b*-PAA<sub>30</sub>, PEO<sub>210</sub>-*b*-PAA<sub>40</sub> and  
 211 PEO<sub>210</sub>-*b*-PAA<sub>50</sub> (see Table 1). The degrees of polymerization of the commercial starting PEO have  
 212 been determined by <sup>1</sup>H NMR<sup>32</sup> and are presented in Table 1.

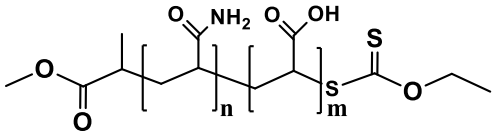
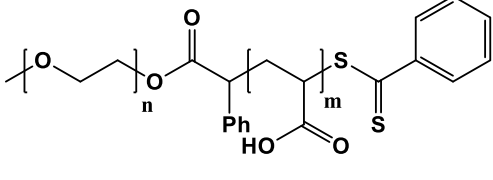
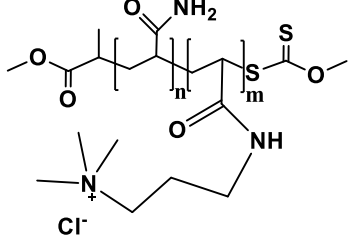
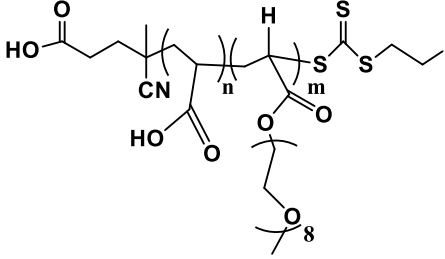
### 213 3.2.4 Synthesis of poly(acrylic acid)-*b*-poly(poly(ethylene glycol) methyl ether acrylate)

#### 214 Aqueous RAFT polymerization of AA and PEGA

215 5,7-dithia-6-thio-4-methyl-4-cyanodecanoic acid (CTPPA) was obtained by reaction of ACPA  
 216 with bis(propylsulfanylthiocarbonyl) disulfide according to literature.<sup>34</sup> Synthesis of PAA<sub>21</sub>-*b*-  
 217 P(PEGA)<sub>12</sub> was performed as follows: PAA-CTPPA chain transfer agent was synthesized according to  
 218 the process described in literature<sup>35</sup>: in a round bottom flask, CTPPA (0.8 g, 2.57 mmol, purity=89%),  
 219 acrylic acid (3.9g, 54.1 mmol), ACPA (0,072 g, 0.26 mmol) and half of the amount of water (7.5 g) are  
 220 stirred until dissolution of CTPPA. The remaining water (7.5 g) was introduced and the mixture was  
 221 degassed with argon for 40 min. The mixture was then heated in an oil bath at 70°C for 5.5 h. For the  
 222 synthesis of PAA-*b*-P(PEGA), ACPA (0.0715 g; 0.26 mmol) and poly(ethylene glycol) methyl ether  
 223 acrylate (12.8 g, 26.4 mmol) were added to the PAA-CTPPA reaction medium and the mixture was  
 224 degassed with argon for 40 min. The mixture was then heated in an oil bath at 70°C for 5 h. Conversion  
 225 was followed by <sup>1</sup>H NMR. At the end of the polymerization, water was evaporated under reduced  
 226 pressure and the polymer washed with diethyl ether. NMR sample preparation: 0.6 mL of D<sub>2</sub>O was  
 227 added to 0.1 mL of polymerization medium and quenched in liquid nitrogen. Two DHBC were  
 228 synthesized according to this procedure: P(PEGA)<sub>12</sub>-*b*-PAA<sub>21</sub> and P(PEGA)<sub>22</sub>-*b*-PAA<sub>45</sub> (see Table 1).

229 **Table 1:** Presentation of the chemical structure and the different DHBC samples synthesized and studied in this  
 230 work. The subscripts in the names correspond to the degree of polymerization of each block.  $MW_{neutral}$  and  $MW_0$   
 231 are the molar masses of the neutral and of the polyelectrolyte block respectively.

Type of DHBC	$MW_{neutral}-MW_0$ as determined by NMR	Chemical structure
PAM <sub>70</sub> - <i>b</i> -PAA <sub>20</sub>	5k-1.4k	
PAM <sub>140</sub> - <i>b</i> -PAA <sub>40</sub>	10k-2.8k	

PAM <sub>140</sub> - <i>b</i> -PAA <sub>60</sub>	10k-4.4k	
PAM <sub>140</sub> - <i>b</i> -PAA <sub>80</sub>	10k-5.6k	
PEO <sub>105</sub> - <i>b</i> -PAA <sub>20</sub>	5k-1.4k	
PEO <sub>105</sub> - <i>b</i> -PAA <sub>30</sub>	5k-2.2k	
PEO <sub>210</sub> - <i>b</i> -PAA <sub>40</sub>	10k-2.8k	
PEO <sub>210</sub> - <i>b</i> -PAA <sub>50</sub>	10k-3.6k	
PAM <sub>70</sub> - <i>b</i> -PAPTAC <sub>30</sub>	5k-5k	
PAM <sub>70</sub> - <i>b</i> -PAPTAC <sub>60</sub>	5k-10k	
PAM <sub>140</sub> - <i>b</i> -PAPTAC <sub>60</sub>	10k-10k	
PAM <sub>140</sub> - <i>b</i> -PAPTAC <sub>120</sub>	10k-20k	
P(PEGA) <sub>12</sub> - <i>b</i> -PAA <sub>21</sub>	5.7k-1.5k	
P(PEGA) <sub>22</sub> - <i>b</i> -PAA <sub>45</sub>	10.6k-3.2k	

### 232 3.3 Capillary electrophoresis

#### 233 *Instrumentation and method*

234 Capillary electrophoresis experiments were performed on an Agilent 7100 capillary electrophoresis  
 235 instrument with a diode array UV detector. Fused silica capillaries of 50/375  $\mu\text{m}$  I.D./O.D. with  
 236 polyimide outer coating (cat. no. TSP050375) were from Polymicro Technologies (Phoenix, AZ, USA).  
 237 Capillary dimensions were 38.5 cm long (30 cm to detection window). New capillaries were conditioned  
 238 by performing the following washes at 1 bar: 1M NaOH for 30 min and water for 15 min. The  
 239 temperature of the capillary cartridge was set at 25 °C.

240 In the case of PAM-*b*-PAA, an electrolyte consisting of 20 mM MES and 14 mM ammonium diethyl imidazole  
 241 was used. 0.1 g/L anisic acid was added in the sample as a mobility marker. The same background electrolyte  
 242 was used for PAM-*b*-PAPTAC, but with a different mobility marker (imidazole 0.1 g/L). In the case of  
 243 PEO-*b*-PAA and P(PEGA)-*b*-PAA, an electrolyte constituted of 6 mM anisic acid and 12 mM BIS-

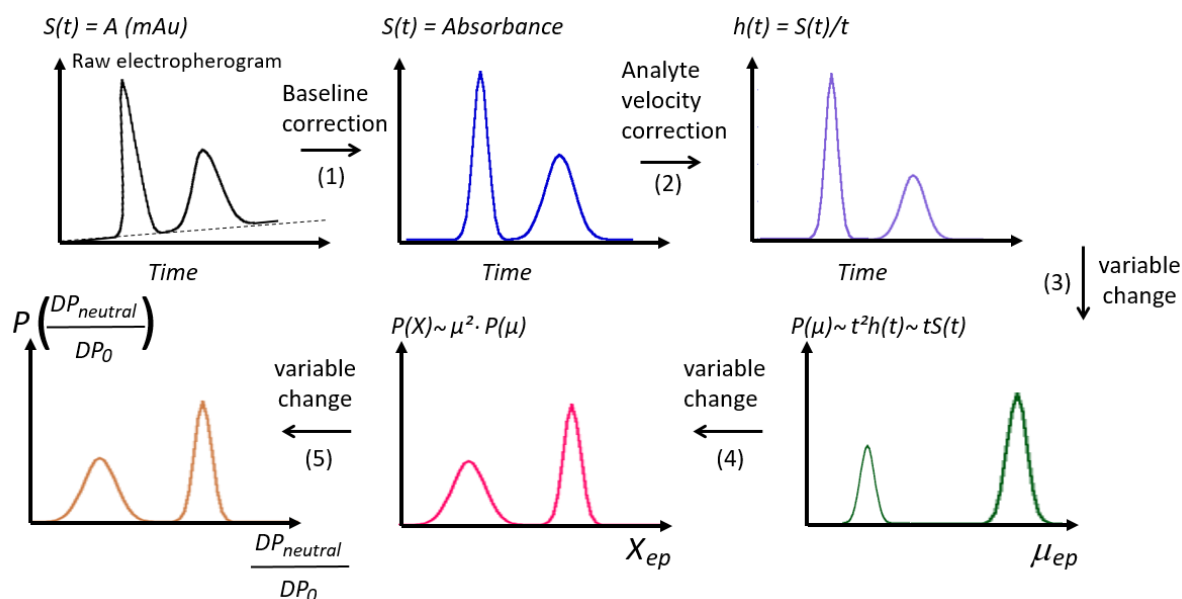
244 TRIS, pH 6.5 was used as buffer, with MES at 0.5 g/L as mobility marker in the case of P(PEGA)-*b*-  
245 PAA.

246 All copolymers were dissolved in water at a concentration of 5 g/L. Samples were injected  
247 hydrodynamically on the inlet side of the capillary by applying 30 mbar for 5 s. Separations were carried  
248 out by applying a +20 kV voltage. For PAM-*b*-PAA, PEO-*b*-PAA and P(PEGA)-*b*-PAA and PAM-*b*-  
249 PAPTAC, detection was realized at 192 +/- 2 nm (reference off).

250 For PAM-*b*-PAA, PEO-*b*-PAA and P(PEGA)-*b*-PAA, the capillary was rinsed between each run by  
251 flushing the capillary for 2 min with the background electrolyte, 2 min with 0.1 M NaOH, 2 min with  
252 ultra-pure water and 2 min with background electrolyte. For the analysis of the cationic polymer PAM-  
253 *b*-PAPTAC, and in order to reduce the adsorption on the capillary wall, surface of the capillary was  
254 modified using UltraTrol™ LN (Target Discovery, Inc., Palo Alto, CA), which is a commercial neutral  
255 semi-permanent coating based on polyacrylamide derivatives. The coating procedure was performed  
256 using the following successive flushes: methanol for 2 min at 1 bar, water for 2 min at 3 bar, 1 M NaOH  
257 for 2 min at 3 bar, 0.1 M NaOH for 2 min at 1 bar, 1 M HCl for 5 min at 1 bar, water for 5 min at 1 bar,  
258 UltraTrol™ LN solution for 5 min at 1 bar, wait for 5 min, water for 2 min at 1 bar. Prior to each analysis  
259 of PAM-*b*-PAPTAC, the capillary was rinsed with the background electrolyte for 2 min at 1 bar.

260

261 **Electropherogram data treatment**



**Figure 2.** General scheme for changing a time-scale electropherogram into a mobility-scale and  $X_{exp}$ -scale distributions. The raw electropherogram is first corrected from baseline shift (1). The time-scale electropherogram is then corrected from the differences in analyte velocities (2). The time-corrected electropherogram is converted into the effective mobility-scale distribution (3). The mobility-scale electropherogram is changed into a  $X_{exp}$ -scale distribution (4) and finally to a compositional  $\frac{DP_{neutral}}{DP_0}$  ratio (5).

$S(t)$  is the UV absorbance signal (in mAU).  $h(t)$  is the time-corrected UV absorbance.  $P(\mu_{ep})$  is the effective mobility distribution.  $P(X_{exp})$  is the distribution in  $X_{exp}$  (see section 4.2) and  $P(\frac{DP_{neutral}}{DP_0})$  is the distribution in  $\frac{DP_{neutral}}{DP_0}$ .

$\frac{DP_{neutral}}{DP_0}$ . Adapted from<sup>11</sup> for the characterization of diblock copolymers.

262 **Scale transformations.** In this section, the transformations of the electropherograms into distributions  
 263 of the parameter of interest are described following a previously published protocol<sup>11</sup>. Briefly,  
 264 experimental raw time-scale electropherograms, were first corrected from any baseline shift using  
 265 Origin (Origin 2016, OriginLab, USA) as depicted in step 1, Figure 2. For quantitative purpose, the  
 266 absorbance signal  $S(t)$  was next divided by the migration time ( $t$ ) to correct the differences in analyte

267 velocity (Figure 2, step 2)<sup>11</sup>. Next, the time-corrected electropherogram  $h(t)$  was changed into an  
 268 effective mobility distribution  $P(\mu_{ep}) = t \times S(t)$  (Figure 2, step 3)<sup>11</sup>, which requires the  
 269 transformations of both the  $x$  and  $y$  axis<sup>11</sup>. Note that  $\mu_{ep}$  is obtained by equation (5):

$$270 \quad \mu_{ep} = \frac{lL}{V} \left( \frac{1}{t} - \frac{1}{t_{eo}} \right) \quad (5)$$

271 where  $l$  is the effective capillary length,  $L$  is the total capillary length,  $t$  is the migration time,  $t_{eo}$  is the  
 272 EOF marker migration time and  $V$  is the separation voltage.

273 **Moments of the electrophoretic mobility distribution** The average effective mobility of the diblock  
 274 copolymer  $\overline{\mu_{ep}^{diblock}}$  was obtained by integration of the peak of the copolymer in the effective mobility  
 275 scale according to:

$$276 \quad \overline{\mu_{ep}^{diblock}} = \frac{\int P(\mu_{ep}) \mu_{ep} d\mu_{ep}}{\int P(\mu_{ep}) d\mu_{ep}} \approx \frac{\sum_i P(\mu_{ep,i}) \mu_{ep,i} (\mu_{ep,i+1} - \mu_{ep,i})}{\sum_i P(\mu_{ep,i}) (\mu_{ep,i+1} - \mu_{ep,i})} \quad (6)$$

277 where integration is carried out over the peak. In practice the integration is done numerically and the  $i$   
 278 index represents the digitized experimental data points. The summation is carried out over values  
 279 of  $P(\mu_{ep,i})$  greater than the median of the base line added to its standard deviation. Calculation of  
 280  $\overline{\mu_{ep}^{diblock}}$  was performed using Excel 2016 (Microsoft, USA), following the discrete form of equation (6).

281 Variance of the diblock electrophoretic mobility was obtained by the following equation:

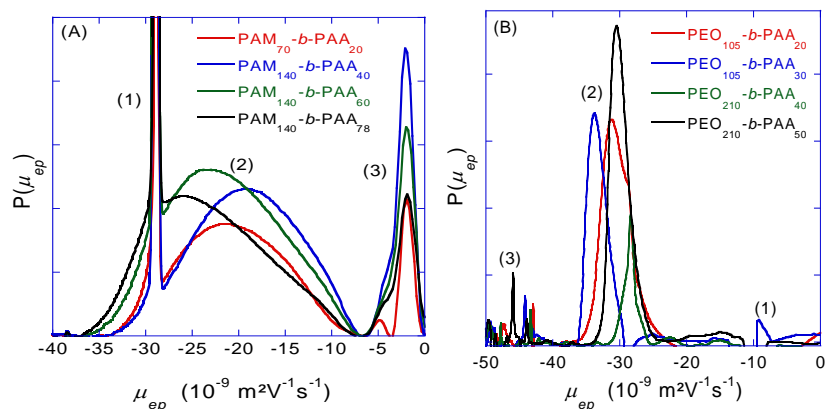
$$282 \quad \sigma_{\mu}^2 = \frac{\int P(\mu_{ep}) \left( \mu_{ep} - \overline{\mu_{ep}^{diblock}} \right)^2 d\mu_{ep}}{\int P(\mu_{ep}) d\mu_{ep}} = \frac{\sum_i P(\mu_{ep,i}) (\mu_{ep,i} - \overline{\mu_{ep}^{diblock}})^2 (\mu_{ep,i+1} - \mu_{ep,i})}{\sum_i P(\mu_{ep,i}) (\mu_{ep,i+1} - \mu_{ep,i})} \quad (7)$$

283

284 **4. Results and discussion**

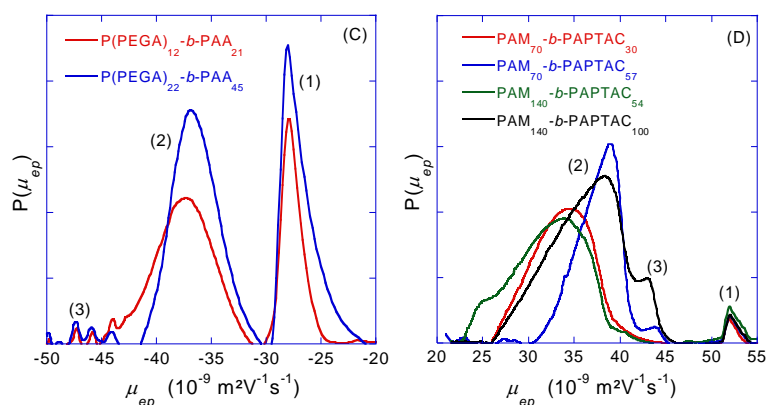
285 **4.1. Electrophoretic separation of the DHBC**

286 The main goal of the CE characterization is to provide information about the chemical composition  
287 distribution of the DHBC and about the purity of the DHBC in terms of possible presence of  
288 homopolymers. The separation of the DHBC by CE requires an appropriate background electrolyte,  
289 depending on the nature of the copolymer. For copolymers absorbing in UV (i.e. those with a PAM  
290 neutral block), direct UV detection was possible and a background electrolyte based on 20 mM MES  
291 and 14 mM ammonium at pH 6.5 was used, with a UV detection at 192 nm. For DHBC copolymers that  
292 do not absorb UV enough to ensure sensitivity (i.e. PEO-*b*-PAA or P(PEGA)-*b*-PAA), an indirect  
293 detection mode based on a 6 mM anisic acid and 12 mM BIS TRIS at pH 6.5 was used. At this pH about  
294 60% of the carboxylic acid groups of the PAA are ionized, and this ensures appropriate selectivity of  
295 separation between PAA homopolyelectrolyte and the DHBC. Uncoated fused silica capillary was used  
296 for the characterization of all anionic DHBC. Semi-permanent UltraTrolLN neutral coating was used  
297 for the characterization of the cationic PAM-*b*-PAPTAC DHBC, to avoid any copolymer adsorption on  
298 the capillary surface. To correct the apparent mobility from the electroosmotic mobility, a mobility  
299 marker (anisic acid for PAM-*b*-PAA, MES for P(PEGA)-*b*-PAA, and imidazolium for PAM-*b*-  
300 PAPTAC) of known effective mobility ( $\mu_{ep, MES} = -28$  TU (where TU, Tiselius Unit, stands for  $10^{-9} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$ )  
301 and  $\mu_{ep, imidazolium} = 52$  TU) was co-injected. For PEO-*b*-PAA, the electroosmotic mobility was  
302 estimated from the electroosmotic flow (EOF) peak. The distributions of effective mobility (DEM) of  
303 PAM-*b*-PAA, PEO-*b*-PAA, P(PEGA)-*b*-PAA and PAM-*b*-PAPTAC are displayed in Figure 3.



304





306

307 **Figure 3.:** Distributions of effective electrophoretic mobility obtained for PAM-*b*-PAA (A), PEO-*b*-  
 308 PAA (B), P(PEGA)-*b*-PAA (C), and PAM-*b*-PAPTAC (D).-Electrophoretic conditions: fused silica  
 309 capillary (A, B, C) or coated with UltraTrolLN<sup>TM</sup> (D), 50  $\mu\text{m}$  I.D.  $\times$  38.5 cm (effective length, 30 cm).  
 310 Electrolytes: 20 mM MES, 14 mM ammediol, pH 6.5 (A, D); 6 mM anisic acid, 12 mM BIS TRIS, pH  
 311 6.5 (B, C). Applied voltage: +20 kV. Hydrodynamic injection: 30 mbar, 5 s. Direct (A, D) or indirect  
 312 (B, C) UV detection at 192 $\pm$  2 nm. Temperature: 25  $^{\circ}\text{C}$ . Samples: 5 g/L DHBC. Assignment of the  
 313 peaks: PAM-*b*-PAA (A): anisic acid (1), DHBC (2), PAM homopolymer (3); PEO-*b*-PAA (B): system  
 314 peak (1), DHBC (2), PAA oligomers (3); P(PEGA)-*b*-PAA (C): MES (1), DHBC (2), PAA oligomers  
 315 (3); PAM-*b*-PAPTAC (D): Imidazolium (1), DHBC (2), PAPTAC (3). The degree of polymerization of  
 316 each block is specified on the graph.

317 The DEM in the series PAM-*b*-PAA (Figure 3A) show three peaks, two sharp at -29 TU (peak 1) and -2  
 318 TU (peak 3) and one broad (peak 2) between -7 and -37.5 TU, the latter being assigned to the copolymer  
 319 of interest. The peak at -29 TU is assigned to anisic acid (electrophoretic mobility marker) and the one  
 320 at -2 TU corresponds to homopolymer of PAM. The non-zero electrophoretic mobility of the PAM  
 321 homopolymer is explained by the incorporation of the negatively charged initiator 4,4'-azobis(4-  
 322 cyanopentanoic) acid. The mass proportion of this PAM population of dead chains has been quantified  
 323 by external calibration based on time-corrected peak areas using direct injections of PAM solutions of  
 324 known concentration in the same condition as the DHBC. The proportion of PAM homopolymer  
 325 amounts to 21wt% in the solid form polymer sample for PAM<sub>70</sub>-*b*-PAA<sub>20</sub>, 15% for PAM<sub>140</sub>-*b*-PAA<sub>40</sub>

326 and PAM<sub>140</sub>-*b*-PAA<sub>60</sub> and 8% for PAM<sub>140</sub>-*b*-PAA<sub>78</sub>. The copolymer peak is broad and, as expected, the  
327 DEM shifts further from zero as the proportion of charged monomer increases in the composition of the  
328 copolymers. This can be verified by comparing the average electrophoretic mobility value  $\overline{\mu_{ep}^{diblock}}$  (given  
329 in Table 2) which varies between -19.5 TU and -24.1 TU from PAM<sub>140</sub>-*b*-PAA<sub>40</sub> to PAM<sub>140</sub>-*b*-PAA<sub>78</sub>.  
330 The greater the average molar mass of the polymer, the more dispersed its electrophoretic mobility, as  
331 demonstrated by the standard deviation  $\sigma_{\mu}$  which varies from 3.9 TU for PAM-*b*-PAA 70-20, to 6.2 TU  
332 for PAM-*b*-PAA 140-60.

333 The DEM of PEO based copolymers are presented in Figure 3B for linear PEO and Figure 3C for PEO  
334 grafted polyacrylates (P(PEGA)). Three populations are observed in both series: several small peaks  
335 associated with large electrophoretic mobility at -45TU are assigned to short oligomers of PAA, the  
336 weight percent of which is estimated to be lower than 10%. The sensitivity of the UV detection is too  
337 low to conclude about the presence / absence of PEO or P(PEGA) in the DHBC. The least mobile species  
338 at -28TU in Figure 3C corresponds to the MES used as mobility marker. The peak at intermediate values  
339 of mobility corresponds to the DHBC. The electrophoretic mobility of PEO-*b*-PAA ( $\overline{\mu_{ep}^{diblock}}$  ranging  
340 from -28 to -33 TU, Table 2) is significantly closer to zero than that of P(PEGA)-*b*-PAA copolymers (  
341  $\overline{\mu_{ep}^{diblock}}$  ranging from -36 to -38 TU, Table 2), although the molar masses are close. This is because  
342 P(PEGA), a comb-like polymer, is more compact than linear PEO of the same molar mass. As a  
343 consequence, the drag force due to the neutral block is lower for P(PEGA) than for PEO.

344 As for PAM-*b*-PAPTAC copolymer, PAPTAC homopolymer was detected at about +43TU, as a  
345 shoulder merged in the copolymer distribution, only for the  $DP_{neutral}/DP_0$  equal to 140/100 and 70/57  
346 samples. Figure 3D displays DEM ranged between +22 and +41 TU, with higher effective mobilities  
347 for the DHBC of highest charge. Comparison of PAM-*b*-PAA series with PAM-*b*-PAPTAC series  
348 illustrates the importance of the nature of the blocks on the drag effect of the neutral block. This effect  
349 is discussed in more detail in section 4.2.

350 As a general trend, electrophoretic mobilities of DHBC are always closer to zero than those of the  
351 homopolyelectrolyte which are:  $\mu_{\text{PAA}} = -42$  TU;  $\mu_{\text{PAPTAC}} = +44$  TU, and the electrophoretic mobility of  
352 the DHBC increases as the proportion of charged monomers in the DHBC increases (see Figure SI 20).  
353 In terms of EM dispersion, the least dispersed series is the P(PEGA)-*b*-PAA, with relative standard  
354 deviation of EM  $\sigma_{\mu} / \overline{\mu_{ep}^{diblock}}$  between 6.5% to 9%, followed by the PEO-*b*-PAA ( $\sigma_{\mu} / \overline{\mu_{ep}^{diblock}} \sim 5\%$  to  
355 16%) and the most disperse series is the PAM-*b*-PAA series with 20% to 30% relative standard deviation  
356 of the electrophoretic mobility. This dispersion in mobility results from both the level of control of the  
357 polymerization, and from the spatial extension of the polymer in the solvent. It can be explained by the  
358 chemistry of the RAFT polymerization (chain transfer agent R-SC(S)Z where Z is the activating group  
359 and R is the leaving group), for which the polymerization of acrylates is better controlled by  
360 dithiobenzoates (Z: -SC(S)Ph) ( $\mathcal{D} < 1.2$ ) than by ethyl xanthate (Z: -SC(S)OEt) ( $\mathcal{D} > 1.3$ ). Besides, the  
361 2-phenylacetate ester of PEO is a better homolytic leaving group than PAM.<sup>36</sup> Furthermore, the synthesis  
362 of PAM-*b*-PAA cumulates two successive RAFT/MADIX polymerizations of AM and AA, whereas the  
363 synthesis of PEO-*b*-PAA starts from a narrow PEO-CTA ( $\mathcal{D} = 1.04$ ) (PEO obtained by anionic  
364 polymerization) to perform a single RAFT polymerization of AA. This is consistent with the higher  
365 dispersity of PAM-*b*-PAA compared to PEO-*b*-PAA<sup>31</sup>. In addition, in reversible-deactivation radical  
366 polymerization<sup>37</sup>, at full conversion, the dispersity as defined by the ratio of the weight average molar  
367 mass over the number average molar mass, decreases when the *DP* increases<sup>38</sup>:

$$368 \quad \mathcal{D} = 1 + \frac{1}{DP} + \frac{1}{C_{ex}} \quad (8)$$

369 where *DP* is the targeted polymerization degree and  $C_{ex}$  is the degenerative chain transfer constant  
370 between dormant and active chains<sup>39, 40</sup>, which is consistent with a higher dispersity for a shorter  
371 poly(acrylic acid) block in PEO-*b*-PAA.

372 To get a better description of the copolymer distribution, it would be interesting to get a distribution of  
373 a new parameter which is directly related to the chemical composition of the copolymer instead of the

374 electrophoretic mobility, which is not linearly dependent on the copolymer composition. This is the  
 375 purpose of the two following sections.

376

	$DP_{neutral}$ $DP_0$	$\mu_{ep}^{diblock}$ peak max (TU)	$\overline{\mu_{ep}^{diblock}}$ integration (TU)	$\sigma_{\mu}$ (TU)	$X_{exp}$ peak max	$\overline{X_{exp}}$ by integration	$\sigma_{X_{exp}}$
<b>PAM-<i>b</i>-PAA</b>	70-20	-22	-19.9	3.89	0.61	1.12	0.45
	140-40	-19.1	-19.5	5.44	0.74	1.26	0.73
	140-60	-23.3	-21.4	6.19	0.58	1.05	1.0
	140-78	-25.3	-24.1	5.68	0.41	0.99	0.56
<b>PEO-<i>b</i>-PAA</b>	105-20	-31	-30.2	4.83	0.28	0.33	0.12
	105-30	-33.8	-33.2	2.45	0.18	0.21	0.06
	210-40	-28	-28.4	1.36	0.40	0.41	0.06
	210-50	-30.5	-30	1.97	0.30	0.34	0.64
<b>P(PEGA)-<i>b</i>-PAA</b>	21-11.5	-37.6	-38.6	3.61	0.059	0.043	0.09
	44.9-22.2	-37	-36.6	2.41	0.079	0.098	0.08
<b>PAM-<i>b</i>-PAPTAC</b>	70-30	34.6	33.9	3.18	0.19	0.25	0.12
	70-60	39.1	37.1	3.2	0.08	0.11	0.05
	140-60	34.2	32	4.1	0.21	0.32	0.39
	140-120	38.5	36.3	4.1	0.09	0.164	0.13

377 **Table 2.** Electrophoretic mobility  $\mu_{ep}^{diblock}$  at peak maximum and average value  $\overline{\mu_{ep}^{diblock}}$  obtained by peak  
 378 integration, standard deviation of the electrophoretic mobility distribution  $\sigma_{\mu}$ ,  $X_{exp}$  value at peak maximum and  
 379 average value  $\overline{X_{exp}}$  obtained by peak integration, standard deviation of the  $X_{exp}$  distribution  $\sigma_{X_{exp}}$  of all DHBC

380 studied in this work. Note that the peak of anisic acid was first subtracted before integration for the calculation of

381  $\overline{\mu_{ep}^{diblock}}$  and  $\sigma_{\mu}$  for PAM-*b*-PAA.

382

### 383 4.2. Change of variable from $\mu_{ep}$ to the retardation parameter $X_{exp}$

384 The drag effect of the neutral block can be expressed by the retardation parameter  $X_{exp}$  defined as :

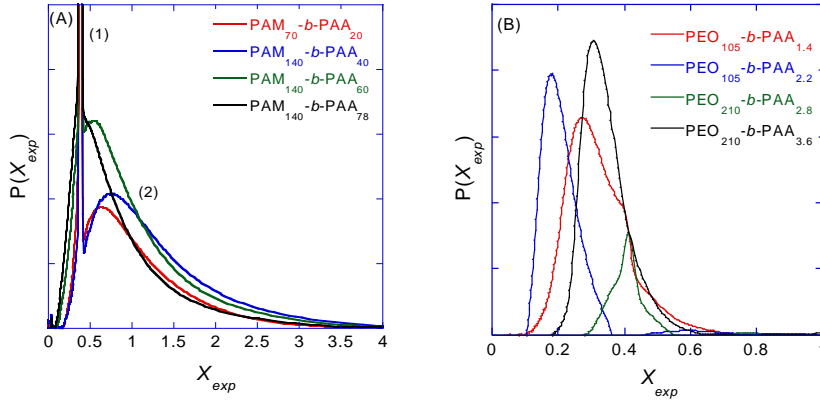
$$385 \quad X_{exp} = \frac{\mu_{ep}^0 - \mu_{ep}^{diblock}}{\mu_{ep}^{diblock}} = \frac{\mu_{ep}^0}{\mu_{ep}^{diblock}} - 1 \quad (9)$$

386 where  $\mu_{ep}^0$  is the electrophoretic mobility of the homopolyelectrolyte;  $\mu_{ep}^{diblock}$  is the electrophoretic

387 mobility of the copolymer.  $X_{exp}$  expresses the relative decrease of mobility due to the presence of the

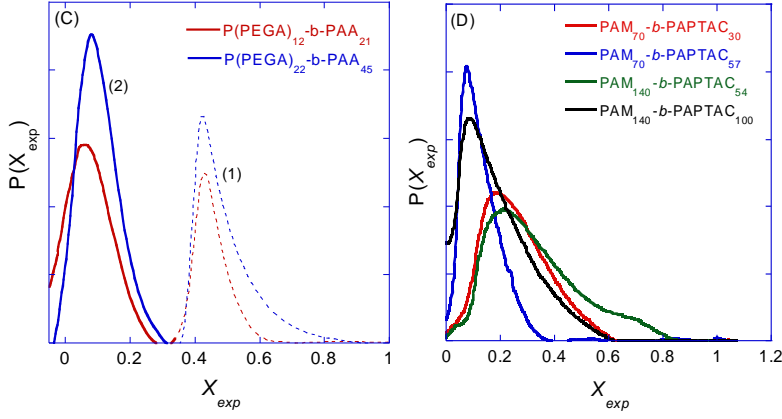
388 neutral block. It is positive and increases as the drag effect increases.

389



390

391



392

393 **Figure 4.** Distribution of retardation parameter  $X_{exp}$  for PAM-*b*-PAA (A) PEO-*b*-PAA (B), P(PEGA)-  
 394 *b*-PAA (C), and PAM-*b*-PAPTAC (D). Experimental conditions as in Figure 3  $X_{exp}$  was determined using  
 395 eq. (8), eq. (12) and  $\mu_{ep,PAA}^0 = -42TU$ ;  $\mu_{ep,PAPTAC}^0 = 44 TU$ . Assignment of the peaks: PAM-*b*-PAA (A):  
 396 anisic acid (1), DHBC (2); P(PEGA)-*b*-PAA (C): MES (1), DHBC (2). The degree of polymerization of  
 397 each block is specified on the graph.

398

399 The new experimental variable,  $X_{exp}$ , not only points out the friction due to the neutral block but is also  
 400 more directly related to the composition of the DHBC. Introducing equation (9) in the various  
 401 expressions of the electrophoretic mobility (equations 1 to 3),  $X_{exp}$ , can be expressed as a function of the  
 402 ratio between the degrees of polymerization of the neutral  $DP_{neutral}$  and the charged blocks  $DP_0$ . Taking  
 403 into account the hydrodynamic coupling (model 1),  $X_{exp}$  reads:

$$404 \quad X_{model,1} = \frac{1}{N_{blob}} = \frac{\alpha}{DP_0} \quad (10a)$$

405 and can be further developed as a function of the Kuhn lengths of the neutral block,  $b_{K_1}$ , and of the  
 406 polyelectrolyte,  $b_{K_0}$ :<sup>15, 41</sup>

$$407 \quad X_{model,1} = \alpha_1 \frac{DP_{neutral}}{DP_0} \quad (10b)$$

408 with  $\alpha_1 = \frac{b_1 b_{K_1}}{b_0 b_{K_0}}$  (10c)

409 where  $b_l$  is the neutral monomer size. The Kuhn statistical segment length (which is twice the persistence  
 410 length) is a measure of the polymer stiffness. Parameter  $\alpha_l$  in Equation (10b) is a relative friction  
 411 coefficient and it is non-dimensional. Since the polyelectrolyte is generally stiffer than the neutral block,  
 412  $\alpha_l$  is often much smaller than unity<sup>15</sup>.

413 As for model 2, it is clear from equation (2) that the  $X$  parameter is directly expressed as the ratio of the  
 414 hydrodynamic radius of each block:

415  $X_{model,2} = \frac{R_h^{neutral}}{R_h^0}$  (11a)

416 which can be rewritten as a function of the degrees of polymerization of each block by:

417  $X_{model,2} = \frac{C_1 DP_{neutral}^{a_1}}{C_0 DP_0^{a_0}}$  (11b)

418 where  $C_1$  (resp.  $C_2$ ) and  $a_1$  (resp.  $a_2$ ) are, respectively, the prefactors and exponents for the neutral (resp.  
 419 charged) block in the relationship between  $R_h$  and  $DP$ . Note that  $a_0$  and  $a_1$  are supposed to be close to  
 420 0.5-0.6 for coil conformations, and slightly higher for more extended conformations.

421 As for model 3 (see equation (3)), the  $X$  parameter is directly expressed as:

422  $X_{model,3} = \frac{2R_h^{neutral} \ln DP_0}{b_0 DP_0}$  (12a)

423 Injecting  $R_h^{neutral}$  in equation (9a) leads to:

424  $X_{model,3} = \frac{2C_1 DP_{neutral}^{a_1} \ln DP_0}{b_0 DP_0}$  (12b)

425 Finally, equations (10b) (11b) and (12b) demonstrates that, whatever the considered model, the  $X$   
 426 parameter is related to a compositional ratio between the neutral and the charged blocks with, however,  
 427 different scaling dependences with the  $DP$  of each block, and with an additional logarithmic term in  
 428 model 3. It is worth noting that in the case of hydrodynamic coupling (model 1), the newly introduced  
 429 variable varies linearly with the ratio of degree of polymerization of the two blocks.

430 The distributions of the  $X_{exp}$  parameter are simply deduced from the distribution of electrophoretic  
 431 mobility using the following equation (Figure 2, step 4)<sup>11</sup>:

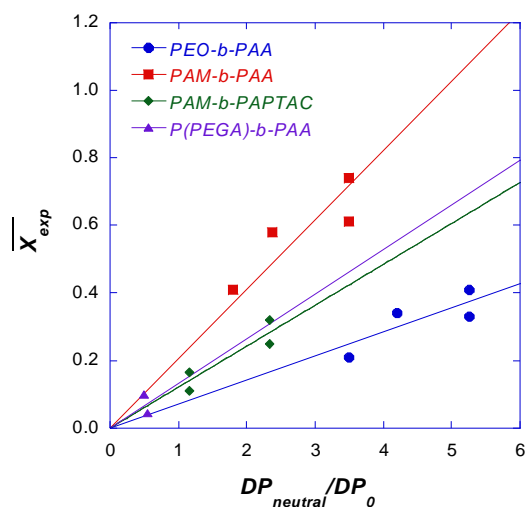
$$432 \quad P(X_{exp}) = \left| \frac{1}{\frac{\partial X_{ep}}{\partial \mu_{ep}}} \right| P(\mu_{ep}) = \mu_{ep}^2 P(\mu_{ep}) \quad (13)$$

433 All the  $X_{exp}$  distributions are presented in Figure 4. Since  $\mu_{ep}$  and  $X_{exp}$  are not linearly related, the change  
 434 of the variable from  $\mu_{ep}$  to  $X_{exp}$  modify the form of the distribution. The different moments characterizing  
 435 the distribution of  $X_{exp}$  are calculated using similar relations as equations (6) and (7) and are reported in  
 436 Table 2.

437  $X_{exp}$  range varies between 0.1-3 for PAM-*b*-PAA, 0.1-0.7 for PEO-*b*-PAA, 0-0.3 for P(PEGA)-*b*-PAA  
 438 and 0-0.8 for PAM-*b*-PAPTAC. The dispersion of the retardation parameter  $X_{exp}$  expressed as  $\sigma_{X_{exp}}$   
 439 values (Table 2) follows the following order: P(PEGA)-*b*-PAA < PEO-*b*-PAA ~ PAM-*b*-PAPTAC <  
 440 PAM-*b*-PAA. The dispersion of the retardation parameter cannot be interpreted as a dispersity in molar  
 441 mass or in composition since the retardation parameter will change with these chemical features in a  
 442 way that depends on the conformation of the blocks. So, a further step is needed to get the composition  
 443 dispersion.



444 **4.3. Change of variable from  $X_{exp}$  to chemical composition ratio**



445  
 446 **Figure 5.** Plot of  $\overline{X}_{exp}$  against  $\frac{DP_{neutral}}{DP_0} \cdot \overline{X}_{exp}$  was determined by using eq.(6) after replacing  $\mu_{ep}$  by

447  $X_{exp} \cdot \frac{DP_{neutral}}{DP_0}$  was obtained by NMR (see Table 1). Least-square linear regressions provide the following  
 448 experimental slopes: 0.071+/-0.005 for PEO-b-PAA; 0.12+/-0.01 for PAM-b-PAPTAC; 0.13 +/- 0.01  
 449 for P(PEGA)-b-PAA; 0.21+/-0.02 for PAM-b-PAA.

450  
 451 To go further in the interpretation and in the process of the experimental data, it is crucial to identify the  
 452 model which is best adapted to describe the electrophoretic behavior of the DHBC investigated in this  
 453 work. To assess the validity of model 1 (hydrodynamic coupling between blocks, see section 2.3),  $\overline{X}_{exp}$   
 454 was plotted against  $\frac{DP_{neutral}}{DP_0}$  in Figure 5 for the four DHBC families.

455 **Table 3.** Characteristic parameters of neutral and charged blocks constituting the DHBC studied in this work.  $M_w$   
 456 are expressed in g/mol.

	$b_l$ (nm)	$b_{k_1}$ (nm)	$R_h^{neutral}$ (nm) <sup>a</sup>	457
PAM	0.25	0.6 <sup>42</sup>	$0.01447 \times M_w^{0.57}$ <sup>43</sup>	458
PEO	0.3 <sup>44</sup>	0.74 <sup>44</sup>	$0.02398 \times M_w^{0.53}$ <sup>45</sup>	459
	$b_0$ (nm)	$b_{k_0}$ (nm)	$R_h^0$ (nm)	460
PAA	0.25	2.5 <sup>46</sup>	$0.007906 \times M_w^{0.585}$ <sup>2</sup>	461
PAPTAC	approximated as PAA			462

463

464 <sup>a</sup> From Mark-Houwink parameters using  $R_h = \left( \frac{3[\eta]M}{10\pi N_A} \right)^{1/3}$ , where  $[\eta]$  is the intrinsic viscosity and  $N_A$  is the

465 Avogadro number. from ref<sup>46</sup> (see Table 1 and Figure 13(a) herein).

466

467 The results are consistent with model 1 which predicts a linear dependence of the retardation parameter

468  $\overline{X_{exp}}$  on the ratio of degree of polymerization  $\frac{DP_{neutral}}{DP_0}$ . The slopes determined from the graph in Figure

469 5 correspond to the parameter  $\alpha_1$  in equation (10b) which can be calculated from equation (10c).

470 Experimentally, the numerical values of the slopes  $\alpha_{1,exp}$  are in the range of ~0.1-0.2. Taking the

471 characteristic parameters (Kuhn lengths, monomer dimensions) given in Table 3 leads to  $\alpha_l=0.24$  (vs

472  $\alpha_{1,exp}=0.21\pm 0.02$  experimentally obtained) for PAM-*b*-PAA,  $\alpha_l=0.36$  (vs  $\alpha_{1,exp}=0.071\pm 0.005$ ) for

473 PEO-*b*-PAA, and  $\alpha_l=0.24$  (vs  $\alpha_{1,exp}=0.12\pm 0.01$ ) for PAM-*b*-PAPTAC. Theoretical values of  $\alpha_l$  are in

474 a reasonably good agreement with the experimental ones, knowing the uncertainty on the persistence

475 length (notably for the polyelectrolyte blocks) and monomer sizes. As for P(PEGA)-*b*-PAA, we only

476 get an estimation of  $\alpha_{1,exp}=0.13$ , since the P(PEGA) Kuhn length is not available in the literature. From

477 Figure 5, we can conclude that the linear correlation between  $\overline{X_{exp}}$  and  $\frac{DP_{neutral}}{DP_0}$  is confirmed and that

478 model 1 (with hydrodynamic coupling between the two blocks) can be used to transform the  $X_{exp}$

479 distributions into compositional  $\frac{DP_{neutral}}{DP_0}$  distributions. As for models 2 and 3, they lead to poor

480 correlations between theoretical  $X_{model,i}$  versus experimental  $\overline{X_{exp}}$  values (see Figure 6).

481 The knowledge of  $\alpha_l$  provides the last relation necessary to carry on the general scheme presented in

482 Figure 2 to its end and which leads to the distribution of ratio of chemical composition. In practice, we

483 used  $\alpha_{l,exp}$  obtained in Figure 5 together with equation (10b) to transform the data of Figures 4A to 4D

484 into the distributions presented in Figures 7A to 7D, using the following equation:

485 
$$P\left(\frac{DP_{neutral}}{DP_0}\right) = \frac{P(X)}{\frac{\partial\left(\frac{DP_{neutral}}{DP_0}\right)}{\partial X}} = \alpha_l P(X) \quad (14)$$

486 Since  $X_{exp}$  and  $\frac{DP_{neutral}}{DP_0}$  are linearly correlated, the shapes of both distributions are similar. However,

487 reading  $\frac{DP_{neutral}}{DP_0}$  axis, which corresponds to a compositional ratio, is more convenient for the practitioners

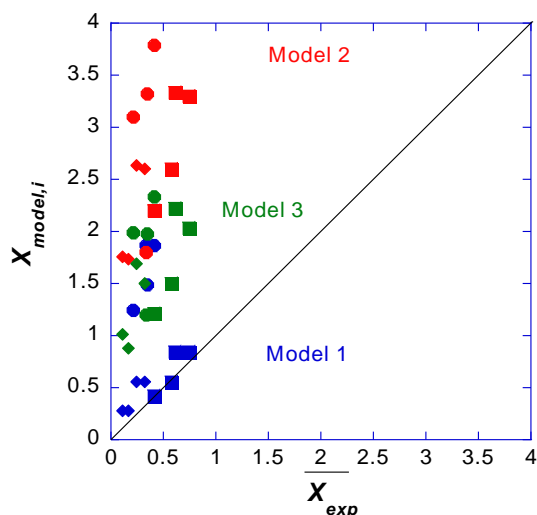
488 than keeping the  $X_{exp}$  scale. Moreover, and as previously anticipated, since the  $\alpha_l$  coefficients are

489 different from one DHBC to another, the distribution in  $\frac{DP_{neutral}}{DP_0}$  allows a better comparison between

490 them. On the whole, the dispersion of the composition ratio are in the order of: P(PEGA)-*b*-PAA <

491 PAM-*b*-PAPTAC ~ PEO-*b*-PAA < PAM-*b*-PAA.

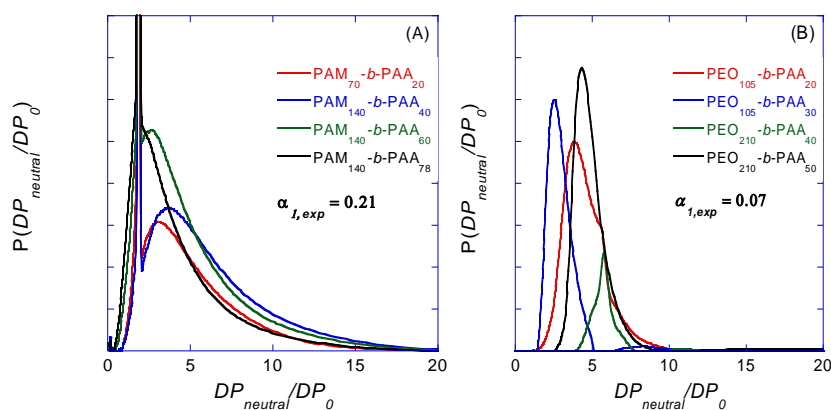
492



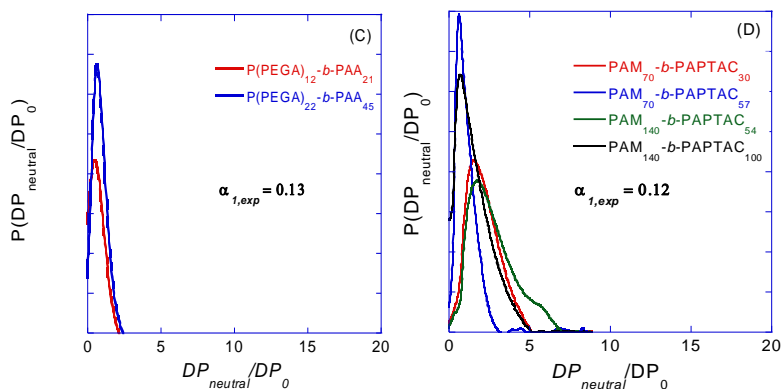
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494 **Figure 6.** Comparison between  $X_{model,i}$  and  $\overline{X}_{exp}$  for the three different models using theoretical  
 495 parameters given in Table 3. PAM-*b*-PAPTAC (◆); PEO-*b*-PAA (●); PAM-*b*-PAA (■).  $\overline{X}_{exp}$  was  
 496 determined by integration of the DHBC peak (in  $X$  scale). For all  $X_{model,i}$  calculations, theoretical  $DP_{neutral}$   
 497 and  $DP_0$  were used.  $X_{model,1}$  was determined according to equations (10b) and (10c),  $X_{model,2}$  according  
 498 to equation (11a) and  $X_{model,3}$  according to equations (12a), with the characteristic numerical parameters  
 499 given in Table 3.

500



501



502

503 **Figure 7.** Distribution of composition in terms of the ratio of the degrees of polymerization of both  
 504 blocks for PAM-*b*-PAA (A), PEO-*b*-PAA (B), P(PEGA)-*b*-PAA (C), and PAM-*b*-PAPTAC (D).

505 Experimental conditions as in Figure 3.  $\frac{DP_{neutral}}{DP_0}$  was determined using eq. (10b) and  $p\left(\frac{DP_{neutral}}{DP_0}\right)$  was  
 506 obtained using eq. (14). In (C), the MES peak has been removed. In (A), the sharp peak is a mobility  
 507 marker (anisic acid) and was deleted before peak integration.

508

## 509 Conclusion

510 In an effort to make information provided by capillary electrophoresis more directly useful for polymer  
 511 chemists, a protocol was proposed to convert electrophoretic mobility distributions of double  
 512 hydrophilic block copolymers into distributions of chemical composition ratios. This ratio of  
 513 composition is expressed as the ratio of the degrees of polymerization of each block  $\frac{DP_{neutral}}{DP_0}$ . To get this  
 514 composition ratio, we have introduced the retardation parameter  $X$  which takes into account the drag  
 515 force exerted by the neutral block on the polyelectrolyte. The distribution of  $X$  that characterizes a DHBC  
 516 is readily obtained from the experimental electropherogram and the relation between  $X$  and the ratio of  
 517  $DP$ . The latter is available from different models for electrophoretic mobility of composite objects. A  
 518 linear relation has been found experimentally between the retardation parameter  $X$  and the ratio of  $DP$ s,  
 519 within each of the four families of DHBC studied in this work. This result is consistent with the model  
 520 of electrophoretic mobility of Long *et al.* that takes into account hydrodynamic coupling, although the

521 prefactors are slightly overestimated. Our experimental findings not only support the theoretical  
522 prediction, but also facilitate the last step of data transformation, from distribution of  $X$  into distributions  
523 of ratios of  $DP$ .

524 The dispersions in composition are in the order of: P(PEGA)-*b*-PAA < PEO-*b*-PAA ~ PAM-*b*-PAPTAC  
525 < PAM-*b*-PAA. Therefore, we can conclude that in the DHBC families, the PAM block leads to broader  
526 composition ratio distributions compared to a PEO block, when associated to a PAA block. Similarly,  
527 the P(PEGA) block lead to less disperse composition ratio distributions compared to a PEO block, when  
528 associated to a PAA block. Finally, PAA associated with PAM leads to broader composition ratio  
529 distributions compared to PAPTAC associated with PAM. The relatively low composition dispersity of  
530 the PEO-PAA block copolymer is most likely due to the low dispersity of the PEO block, prepared by  
531 anionic polymerization, and the use of a dithiobenzoate chain transfer agent, which has a higher chain  
532 transfer constant and thus gives narrower molar mass distributions than the xanthate chain transfer agent  
533 used to prepare the PAM-PAA and PAM-PAPTAC block copolymers. The use of a trithiocarbonate  
534 chain transfer agent and a relatively short P(PEGA) block leads to a fairly narrow composition  
535 distribution for P(PEGA)-PAA block copolymers.

536 Finally, the transformation of electrophoretic mobility distributions into composition ratio distributions  
537 significantly improved the comparison of the distributions between the different copolymer families,  
538 since it takes into account the differences in expansion and drag force according to the chemical nature  
539 of the blocks.

#### 540 **Supporting Information.**

541 Synthetic pathway, SEC and NMR characterizations, raw electropherograms are provided for all dibloc  
542 copolymers studied in this work.

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546 **References**

- 547 1. Thevarajah, J. J.; Sutton, A. T.; Maniego, A. R.; Whitty, E. G.; Harrison, S.; Cottet, H.;  
548 Castignolles, P.; Gaborieau, M., Quantifying the Heterogeneity of Chemical Structures in Complex  
549 Charged Polymers through the Dispersity of Their Distributions of Electrophoretic Mobilities or of  
550 Compositions. *Anal. Chem.* **2016**, *88* (3), 1674-1681.
- 551 2. Morel, A.; Cottet, H.; In, M.; Deroo, S.; Destarac, M., Electrophoretic Behavior of Amphiphilic  
552 Diblock Copolymer Micelles. *Macromolecules* **2005**, *38* (15), 6620-6628.
- 553 3. Sutton, A. T.; Read, E.; Maniego, A. R.; Thevarajah, J. J.; Marty, J. D.; Destarac, M.; Gaborieau,  
554 M.; Castignolles, P., Purity of Double Hydrophilic Block Copolymers Revealed by Capillary  
555 Electrophoresis in the Critical Conditions. *J. Chromatogr. A* **2014**, *1372C*, 187-195.
- 556 4. Javakhishvili, I.; Jankova, K.; Hvilsted, S., Neutral, Anionic, Cationic, and Zwitterionic Diblock  
557 Copolymers Featuring Poly(2-methoxyethyl acrylate)“Hydrophobic” Segments. *Polym. Chem.-UK*  
558 **2013**, *4* (3), 662-668.
- 559 5. Delplace, V.; Harrison, S.; Tardy, A.; Gimes, D.; Guillaeneuf, Y.; Nicolas, J., Nitroxide-  
560 Mediated Radical Ring-Opening Copolymerization: Chain-End Investigation and Block Copolymer  
561 Synthesis. *Macromol. Rapid Comm.* **2014**, *35* (4), 484-491.
- 562 6. Nejad, E. H.; Castignolles, P.; Gilbert, R. G.; Guillaeneuf, Y., Synthesis of Methacrylate  
563 Derivatives Oligomers by Dithiobenzoate-RAFT-Mediated Polymerization. *J. Polym. Sci. A1* **2008**, *46* (6),  
564 2277-2289.
- 565 7. Jacquin, M.; Muller, P.; Cottet, H.; Crooks, R.; Théodoly, O., Controlling the Melting of  
566 Kinetically Frozen Poly(butyl acrylate-*b*-acrylic acid) Micelles via Addition of Surfactant. *Langmuir* **2007**,  
567 *23* (20), 9939-9948.

- 568 8. Jacquin, M.; Muller, P.; Lizarraga, G.; Bauer, C.; Cottet, H.; Théodoly, O., Characterization of  
569 Amphiphilic Diblock Copolymers Synthesized by MADIX Polymerization Process. *Macromolecules* **2007**,  
570 *40* (8), 2672-2682.
- 571 9. Jacquin, M.; Muller, P.; Cottet, H.; Théodoly, O., Self-Assembly of Charged Amphiphilic Diblock  
572 Copolymers with Insoluble Blocks of Decreasing Hydrophobicity: From Kinetically Frozen Colloids to  
573 Macrosurfactants. *Langmuir* **2010**, *26* (24), 18681-18693.
- 574 10. Anik, N.; Airiau, M.; Labeau, M.-P.; Vuong, C.-T.; Reboul, J.; Lacroix-Desmazes, P.; Gérardin,  
575 C.; Cottet, H., Determination of Polymer Effective Charge by Indirect UV Detection in Capillary  
576 Electrophoresis: Toward the Characterization of Macromolecular Architectures. *Macromolecules*  
577 **2009**, *42* (7), 2767-2774.
- 578 11. Chamieh, J.; Martin, M.; Cottet, H., Quantitative Analysis in Capillary Electrophoresis:  
579 Transformation of Raw Electropherograms Into Continuous Distributions. *Anal. Chem.* **2015**, *87* (2),  
580 1050-1057.
- 581 12. Long, D.; Ajdari, A., Electrophoretic Mobility of Composite Objects in Free Solution: Application  
582 to DNA Separation. *Electrophoresis* **1996**, *17* (6), 1161-1166.
- 583 13. Long, D.; Viovy, J.-L.; Ajdari, A., Simultaneous Action of Electric Fields and Nonelectric Forces  
584 on a Polyelectrolyte: Motion and Deformation. *Phys. Rev. Lett.* **1996**, *76* (20), 3858-3861.
- 585 14. Vreeland, W. N.; Desruisseaux, C.; Karger, A. E.; Drouin, G.; Slater, G. W.; Barron, A. E., Molar  
586 Mass Profiling of Synthetic Polymers by Free-Solution Capillary Electrophoresis of DNA- Polymer  
587 Conjugates. *Anal. Chem.* **2001**, *73* (8), 1795-1803.
- 588 15. Nedelcu, S.; Slater, G. W., Branched Polymeric Labels Used as Drag-Tags in Free-Solution  
589 Electrophoresis of ssDNA. *Electrophoresis* **2005**, *26* (21), 4003-4015.
- 590 16. Chubynsky, M. V.; Slater, G. W., Theory of End-Labeled Free-Solution Electrophoresis: Is the  
591 End Effect Important? *Electrophoresis* **2014**, *35* (5), 596-604.
- 592 17. Chubynsky, M. V.; Slater, G. W., Electrophoresis of Heteropolymers. Effect of Stiffness.  
593 *Macromolecules* **2015**, *48* (16), 5899-5913.



- 594 18. Desruisseaux, C.; Long, D.; Drouin, G.; Slater, G. W., Electrophoresis of Composite Molecular  
595 Objects. 1. Relation between Friction, Charge, and Ionic Strength in Free Solution. *Macromolecules*  
596 **2001**, *34* (1), 44-52.
- 597 19. Schmidt, B. V. K. J., Double Hydrophilic Block Copolymer Self-Assembly in Aqueous Solution.  
598 *Macromol. Chem. Phys.* **2018**, *219* (7), 1700494.
- 599 20. Guragain, S.; Bastakoti, B. P.; Malgras, V.; Nakashima, K.; Yamauchi, Y., Multi-Stimuli-  
600 Responsive Polymeric Materials. *Chem-Eur. J.* **2015**, *21* (38), 13164-74.
- 601 21. Perrier, S., 50th Anniversary Perspective: RAFT Polymerization—A User Guide.  
602 *Macromolecules* **2017**, *50* (19), 7433-7447.
- 603 22. Matyjaszewski K., X. J., Atom Transfer Radical Polymerization. *Chem. Rev.* **2001**, *100*, 2921-  
604 2990.
- 605 23. Nicolas, J.; Guillaeneuf, Y.; Lefay, C.; Bertin, D.; Gigmes, D.; Charleux, B., Nitroxide-Mediated  
606 Polymerization. *Prog. Polym. Sci.* **2013**, *38* (1), 63-235.
- 607 24. Destarac, M., Industrial Development of Reversible-Deactivation Radical Polymerization: is the  
608 Induction Period Over? *Polym. Chem.-UK* **2018**, *9* (40), 4947-4967.
- 609 25. Colfen, H., Double-Hydrophilic Block Copolymers: Synthesis and Application as Novel  
610 Surfactants and Crystal Growth Modifiers. *Macromol. Rapid Comm.* **2001**, *22*, 219-252.
- 611 26. Loh, X. J.; del Barrio, J.; Toh, P. P. C.; Lee, T.-C.; Jiao, D.; Rauwald, U.; Appel, E. A.; Scherman,  
612 O. A., Triply Triggered Doxorubicin Release From Supramolecular Nanocontainers. *Biomacromolecules*  
613 **2012**, *13* (1), 84-91.
- 614 27. Baccile, N.; Reboul, J.; Blanc, B.; Coq, B.; Lacroix-Desmazes, P.; In, M.; Gerardin, C., Ecodesign  
615 of Ordered Mesoporous Materials Obtained with Switchable Micellar Assemblies. *Angew. Chem. Int.*  
616 *Edit.* **2008**, *47*, 8433-8437.
- 617 28. Desruisseaux, C.; Drouin, G.; Slater, G. W., Electrophoresis of Composite Molecular Objects. 2.  
618 Competition between Sieving and Frictional Effects in Polymer Solutions. *Macromolecules* **2001**, *34*  
619 (15), 5280-5286.

- 620 29. Long, D.; Dobrynin, A. V.; Rubinstein, M.; Ajdari, A., Electrophoresis of polyampholytes. *The J.*  
621 *Chem. Phys.* **1998**, *108* (3), 1234-1244.
- 622 30. Layrac, G.; Gérardin, C.; Tichit, D.; Harrisson, S.; Destarac, M., Hybrid Polyion Complex  
623 Micelles from Poly(Vinylphosphonic Acid)-Based Double Hydrophilic Block Copolymers and Divalent  
624 Transition Metal Ions. *Polymer* **2015**, *72*, 292-300.
- 625 31. Taton, D.; Wilczewska, A.-Z.; Destarac, M., Direct Synthesis of Double Hydrophilic Statistical  
626 Di- and Triblock Copolymers Comprised of Acrylamide and Acrylic Acid Units via the MADIX Process.  
627 *Macromol. Rapid Comm.* **2001**, *22* (18).
- 628 32. Bathfield, M.; Warnant, J.; Gérardin, C.; Lacroix-Desmazes, P., Asymmetric Neutral, Cationic  
629 and Anionic PEO-Based Double-Hydrophilic Block Copolymers (DHBCs): Synthesis and Reversible  
630 Micellization Triggered by Temperature or pH. *Polym. Chem.-UK* **2015**, *6* (8), 1339-1349.
- 631 33. Kuhnel, E.; Laffan, D. D.; Lloyd-Jones, G. C.; Martinez Del Campo, T.; Shepperson, I. R.;  
632 Slaughter, J. L., Mechanism of Methyl Esterification of Carboxylic Acids by Trimethylsilyldiazomethane.  
633 *Angew. Chem. Int. Edit* **2007**, *46* (37), 7075-8.
- 634 34. Boursier, T.; Chaduc, I.; Rieger, J.; D'Agosto, F.; Lansalot, M.; Charleux, B., Controlled Radical  
635 Polymerization of Styrene in Miniemulsion Mediated by PEO-based Trithiocarbonate Macromolecular  
636 RAFT Agents. *Polym. Chem.-UK* **2011**, *2* (2), 355-362.
- 637 35. Chaduc, I.; Crepet, A.; Boyron, O.; Charleux, B.; D'Agosto, F.; Lansalot, M., Effect of the pH  
638 on the RAFT Polymerization of Acrylic Acid in Water. Application to the Synthesis of Poly(acrylic acid)-  
639 Stabilized Polystyrene Particles by RAFT Emulsion Polymerization. *Macromolecules* **2013**, *46* (15),  
640 6013-6023.
- 641 36. Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process ? A  
642 Third Update. *Aust. J. of Chem.* **2012**, *65* (8), 985.
- 643 37. Jenkins, A. D.; Jones, R. G.; Moad, G., Terminology for Reversible-Deactivation Radical  
644 Polymerization Previously Called "Controlled" Radical or "Living" Radical Polymerization (IUPAC  
645 Recommendations 2010). *Pure Appl. Chem.* **2009**, *82* (2).

- 646 38. Harrisson, S., The Downside of Dispersity: Why the Standard Deviation is a Better Measure of  
647 Dispersion in Precision Polymerization. *Polym. Chem.-UK* **2018**, *9* (12), 1366-1370.
- 648 39. Goto, A.; Fukuda, T., Kinetics of Living Radical Polymerization. *Prog. Polym. Sci.* **2004**, *29* (4),  
649 329-385.
- 650 40. Molina, E.; Warnant, J.; Mathonnat, M.; Bathfield, M.; In, M.; Laurencin, D.; Jerome, C.;  
651 Lacroix-Desmazes, P.; Marcotte, N.; Gerardin, C., Drug-Polymer Electrostatic Complexes as New  
652 Structuring Agents for the Formation of Drug-Loaded Ordered Mesoporous Silica. *Langmuir* **2015**, *31*  
653 (47), 12839-12844.
- 654 41. McCormick, L.; Slater, G.; Karger, A.; Vreeland, W.; Barron, A.; Desruisseaux, C.; Drouin, G.,  
655 Capillary Electrophoretic Separation of Uncharged Polymers Using Polyelectrolyte Engines: Theoretical  
656 Model. *J. Chromatogr. A* **2001**, *924* (1-2), 43-52.
- 657 42. Zhang, W.; Zou, S.; Wang, C.; Zhang, X., Single Polymer Chain Elongation of Poly(N-  
658 isopropylacrylamide) and Poly(acrylamide) by Atomic Force Microscopy. *J. Phys. Chem. B* **2000**, *104*  
659 (44), 10258-10264.
- 660 43. J. Brandrup, E. H. I., E. A. Grulke *Polymer Handbook, Fourth Edition, Vol. 2.* John Wiley and Sons,  
661 Hoboken, New Jersey ed.; 1999; Vol. 2.
- 662 44. Lee, H.; Venable, R. M.; MacKerell, A. D.; Pastor, R. W., Molecular Dynamics Studies of  
663 Polyethylene Oxide and Polyethylene Glycol: Hydrodynamic Radius and Shape Anisotropy. *Biophys. J.*  
664 **2008**, *95* (4), 1590-1599.
- 665 45. Armstrong, J. K.; Wenby, R. B.; Meiselman, H. J.; Fisher, T. C., The Hydrodynamic Radii of  
666 Macromolecules and Their Effect on Red Blood Cell Aggregation. *Biophys. J.* **2004**, *87* (6), 4259-4270.
- 667 46. Cranford, S. W.; Buehler, M. J., Variation of Weak Polyelectrolyte Persistence Length through  
668 an Electrostatic Contour Length. *Macromolecules* **2012**, *45* (19), 8067-8082.

669

670 **For TOC only:**

### Composition distributions by Capillary Electrophoresis

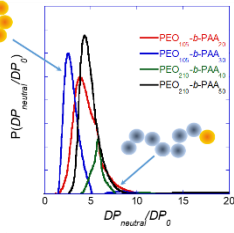
neutral and charged diblock copolymers

- Retardation parameter:

$$X_{\text{sep}} = \frac{\mu_{\text{sp}}^0}{\mu_{\text{sp}}^{\text{block}}} - 1$$

- Composition ratio:

$$\frac{DP_{\text{neutral}}}{DP_0}$$



671

672