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3 **Water structure change-induced expansion and collapse of zwitterionic polymers**
4 **surface-grafted onto carbon black**

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17
18 Keywords: polymer brush; brush collapse; carbon black colloidal stability;
19 poly(sulfobetaine)s; urea

20
21 Running head: surface-grafted polyzwitterions on carbon black

22
23 **ABSTRACT**

24 We demonstrate the expansion and collapse of surface-grafted zwitterionic polymer brushes
25 in water caused by the addition of urea. We hypothesise that at low urea concentration this is
26 an effect of an ion-dipole interaction between urea and the polymer and at high urea
27 concentration an effect of a change of water structure causing change of solvation of the
28 brushes and hence a change in the dipole-dipole interaction, and that it is analogous to the
29 effects of urea on protein stability.

30 -----
31 In this work we report grafting of zwitterionic polymer brushes onto carbon black by surface-
32 initiated atom transfer radical polymerization (SI-ATRP)^[1-4] and the effect of urea on the
33 colloidal stability in water. Zwitterionic polymer brushes have been the subject of intensive
34 research due to their unique properties.^[5-9] Compared to these polymers attached to flat
35 surfaces, spherical zwitterionic polymer brushes may exhibit some interesting solution
36 properties because of an effect of surface curvature.^[10] Temperature- and ionic strength-
37 induced phase behavior of poly(sulfobetaine)-grafted polymer colloidal particles^[11] and silica

38 particles^[12-13] have been investigated. Urea is well known for the induction of protein
39 unfolding, enhancing solvation of ionic groups and reducing aggregation of ion pairing
40 properties as a consequence of the effect on hydrophobic interactions.^[14-15] Urea at
41 concentrations up to ~2.5M can also lower the upper critical solution temperature (UCST) and
42 promote water solubility of poly(sulfobetaine)s. Despite a large volume of work on the
43 solvation of poly(sulfobetaine)s^[16], these effects of urea have only been sketchily studied and
44 attributed to changes in hydrogen bonding to the sulfonate group.^[17-18] The present work
45 presents a study of a colloidal-polymer system that consists of a spherical carbon black (CB)
46 colloidal core with attached sulfobetaine-based zwitterionic polymer chains. The colloidal
47 stability of polyzwitterion-grafted CB nanoparticles strongly depended on the concentration
48 of urea: a small addition of urea increased the water dispersibility while a large addition
49 resulted in an unstable suspension. We deduce that the brush, collapsed in pure water, is
50 expanded in the presence of a low concentration of urea and collapsed at high concentration
51 and attribute the effect to a change in solvation of the zwitterion dipoles caused by the
52 interaction of urea both with the zwitterionic groups and with water.

53

54 In order to graft polymer brushes from carbon black (CB) surfaces, carboxylic acid-
55 functionalized CB nanoparticles were firstly obtained by chemical treatment with nitric acid
56 for 24 h. The carboxylate group on the oxidized CB nanoparticles was then successively
57 converted to hydroxyl group by a carbodiimide-facilitated coupling reaction, followed by the
58 attachment of the ATRP initiator via a nucleophilic substitution reaction (figure 1).

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64 **Table 1.** Elemental analysis of bare CB, CB-Br and CB-PMPDSAHA nanoparticles.
65

Sample	C [w/w%]	N [w/w%]	S [w/w%]	Br [w/w%]
Bare CB	45.14	0.44	—	—
CB-Br	48.46	9.24	—	20.80
CB-PMPDSAHA	40.29	5.18	0.97	3.32

66 Analysis performed by The Campbell Microanalytical Laboratory, University of Otago, New Zealand.
67

68
69 Surface-initiated ATRP polymerization on the CB nanoparticles to form brushes of poly(3-
70 (methacryloylamido)propyl)-N,N'-dimethyl(3-sulfopropyl)ammonium hydroxide
71 (PMPDSAHA) was carried out in water/methanol (4/1, v/v) at room temperature with
72 CuBr/CuBr₂/Bipyridine as catalyst. Table 1 shows the elemental analysis of the powder at
73 different stages of the preparation. The "halogen exchange" technique of CuBr catalyst with a
74 bromo initiator provides a better control of the polymerization.^[19] The addition of [Cu^I] in
75 polymerization can control the rate of deactivation and hence avoid coupling of the organic
76 radicals which causes an increase in the deactivator concentration.^[20] Huck et al.^[21] have
77 reported that the internal structure of polymer brushes could be affected by the [Cu^I]/[Cu^{II}]
78 ratio. Here, zwitterionic polymer brushes were grafted from CB surfaces using [Cu^I]/[Cu^{II}] =
79 10. The polymerization was ceased after 15 h and chemical composition of the resulting CB-
80 polymer nanoparticles was characterized by elemental analysis and FTIR spectra. FTIR
81 spectra confirmed the successful growth of poly(sulfobetaine), as shown in Figure 2: in the
82 spectrum of the CB-COOH nanoparticles (Figure 2b), the peak at ~1720 cm⁻¹ is attributed to
83 the C=O stretch of the carboxylic (COOH) group, which is absent in the bare CB
84 nanoparticles (Figure 2c); the S=O symmetric (~1205 cm⁻¹) and symmetric stretching
85 vibration (~1038 cm⁻¹) of the sulfonate group,^[22] are observable in the spectrum of
86 PMPDSAHA-CB nanoparticles; the peak at ~965 cm⁻¹ related to quaternary ammonium (-N⁺-

87 $(\text{CH}_3)_2^-$ ^[23] further confirms the successful grafting of sulfobetaine polymer brushes (Figure
88 2). The elemental analysis of bare CB, CB-Br and CB-PMPDSAH nanoparticles (table 1) first
89 confirms, through the increased amount of nitrogen and the significant presence of bromine in
90 CB-Br, a successful attachment of ATRP initiator. From the known molecular composition,
91 the calculation presented in the SI shows that the particle mass is dominated by that of bound
92 initiator, of which ~40 mol% retained the bromine: the remainder is likely to have been lost
93 by hydrolysis to the tertiary alcohol. The presence of polyzwitterion grafts is confirmed by
94 the observation of sulfur. The yield of polymer attached to particles, calculated from the
95 amount of sulfur, was ~9% based on the amount of monomer added. The mole ratio of
96 polymer to unreacted initiator, calculated from the amounts of N and S, was ≈ 0.2 . The MW
97 of the polymer was estimated by assuming that the kinetics of the surface-attached
98 polymerization were the same as those from initiator in solution, which under the conditions
99 used here yields a polymer of MW $\approx 10,000$ ^[24]. Given that, and the specifications of the
100 carbon nanopowder, we estimate $\sim 2 - 10$ attached polymer chains / particle (see SI).

101 The dispersibility of CB nanoparticles in water was improved by grafting PMPDSAH onto
102 the surface, as shown in Figure 2. Water does not wet the bare CB spherical particles at all
103 due to their hydrophobic nature. However, CB nanoparticles acquired a hydrophilic property
104 after grafting zwitterionic PMPDSAH, leading to the formation of colloidal dispersions in
105 water. The urea-dependent dispersibility of CB-PMPDSAH colloids in aqueous environment
106 was examined by UV-vis spectrometric measurement of the time-dependent turbidity of the
107 solution at 20°C. As the colloid aggregated and settled, the turbidity decreased. We assessed
108 colloidal stability by simply measuring the decrease in optical absorbance of the solution with
109 time, as a consequence of sedimentation of the colloid: Figure 3A. As shown in Figure 3,
110 there was a maximum in the colloidal stability observed for CB-polymer colloids (0.3 g dm^{-3})
111 in aqueous solution containing 1 mol dm^{-3} urea. In the absence of urea, the CB-PMPDAH
112 dispersion showed a steady decrease of the absorbance after stabilizing 2 h at 20°C. A clear

113 improvement of the stability of the CB-PMPDSAH dispersion against agglomeration and
114 sedimentation was obtained with increasing urea concentration from 0.1 mol dm^{-3} to 1 mol
115 dm^{-3} . However, further increase of urea concentration (8 mol dm^{-3}) was detrimental to the
116 colloidal stability. In Figure 3B, the colloidal stability at different urea concentrations is
117 compared by simply plotting the absorbance at a fixed time after mixing. The existence of
118 three states separated from each other by two critical urea concentrations is observable: a first
119 state (i) ranging from $0.001 \text{ mol dm}^{-3}$ to 0.1 mol dm^{-3} , where the absorbance of CB-
120 PMPDSAH colloids was a relatively low value; a second state (ii) for the range $0.5 - 1.2 \text{ mol}$
121 dm^{-3} , where the absorbance sharply increased to a large value; and a third state (iii) where
122 further addition of urea ($1.2 \text{ mol dm}^{-3} < c_{\text{urea}} < 8 \text{ mol dm}^{-3}$) led to a steadily decreasing
123 cloudiness. We note for comparison that PMPDSAH is itself insoluble in pure water.
124 Solubility is promoted by the addition of salt (the anti-polyelectrolyte effect).^[16,25] We
125 checked the effect of addition of urea on the solubility of PMPDSAH in water and noted that
126 indeed addition of urea ($c_{\text{urea}} = 1 \text{ mol dm}^{-3}$) promoted the dissolution of PMPDSAH at 20°C ,
127 consistent with earlier reports on different sulfobetaines^[17,18].
128
129 Colloids may be stabilised by either electrical or steric repulsion of the particles. The
130 polyzwitterion is electrically neutral. Thus the stabilization must be a steric stabilization, due
131 to the extension of the polymer chains from the surface. CB-PMPDSAH suspensions were not
132 unconditionally stable. However, the colloidal stability was greatly improved by the presence
133 of urea. The upper critical solution temperature (UCST) of salt-free PMPDSAH was
134 observed at around 30°C (unpublished results). Therefore, spherical PMPDSAH brushes
135 should be in a partially collapsed state at 20°C , hence steric stabilization of the suspension
136 would not be fully effective. The effect of a small addition of urea can be interpreted as due to
137 an expansion of the polymer chains in the presence of urea: that is, the dipole-dipole
138 interaction that causes the collapse of the chains (and the insolubility of PMPDSAH in pure

139 water) is mitigated by an improved solvation of the ionic groups. The expanded polymer
140 layer would act like a shell on the CB nanoparticle surfaces that stabilizes the interface and
141 cannot be penetrated when two particles touch. This effect could be out-weighed by
142 interactions between oppositely charged quaternized ammonium and sulfonate groups.
143 Expansion of the polymer chains in the presence of urea implies that this electrostatic
144 interaction has been diminished. Thus adding urea served both to expand the polymer chains
145 on individual particles and increase the steric repulsion between different particles. The effect
146 at large concentration of urea was the opposite. The effects can be interpreted from studies of
147 urea-water solutions^[26,27], the interactions of urea with zwitterionic amino acids^[28], and the
148 effects of urea on protein denaturation, which has been extensively studied^[29]. These studies
149 indicate the possibility of a direct ion-dipole interaction between urea and the charged groups
150 of the sulfobetaine. Such an effect would screen the electrostatic interaction between the
151 cationic and anionic groups of the zwitterion and could explain the expansion we have
152 deduced is induced by urea in the lower concentration range. These studies also indicate that
153 one water molecule/urea is strongly hydrogen bonded^[26] so at high concentration of urea
154 there could be a competition for water of solvation and a “breaking” of the water structure^[27],
155 which would decrease the solvation of the charged groups, leading to an increase of the
156 electrostatic interaction and hence the collapse of the polymer chains causing the suspension
157 to become unstable.

158

159 In summary, the preparation of PMPDSAH-grafted CB nanoparticles by SI-ATRP has been
160 demonstrated. The presence of zwitterionic polymer grafts improved the water dispersibility
161 of CB nanoparticles due to the extremely high dipole moment of the graft. Alteration of CB-
162 PMPDSAH colloidal stability was obtained by changing the urea concentration in the solution.
163 The mechanism behind the urea-promoted stabilisation of CB-PMPDAH colloids can be
164 understood as an expansion of sulfobetaine-based spherical polymer brushes on the surfaces,

165 because an ion-dipole interaction with urea changes the solvation of the charged groups,
166 disrupting the inter/intramolecular interactions and stabilizing the colloid through the steric
167 effect. A large addition of urea can “break” the water structure, altering further the solvation
168 of the charged groups, resulting in the electrostatic interactions becoming relatively more
169 important, which causes a collapse of the polymer brush and therefore causes the
170 agglomeration and sedimentation of CB-PMPDSAH nanoparticles. In other work we have
171 demonstrated electrochemical switching of conformation of surface-attached zwitterionic
172 polymer brushes, induced by electrochemical ion-pumping^[24,30]. We anticipate that these
173 stimuli-responsive carbon nanoparticles will be useful to fabricate composite electrode films
174 in which electrochemical-switching of surface properties is achieved, and could therefore find
175 applications in biosensors and microfluidic devices where, for example, hydrophobic-
176 hydrophilic switching can be used to control flow.

177

178 **Experimental**

179 *Materials and Reagents:* All reagents, including carbon black nanopowder (Aldrich, < 50 nm,
180 99+ %), were purchased from Sigma-Aldrich and used as received.

181 *Preparation of PMPDSAH-Grafted Carbon Black Nanoparticles:* CB-PMPDSAH

182 nanoparticles were prepared via ATRP polymerisation. As shown in Figure 1, a suspension of
183 CB nanoparticles (2 g) in 70% nitric acid (20 mL) was sonicated for 30 min and the reaction
184 was carried out under continuous stirring at 100°C for 24 h. After the reaction, the suspension
185 was cooled to room temperature and the resulting CB nanoparticles were washed centrifugally
186 using Milli-Q water (pH = 7). The samples were then dried under vacuum at 50°C for 24 h.
187 The resulting CB-COOH (1) nanoparticles (0.5 g) were dispersed in a solution of 1-ethyl-3-
188 (3-dimethylaminopropyl) carbodiimide (EDC) (1.0 g, 5.25 mmol) and phosphate buffered
189 saline (PBS) (20 mL, pH = 5.2). The reaction mixture was stirred for 15 min, followed by the
190 addition of ethanolamine (0.21 mL). The reaction bottle was then sealed and the suspension

191 was continuously stirred at room temperature for 2 h. After the reactions, the resulting CB-
192 OH (2) particles were washed centrifugally using water and dried under vacuum at 50°C for
193 24 h. The CB-OH (2) nanoparticles (0.40 g) were added into a 25 mL three-necked round
194 bottom flask containing triethylamine (Et₃N) (2.31 mL, 16.20 mmol), 4-
195 dimethylaminopyridine (DMAP) (0.16 g, 1.28 mmol) and 2-bromo-2-methylpropionyl
196 bromide (2.00 mL, 16.20 mmol) in 10 mL anhydrous dichloromethane. The reaction mixture
197 was sonicated for 30 min and stirred for 3 h in an ice/water bath (at 0°C). The reaction was
198 then carried out at room temperature for another 24 h. After the reactions, the resulting CB-Br
199 (3) particles, now carrying the surface initiator for ATRP, were washed centrifugally using
200 dichloromethane, tetrahydrofuran and water, and dried under vacuum at 50°C for 24 h.

201 Zwitterionic homopolymer PMPDSAH-grafted CB nanoparticles were prepared using ATRP
202 polymerisation technique: a Schlenk tube containing CB-Br nanoparticles (0.20 g), Bipy (0.03
203 g, 0.21 mmol), MPDSAH (1.25 g, 4.28 mmol) in a mixture of water (2.00 mL) and methanol
204 (0.50 mL) went through five freeze-pump-thaw cycles to remove oxygen. When the reaction
205 mixture was in the frozen state (in liquid N₂), CuBr (9.80 mg) and CuBr₂ (1.90 mg) were
206 added into the tube, followed by two pump-purge N₂ cycles. The reaction was carried out at
207 room temperature for 20 h. After the polymerization, the resulting particles were washed
208 centrifugally using water and methanol. The resulting particles were dried under vacuum at
209 50°C for 24 h.

210 *Characterization.* The presence of the grafted polymers on CB nanoparticles was confirmed
211 by elemental analysis and FTIR measurements. FTIR spectra were recorded after
212 accumulation of 128 scans at a resolution of 2 cm⁻¹ for a range 700 - 2000 cm⁻¹, using a
213 Continuum FTIR microscope equipped with a liquid nitrogen cooled MCT detector in
214 reflectance mode with aperture size 100 μm x 100 μm, and the Atlus spectroscopic software.
215 The absorption spectra were obtained at 550 nm using a UV-Vis spectrophotometer (UV-
216 1700, SHIMADZU) by equipped with a temperature controller system (S-1700 thermoelectric

217 cell holder, SHIMADZU). All samples (0.9 g dm^{-3}) were kept overnight to allow complete
218 hydration. All samples were stirred for 10 min using a magnetic stirrer before each
219 measurement. All the measurements were performed at 20°C .

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224 Zealand.

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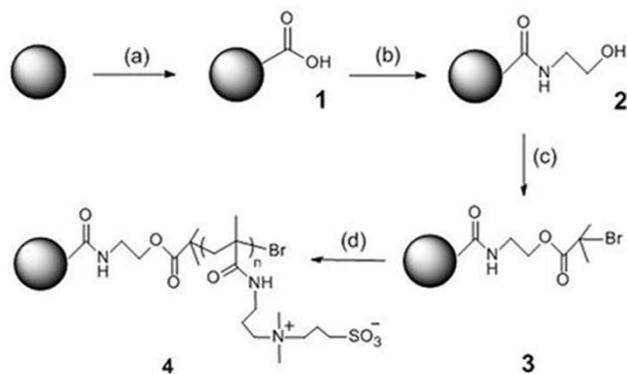
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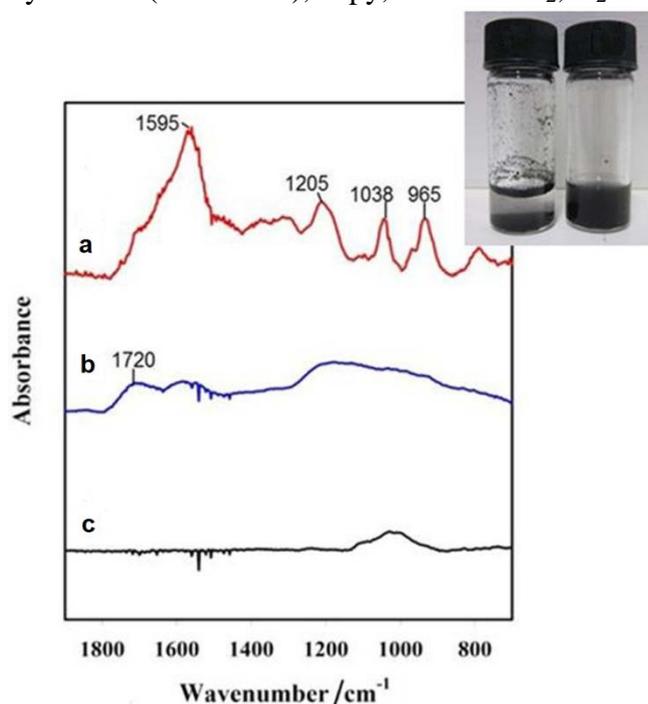
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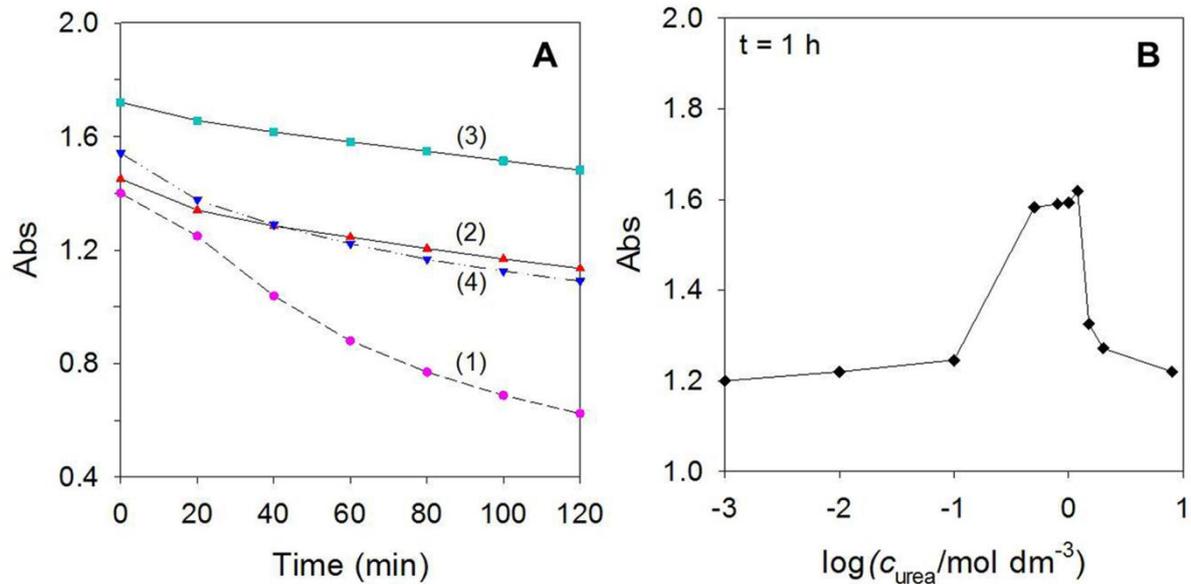
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276 **Figure 1.** Synthesis of PMPDSA-grafted CB nanoparticles (4) via ATRP polymerisation: **a)**
277 HNO₃, 100°C, 24 h; **b)** EDC, ethanolamine, 2 h; **c)** 2-bromo-2-methylpropionyl bromide,
278 Et₃N, DMAP, 24 h; **d)** 3-(methacryloylamino)propyl)-dimethyl(3-sulfopropyl)ammonium
279 hydroxide (MPDSA), Bipy, CuBr/CuBr₂, H₂O/MeOH, 15 h



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Figure 2. IR spectra for (a) CB-PMPDSA, (b) CB-COOH and (c) bare CB nanoparticles.
Inset: images of the aqueous suspension of bare CB (left) and CB-PMPDSA (right)
nanoparticles.



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Figure 3. Uv-vis absorption of (A) CB-PMPDSAHA nanoparticle suspension (0.3 g dm⁻³) with (1) no urea, (2) 0.1 mol dm⁻³, (3) 0.8 mol dm⁻³ and (4) 8 mol dm⁻³ urea. (B) urea concentration-dependent colloidal stability of CB-PMPDSAHA nanoparticles. All samples were measured after standing for 1 h.

297 **The table of contents entry:**

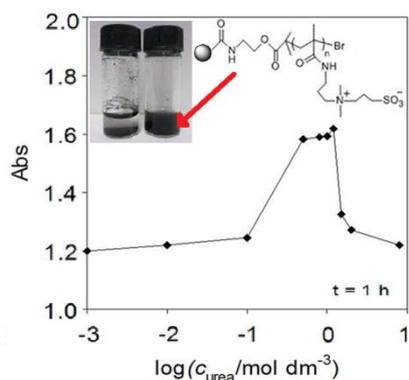
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299 The expansion and collapse of surface-grafted zwitterionic polymer brushes in water caused
300 by the addition of urea is demonstrated. We hypothesise that this is an effect of change of
301 water structure causing change of solvation of the brushes and hence a change in the dipole-
302 dipole interaction, and that it is analogous to the effects of urea on protein stability
303

304 **Keyword:** polymer brush; brush collapse; carbon black colloidal stability; poly(sulfobetaine)s;
305 urea

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