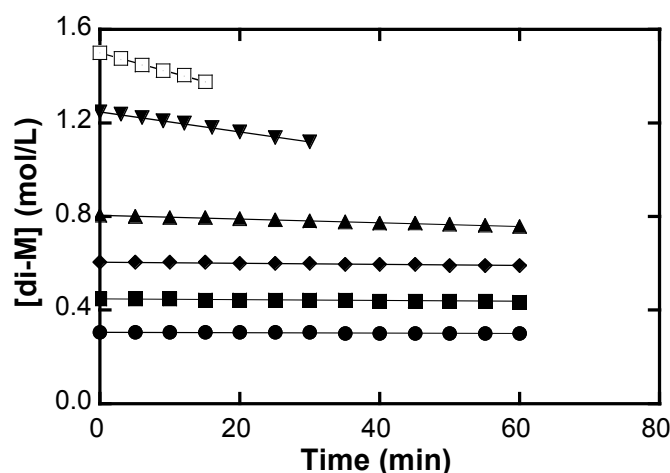


# Supplementary Materials: Effect of Very High Charge Density and Monomer Constitution on the Synthesis and Properties of Cationic Polyelectrolytes

Hamideh Ahmadloo, Ricardo Losada and Christine Wandrey

## 1. Polyelectrolyte Synthesis



**Figure S1.** Influence of the initial monomer concentration  $[di-M]_0$  on the linear period of  $-d[M]/dt$ .  $[di-M]_0 = \bullet 0.3, \blacksquare 0.45, \blacklozenge 0.6, \blacktriangle 0.8, \blacktriangledown 1.25, \square 1.5$  mol/L,  $[I] = 1.6 \times 10^{-2}$  mol/L,  $T = 323$  K.

## 2. Permanently Charged Polyelectrolytes in Solution

Calculation of the Bjerrum length  $l_B$  according to Equation (8):

with  $e = 1.60218 \times 10^{-19}$  C;  $\epsilon_0 = 8.8542 \times 10^{-12}$  s<sup>4</sup>·A<sup>2</sup>/m<sup>3</sup>·kg;  $\epsilon_{0, \text{water}, 293 \text{ K}} = 80.1$ ;  $\epsilon_{0, \text{water}, 298 \text{ K}} = 78.3$ ;

$k_B = 1.3807 \times 10^{-23}$  J/K;

$l_B = 0.712$  nm in water at 293 K

$l_B = 0.714$  nm in water at 298 K

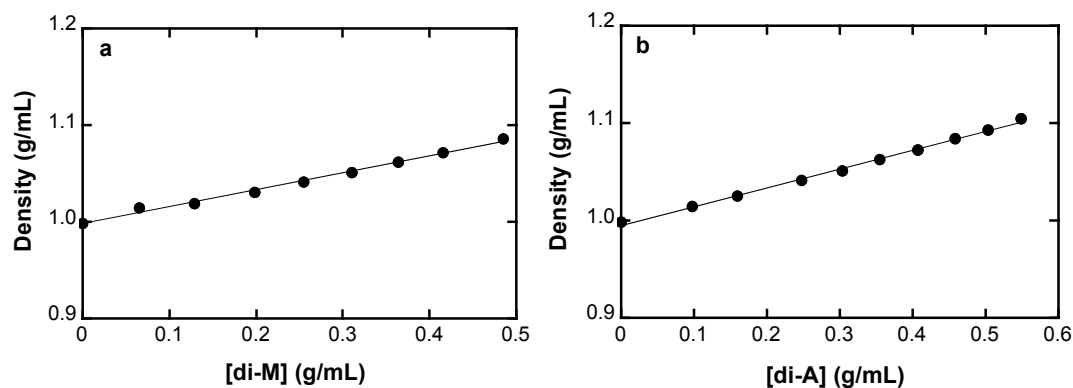
Calculation of the theoretical/structural charge spacing  $b$  (Scheme III):

$b = \text{monomer unit length}/\text{number of charges}$

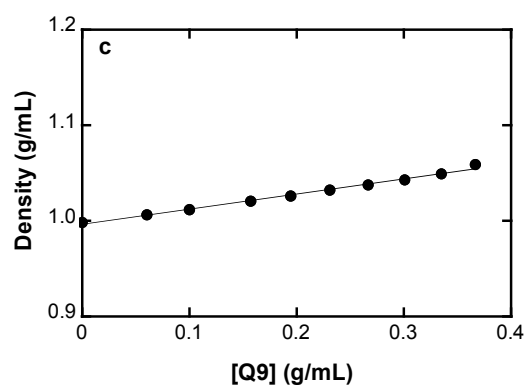
for di-M and di-A:  $b = 0.25/2 = 0.125$  nm (C–C bond length 0.154 nm, bond angle 112°)

for Q9:  $b = 0.25/1 = 0.25$  nm

## 3. Monomer and Monomer Solution Properties



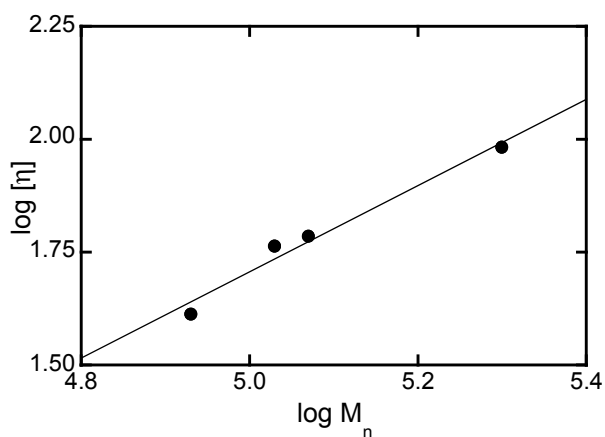
**Figure S2.** Cont.



**Figure S2.** Influence of the monomer concentration on the density of aqueous monomer solutions of (a) di-M; (b) di-A; (c) Q9,  $T = (293 \pm 0.01)$  K.

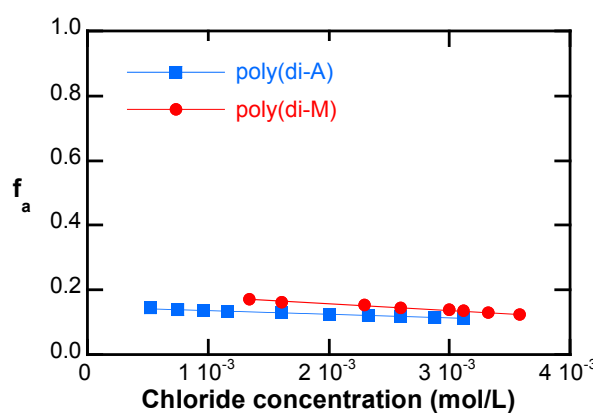
#### 4. Polyelectrolyte and Polyelectrolyte Solution Properties

##### 4.1. Intrinsic Viscosity and Molar Mass



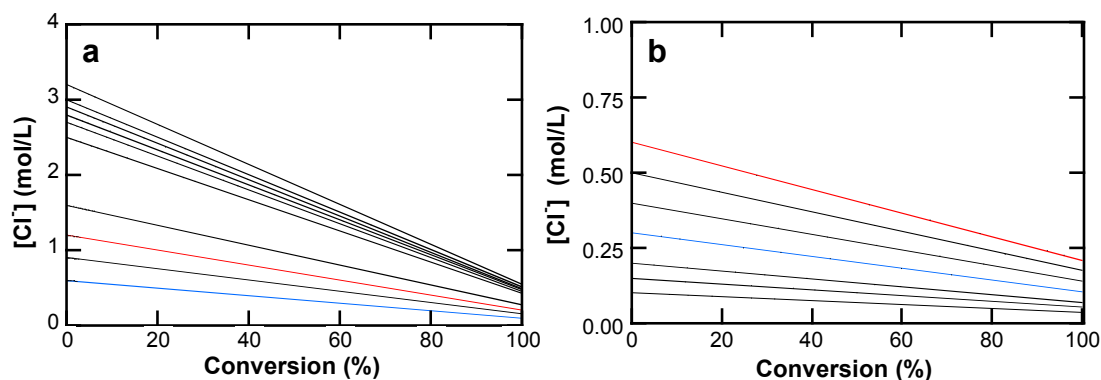
**Figure S3.** Determination of the intrinsic viscosity-molar mass relationship for poly(di-M) in 0.5 mol/L NaCl,  $T = 293$  K,  $8 \times 10^4 < M_n < 2 \times 10^5$  g/mol, by membrane osmometry.

##### 4.2. Counterion Condensation



**Figure S4.** Counterion activity coefficients  $f_a$  of poly(di-A) and poly(di-M) dissolved in water,  $T = 293$  K.

### 5. Autoacceleration

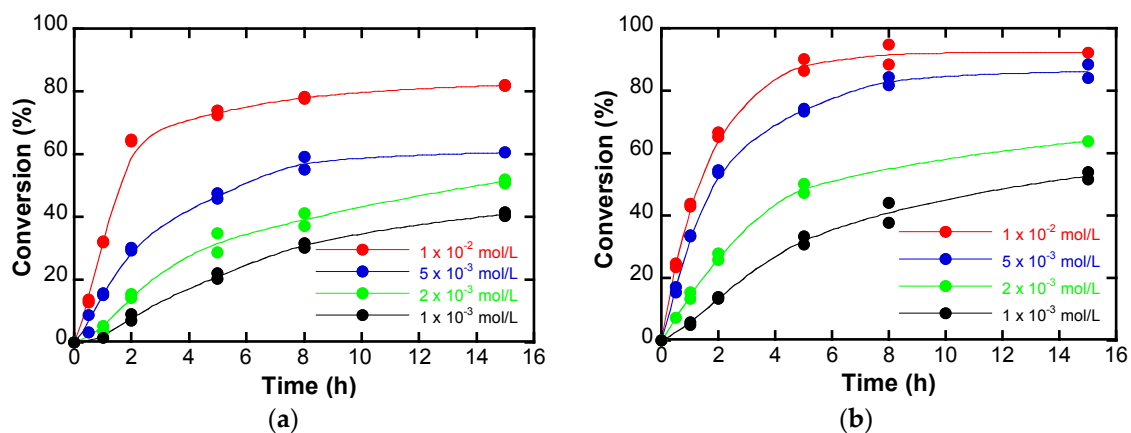


**Figure S5.** Decrease of the free chloride ion concentration  $[Cl^-]$  vs. conversion (a) di-M and di-A:  $0.3 < [M]_0 < 1.6$  mol/L; (b) Q9:  $0.1 < [M]_0 < 0.6$  mol/L. The red and blue lines indicate the same initial monomer concentrations 0.6 and 0.3 mol/L.

Equation (12) was used to quantify the decrease of the ionic strength expressed as the decrease of the concentration of the free chloride ions  $[Cl^-]$ .

$$[Cl^-] = n\{[M] + [P](1/\xi)\} = n\{[M]_0(1 - X_M) + X_M(1/\xi)\} \tag{12}$$

with  $n$  the number of charges per monomer molecule,  $n = 2$  for di-M and di-A, but  $n = 1$  for Q9.  $[M]$  and  $[P]$  are the monomer and polymer concentrations,  $X_M$  is the monomer conversion at time  $t$ , and  $\xi$  is the Manning charge-density parameter defined in Equation (10).



**Figure S6.** Conversion curves of ammonium persulfate-initiated free radical polymerizations of DADMAC in aqueous solution at  $T = 323$  K,  $1.0 \times 10^{-3} < [I] < 1.0 \times 10^{-2}$  mol/L (a)  $[DADMAC]_0 = 3.0$  mol/L; (b)  $[DADMAC]_0 = 4.0$  mol/L.

