Impact of Charge Correlation, Chain Rigidity and Chemical Specific Interactions on the Behavior of Weak Polyelectrolytes in Solution

Andrea Tagliabue,† Lorella Izzo,‡ and Massimo Mella*,†

Dipartimento di Scienza ed Alta Tecnologia, Università degli Studi dell’Insubria, via Valleggio 9, 22100, Como, Italy, and Dipartimento di Biotecnologie e Scienze della Vita, Università degli Studi dell’Insubria, via J. H. Dunant 3, 21100, Varese, Italy

E-mail: massimo.mella@uninsubria.it

*To whom correspondence should be addressed
†Dipartimento di Scienza ed Alta Tecnologia, Università degli Studi dell’Insubria, via Valleggio 9, 22100, Como, Italy
‡Dipartimento di Biotecnologie e Scienze della Vita, Università degli Studi dell’Insubria, via J. H. Dunant 3, 21100, Varese, Italy
Figure S1: $\Delta pK_a$ as function of $\alpha$ for different number of chains in the cell, precisely for $n = 8$ (solid lines, squares), $n = 2$ (dashed lines, circles) and $n = 1$ (dotted-dashed lines, triangles). Since the number of monomers for each chain is $L = 15$, $n = 1, 2, 8$ correspond to values of chains concentration equal to $C \simeq 1.37 \cdot 10^{-3}$ M, $2.74 \cdot 10^{-3}$ M, $1.10 \cdot 10^{-2}$ M, and, since $L = 15$, to values of monomers concentration equal to $C_m \simeq 2.06 \cdot 10^{-2}$ M, $4.11 \cdot 10^{-2}$ M, and $1.65 \cdot 10^{-1}$ M, respectively. The following cases are presented: flexible chains with ($\zeta = 2, k_{bend} = 0$, green) and without ($\zeta = 0, k_{bend} = 0$, black) MB interactions, and semi-rigid chains with ($\zeta = 2, k_{bend} = 2 \cdot 10^{-3} k_B T/\text{deg}^2$, red) and without ($\zeta = 0, k_{bend} = 2 \cdot 10^{-3} k_B T/\text{deg}^2$, light blue) the possibility to form c-H-bonds. The dotted gray line is a guide for the eye useful to discern negative and positive values of $\Delta pK_a$. Standard error bars are smaller than plot symbols when not visible.
Figure S2: Dissociation degree $\alpha$ as function of the control parameter $\text{pH} - pK_a$ for the same cases presented in Figure S1 (the color scheme is maintained). Here, the dotted gray line indicates the ideal behavior predicted by the Henderson-Hasselbalch equation. Standard error bars are smaller than plot symbols when not visible.
Figure S3: Hydrodynamic radius $R_H$ as function of $\alpha$ (top panels) or pH - $pK_a$ (bottom panels) for the same cases presented in Figure S1 (the color scheme is maintained).
Figure S4: End-to-end distance $r_{1N}$ as function of $\alpha$ and pH - p$K_a$. The scheme is the same as in Figure S3.
Figure S5: Pair distribution functions calculated between monomers (both neutral and charged) and counterions, with (dashed lines) and without (solid lines) MB interactions. Shown are data for different dissociation degree values: \( \alpha \approx 0.25 \) (pink), \( \alpha \approx 0.50 \) (blue), \( \alpha \approx 0.75 \) (olive green), \( \alpha \approx 0.90 \) (orange), \( \alpha \approx 1.00 \) (black). (a) flexible chains; (b) semi-rigid chains. Each distribution value has been divided by the corresponding volume element.
Figure S6: Trajectory snapshots for $n = 8$ flexible chains and $\zeta = 0$ interactions with different dissociation degrees: (a) $\alpha = 0.25$, (b) $\alpha = 0.50$, (c) $\alpha = 0.75$, (d) $\alpha = 1.00$. Color scheme: neutral monomers in dark gray, charged monomers in pink, counterions in white; the first and the last monomer of each chain are depicted in red and blue, respectively.
Figure S7: Trajectory snapshots for $n = 8$ semi-rigid chains and $\zeta = 0$ with different dissociation degrees: (a) $\alpha = 0.25$, (b) $\alpha = 0.50$, (c) $\alpha = 0.75$, (d) $\alpha = 1.00$. Color scheme as in Figure S6.
Figure S8: Trajectory snapshots for $n = 8$ flexible chains and $\zeta = 2$ for different dissociation degrees: (a) $\alpha = 0.25$, (b) $\alpha = 0.50$, (c) $\alpha = 0.75$, (d) $\alpha = 0.80$, (e) $\alpha = 0.90$, (f) $\alpha = 1.00$. Color scheme as in Figure S6.
Figure S9: Trajectory snapshots for $n = 8$ semi-rigid chains and $\zeta = 2$ for different dissociation degrees: (a) $\alpha = 0.25$, (b) $\alpha = 0.50$, (c) $\alpha = 0.75$, (d) $\alpha = 0.80$, (e) $\alpha = 0.90$, (f) $\alpha = 1.00$. Color scheme as in Figure S6.
Figure S10: $\Omega$ in kcal/(mol K) as versus: (a), (b) pH - p$K_a$; (c) $\alpha$. 
Figure S11: Dissociation degree $\alpha$ as function of the control parameter pH - p$K_a$ calculated for different $d_{CoM}$ intervals. The color scheme is the same as in Figure S1. Here, the dashed gray line indicates the ideal behavior predicted by the Henderson-Hasselbalch equation. In order to make the chart more readable, error bars has been plotted only for the 'INT 03' case.
Figure S12: Trajectory snapshots for 2 flexible chains and $\zeta = 0$ at different pH - pK$_a$ values and $d_{\text{CoM}s}$ distances. Color scheme as in Figure 6.
Figure S13: Trajectory snapshots for 2 semi-rigid chains and $\zeta = 0$ at different pH - p$K_a$ values and $d_{\text{CoM}s}$ distances. Color scheme as in Figure 6.
Figure S14: Trajectory snapshots for 2 flexible chains and $\zeta = 2$ at different pH - p$K_a$ values and $d_{CoM_s}$ distances. Color scheme as in Figure 6.
Figure S15: Trajectory snapshots for 2 semi-rigid chains and \( \zeta = 2 \) at different pH - pK\(_a\) values and \( d_{\text{CoMs}} \) distances. Color scheme as in Figure 6.
Figure S16: Total potential $U_{\text{tot}}$ (in kcal/mol) as function of $\alpha$ for different intervals of $d_{\text{CoMs}}$. (a) flexible, $\zeta = 0$; (b) semi-rigid, $\zeta = 0$; (c) flexible, $\zeta = 2$; (d) semi-rigid, $\zeta = 2$. 
Figure S17: Total potential energy $U_{\text{tot}}$ as function of pH - pK$\alpha$: (a) $\zeta = 0$, flexible; (b) $\zeta = 0$, semi-rigid; (c) $\zeta = 2$, flexible; (d) $\zeta = 2$, semi-rigid.
Figure S18: End-to-end distance $r_{1N}$ as function of pH - $pK_a$. (a) flexible chains; (b) semi-rigid chains.