ALL-ATOMISTIC MOLECULAR DYNAMICS STUDY OF THE EFFECT OF pH AND MOLECULAR WEIGHT ON STRUCTURE AND DYNAMICS OF WEAK POLYELECTROLYTE POLY(ACRYLIC ACID)

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Abstract

Long detailed all-atomistic Molecular Dynamics (MD) simulations are carried out to investigate the effect of pH (or, equivalently, degree of ionization, α^-, $\alpha^- = 0\%, 50\%, 100\%$), and degree of polymerization *N* (=20, 23, 46, 70, 110) on structure and dynamics of poly(acrylic acid) (PAA) at infinite dilution.

The overarching goal of this study is to address whether a conformational transition with the pH does occur for short chain polyacrylate since this remains a controversial topic in the research community. To ensure the validity and add to the reliability of our research conclusions, a systematic validation of several molecular mechanics force fields is performed. It is observed that the generalized AMBER force field in combination with the RESP charge fitting method best describes both the structural and dynamical behaviour of poly(acrylic acid) in comparison with experimentally obtained data.

It is found that $\left\langle R_g^2 \right\rangle^{0.5}$ exhibits a power law scaling with *N* with an exponent $\nu = 0.27$ at $\alpha^- = 0\%$ degree of ionization (acidic conditions), $\nu = 0.94$ at $\alpha^- = 50\%$ degree of ionization (neutral conditions) and $\nu = 0.87$ at $\alpha^- = 100\%$ degree of ionization (basic conditions). The global shape of the PAA chain in the solution is characterized by the estimation of the eigenvalues of the $\left\langle R_g^2 \right\rangle^{0.5}$ tensor, of the relative shape anisotropy, κ^2, and of the asphericity parameter, b, whereas it is revealed that at $\alpha^- = 0\%$ adopts a sphere like conformation and at $\alpha^- = 50\%$ and $\alpha^- = 100\%$ its conformation is flattened and flexible. In addition, it is revealed that, as the degree of ionization increases, the persistence length L_p increases and shorter PAA chains tend to be locally stiffer. The global and local conformation changes of the PAA chain in the solution with the degree of ionization are found to be highly related to the solvation of the polymer. Lastly, it is revealed that the diffusion coefficient of the center of mass of PAA exhibits a power law scaling with *N* with an exponent $\nu = 0.25$ at $\alpha^- = 0\%$ degree of ionization, $\nu = 0.46$ at $\alpha^- = 50\%$ degree of ionization (neutral conditions) and $\nu = 0.44$ at $\alpha^- = 100\%$ degree of ionization (basic conditions), in excellent agreement with recent experimental data and theoretical predictions[1, 2].

REFERENCES

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