A Combined Experimental and Molecular Dynamics study to Investigate the Effect of Polymer Concentration on the Structure and Dynamics of Short Weak Polyelectrolyte, Poly(*N,N*-dimethylaminoethyl methacrylate) in aqueous solution

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ABSTRACT

A combined experimental and Molecular Dynamics (MD) study is carried out to investigate the effect of polymer concentration on the zero-shear rate viscosity of a salt-free aqueous solution of poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA), a flexible thermo-responsive weak polyelectrolyte with a bulky 3-methyl-1,1-diphenylpentyl unit as a terminal group. The study has been carried out at room temperature (T = 298 K) with relatively short PDMAEMA chains (each containing N = 20 monomers or repeat units) at fixed degree of ionization ($α^+$ = 100%).

For the MD simulations, a thorough validation of several molecular mechanics force fields is first carried out for assessing their capability to accurately reproduce experimental observations and established theoretical laws. The generalized Amber force field in combination with the RESP charge fitting method is eventually adopted. Three characteristic concentration regimes are considered: the dilute (from 5 wt % to 10 wt %), the semi-dilute (from 10 wt % to 20 wt %), and the concentrated (from 20 wt % to 29 wt %); the latter two are characterized by concentrations higher than the characteristic overlap concentration.

The structural behavior of the PDMAEMA chains in the solution is assessed by calculating the square root of their mean square radius-of-gyration, the square root of the average square chain end-to-end distance and the persistence length. It is observed that at low polymer concentrations PDMAEMA chains adopt a stiffer and slightly more expanded conformation due to excluded-volume effects (good solvent is considered in this study) and electrostatic repulsions that arise within the polymer chains. As the polymer concentration increases above 20 wt %, PDMAEMA chains adopt more flexible conformations, since excluded-volume effects seize and charge repulsion in the polymer chains subsides.

The effect of the total polymer concentration on PDMAEMA chain dynamics in the solution is assessed by calculating the chain re-orientational relaxation time, the diffusion coefficient of the molecule's center-of-mass, and the zero-shear rate viscosity; the latter is also measured experimentally here and found to be in excellent agreement with the MD predictions. Our study suggests that short chain length (N = 20), fully ionized, PDMAEMA with a bulky 3-methyl-1,1-diphenylpentyl unit as a terminal group behaves as strong polyelectrolyte in the dilute and semi-dilute concentration regimes. At a concentration around 20 wt %, the electrostatic blobs begin to overlap and thus the PDMAEMA chains behave as uncharged (neutral) polymers in solution.