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Unfolding polyelectrolytes in a strong DC electric field<sup>1</sup> PAI-YI HSIAO, KUN-MAO WU, Department of Engineering and System Science, National Tsing Hua University — The behavior of single polyelectrolytes in multivalent salt solutions under the action of an electric field is investigated by computer simulations. The variation of chain size against the strength of electric field displays a sigmoidal transition, which defines a critical field  $E^*$  to unfold a chain. Above  $E^*$ , the chain is unfolded into a rodlike structure, aligned parallel to the field direction. We show that  $E^*$  is a function of salt concentration and depends on the chain length via the scaling law  $V^{-1/2}$  where V is the ellipsoidal volume occupied by the chain. Moreover, the magnitude of the electrophoretic mobility of chain drastically increases during the unfolding. These findings provide a solid foundation to a newly proposed mechanism to separate long charged homopolymers by their chain length in free-solution electrophoresis via the unfolding transition of globule polyelectrolytes condensed by multivalent salt.

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