

# THE EFFECT OF THE SOLVENT DIELECTRIC CONSTANT ON THE CONFORMATION AND DYNAMICS OF POLYELECTROLYTES IN SOLUTION

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## ABSTRACT

In this study, we investigated the effect of the solvent dielectric constant  $\epsilon_r$  on the counterion condensation for an imidazolium-based polyelectrolyte, poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (PC<sub>4</sub>-TFSI), by measuring the shear viscosity of the PC<sub>4</sub>-TFSI in a series of non-ionic good solvents having dielectric constants ranging from 7.9 for tetrahydrofuran to 178 for *N*-methylformamide. We found that for a given molar concentration  $c_p$  of the PC<sub>4</sub>-TFSI monomers, the specific viscosity  $\eta_{sp}$  decreased significantly with decreasing  $\epsilon_r$ . Moreover, the dependence of  $\eta_{sp}$  on  $c_p$  in solvents at high  $\epsilon_r$  followed the scaling law of  $\eta_{sp}$  for salt-free polyelectrolytes in good solvents, but its scaling relationship gradually shifted to the scaling law of  $\eta_{sp}$  for electrically neutral polymers in good solvents as  $\epsilon_r$  was decreased. Thus, we found that PC<sub>4</sub>-TFSI could behave as both polyelectrolyte and neutral polymer chains by simply changing the solvent dielectric constant. We further analyzed the viscosity data by estimating the overlap monomer concentration  $c_p^*$  as a monomer concentration at which  $\eta_{sp} = 1$ . The value of  $c_p^*$  decreased with increasing  $\epsilon_r$  with a power of  $-3$  for  $\epsilon_r < 70$ , and asymptotically approached a constant value at higher  $\epsilon_r$ . Since the overlap polymer concentration is related to the chain size, i.e.,  $c_p^* \propto 1/R^3$ , the observed result indicates that the chain size increases with increasing  $\epsilon_r$  due to the increase in the charge fraction on the PC<sub>4</sub>-TFSI caused by the counterion condensation. By applying the Dobrynin blob model for  $c_p^*$  of salt-free polyelectrolytes in good solvents<sup>1</sup>, we found that the charge fraction  $f$  was scaled as  $f \propto \epsilon_r^{7/4}$ . The obtained scaling exponent was larger than the value predicted by the classical Manning counterion condensation model<sup>2</sup>, i.e.,  $f \propto \epsilon_r^1$ . Our results provide, for the first time, a valid experimental reference for the study of the counterion condensation process of polyelectrolytes with respect to the varying  $\epsilon_r$ .

1. Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. Scaling Theory of Polyelectrolyte Solutions. *Macromolecules*, **28**, 1859–1871., 1995. <https://doi.org/10.1021/ma00110a021>.
2. Manning, G. S. Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions I. Colligative Properties. *J. Chem. Phys.*, **51**, 924, 1969. <https://doi.org/10.1063/1.1672157>.