

## 1. Introduction

- Polymer Grafted Nanoparticles (PGNPs) in a polymer matrix – reduces mobility of nanoparticles<sup>1</sup>
- PGNPs without free polymer- weak structural properties
- Network formation of PGNPs will enhance structural properties and viscosity of system
- Polyelectrolytes are grafted on nanoparticles (PENPs)
- Charges in polyelectrolyte → Electrostatic interactions controls the solubility and flexibility
- Degree of Ionization controlled by varying pH of solution<sup>2</sup>

## 2. Research Focus

- Effect of degree of ionization, grafting parameters, concentration and stiffness of chain extenders on viscosity and structural properties of polymer nanocomposites

## 3. Models

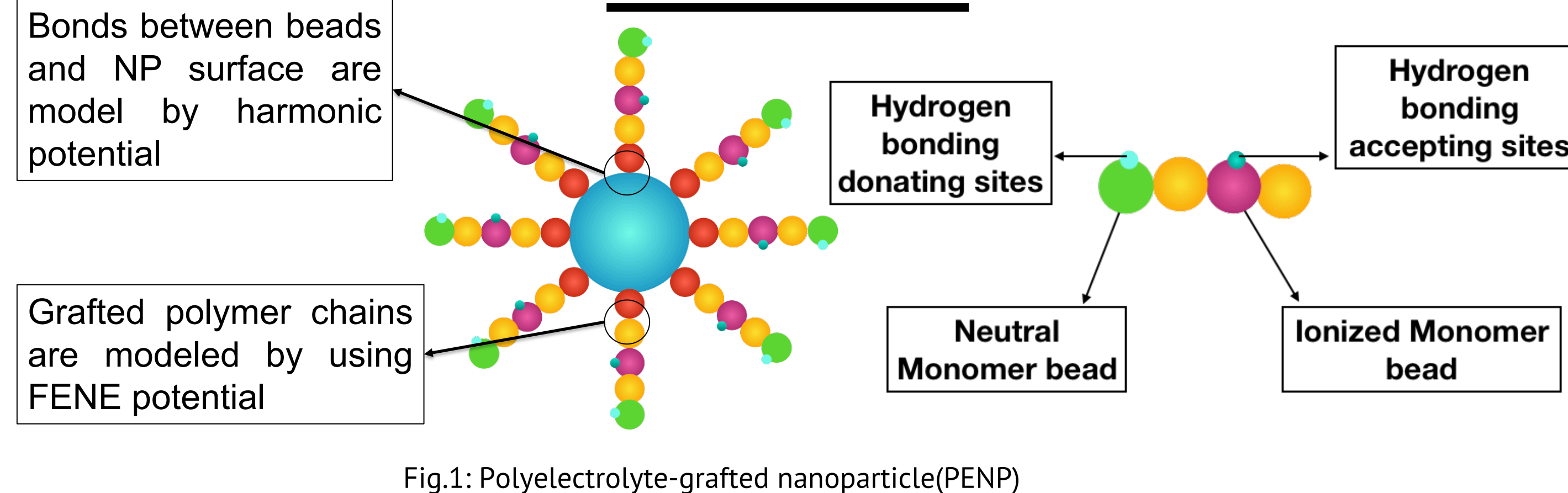


Fig.1: Polyelectrolyte-grafted nanoparticle(PENP)

- Moderate grafting density =  $(0.11 \frac{\text{chains}}{\text{area of nanoparticle}})$
- Concentration of Poly PENPs in solution  $\phi_{penp} = 10\% \text{ v/v}$
- Size of nanoparticle core  $\sigma_{np} \sim 8\text{nm}$

## 4. Results and Discussions

### i. Effect of graft length ( $l_g$ ) of PGNPs

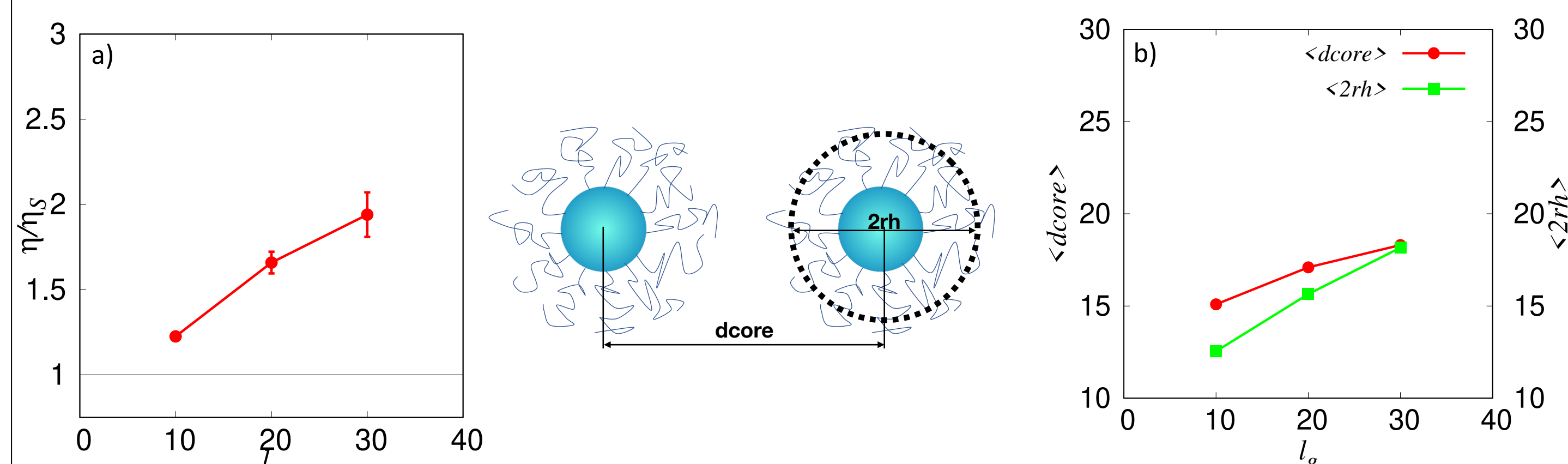


Fig.2: a)Viscosity of polymer nanocomposites as a function of graft length of PGNP.  $\eta_s$  is viscosity of pure solution. b)Ensemble average of distance between any two PGNP cores i.e.  $\langle d_{core} \rangle$  (left axis) and average hydrodynamic size of the PGNP  $2rh$  (right axis) as a function of graft length of PGNP

- Normalized with respect to viscosity of pure solvent ( $\eta_s$ )
- Increase in viscosity of system with graft length
- Hydrodynamic radius (rh) increase with graft length, i.e. brushes interact each other
- Grafting parameters dictates the viscosity of system
- Results are consistent with literature<sup>3</sup>

### ii. Effect of degree of Ionization on PENPs

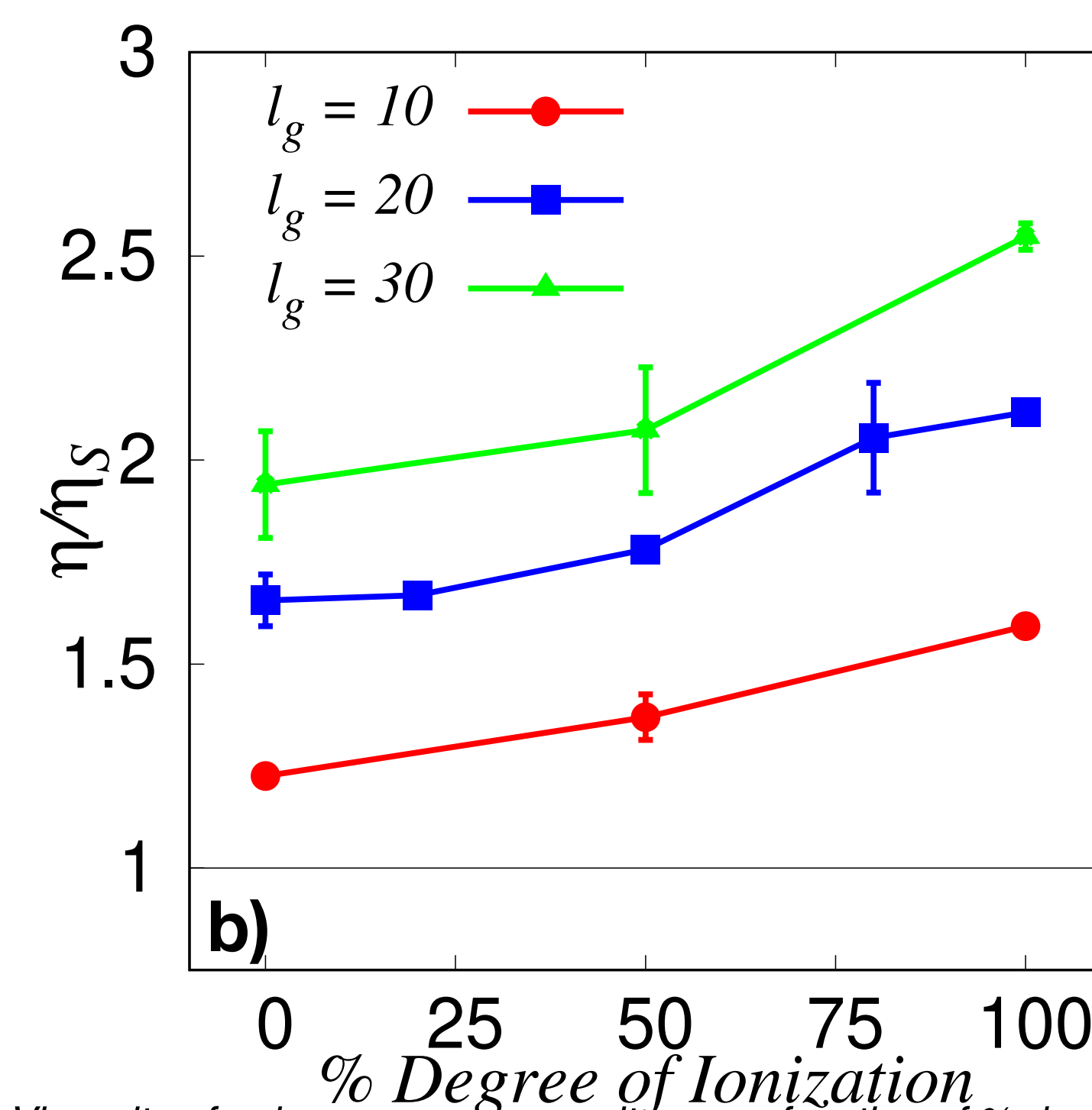


Fig. 3: Viscosity of polymer nanocomposites as a function of % degree of ionization.  $\eta_s$  is viscosity of pure solution.

- Viscosity gradually increase with degree of ionization
- Distance between the PENPs core is higher than hydrodynamic size of PENPs
- Lacking in network formation between the PENPs

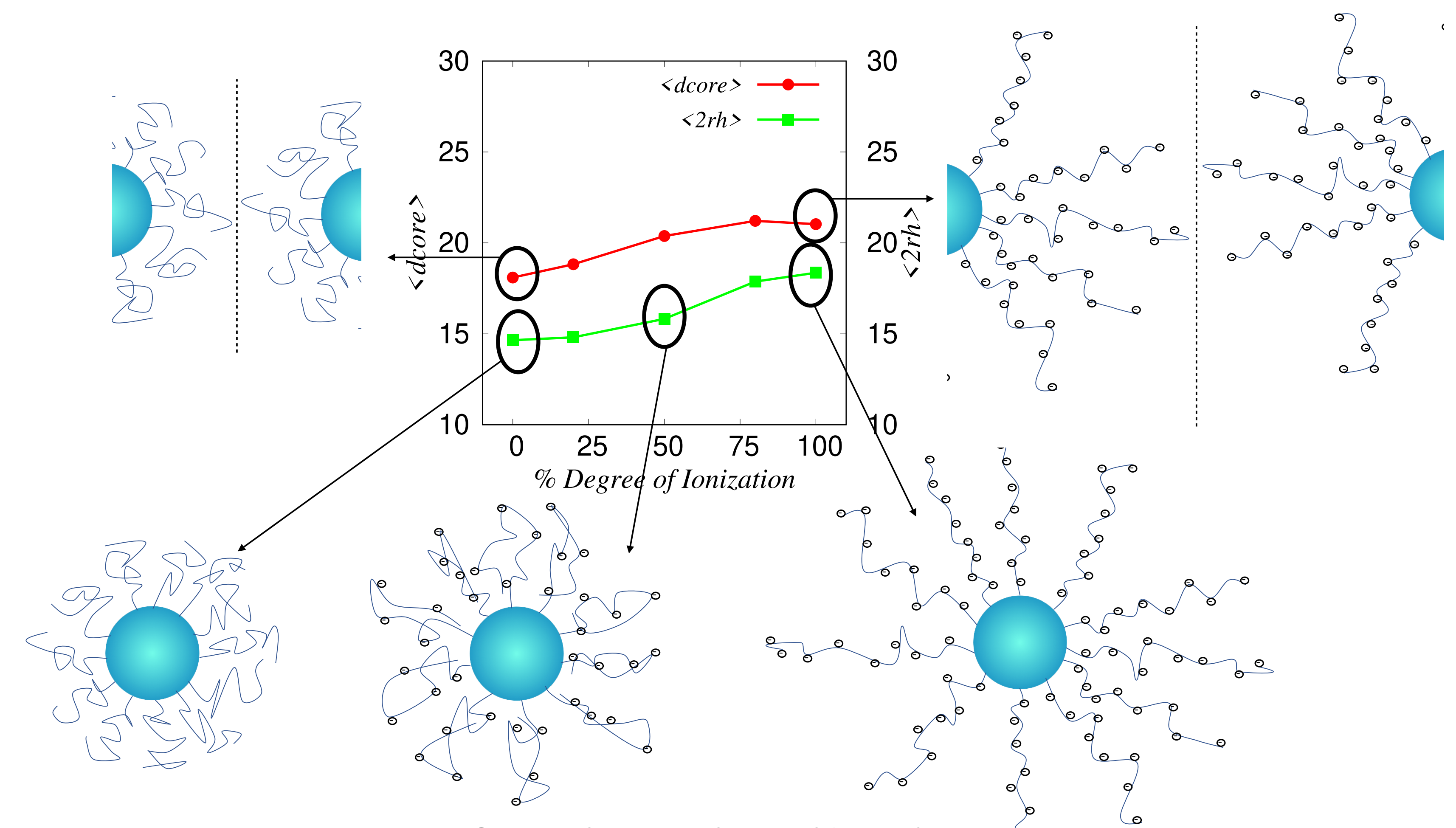


Fig. 4: Structure of PENP as a function of degree of ionization

### iii. Addition of chain extenders

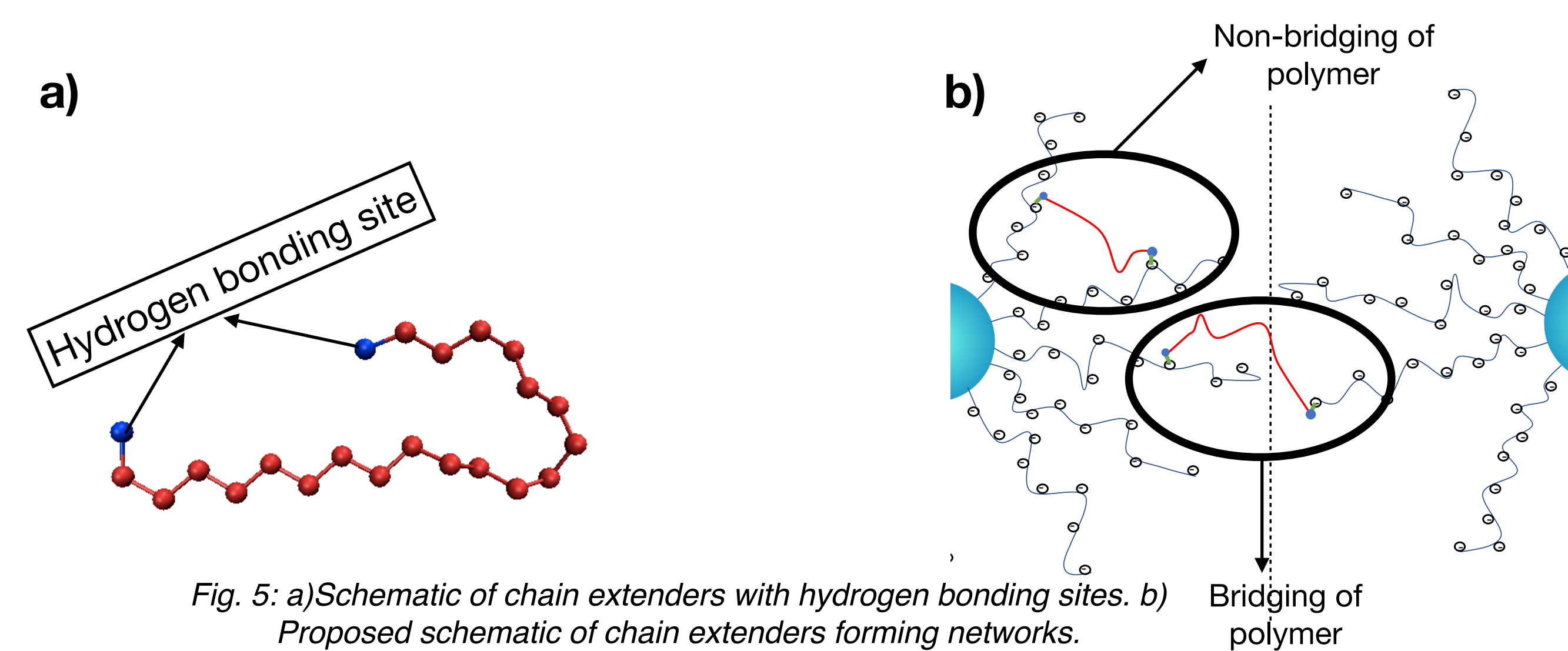
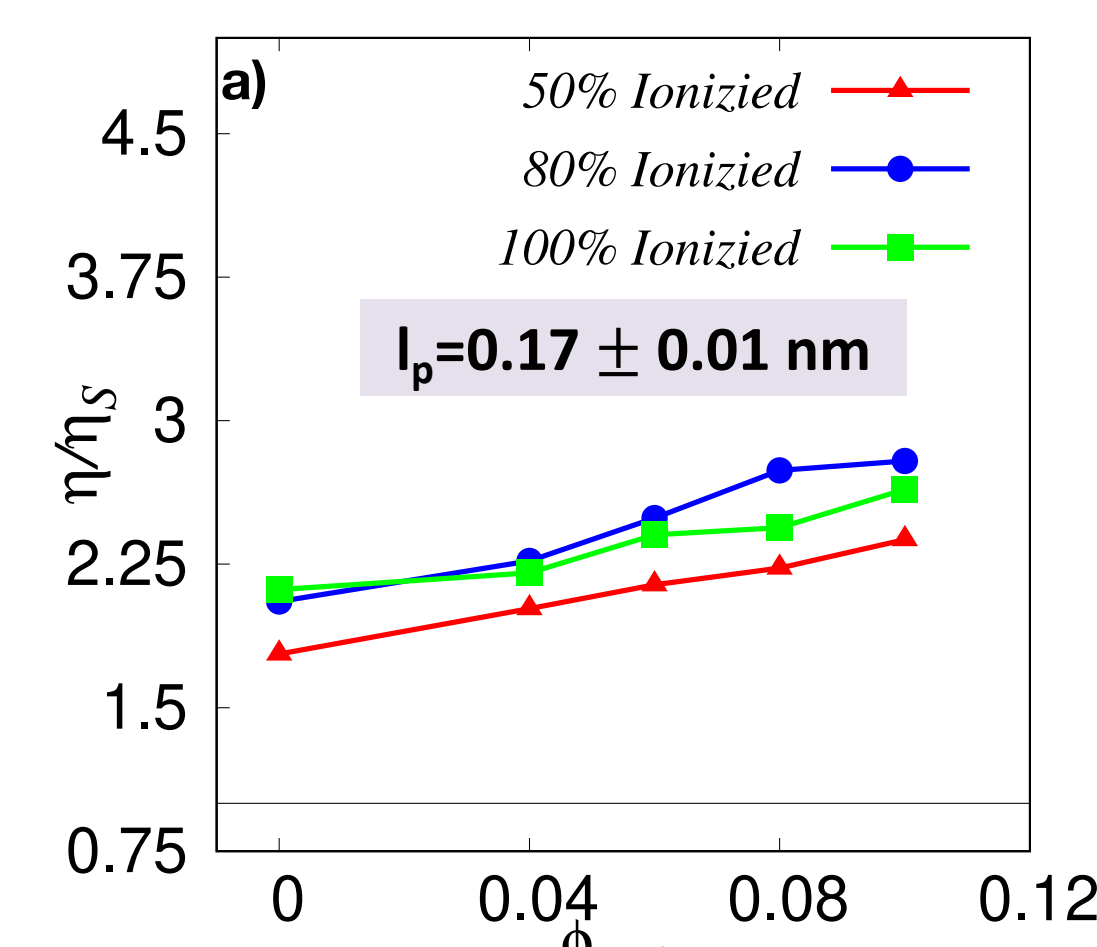


Fig. 5: a) Schematic of chain extenders with hydrogen bonding sites. b) Proposed schematic of chain extenders forming networks.

- Concentration of chain extenders  $\phi_{poly}$  varying from 4 to 10 % v/v
- Stiffness of chain extenders, varying  $l_p$  varying from 0.17 to 0.31nm

#### a. Effect of concentration of chain extenders ( $\phi_{poly}$ )



- Increase in viscosity with concentration of chain extenders
- Low probability of chain extenders to form bridging between PENPs
- Low network formation between PENPs

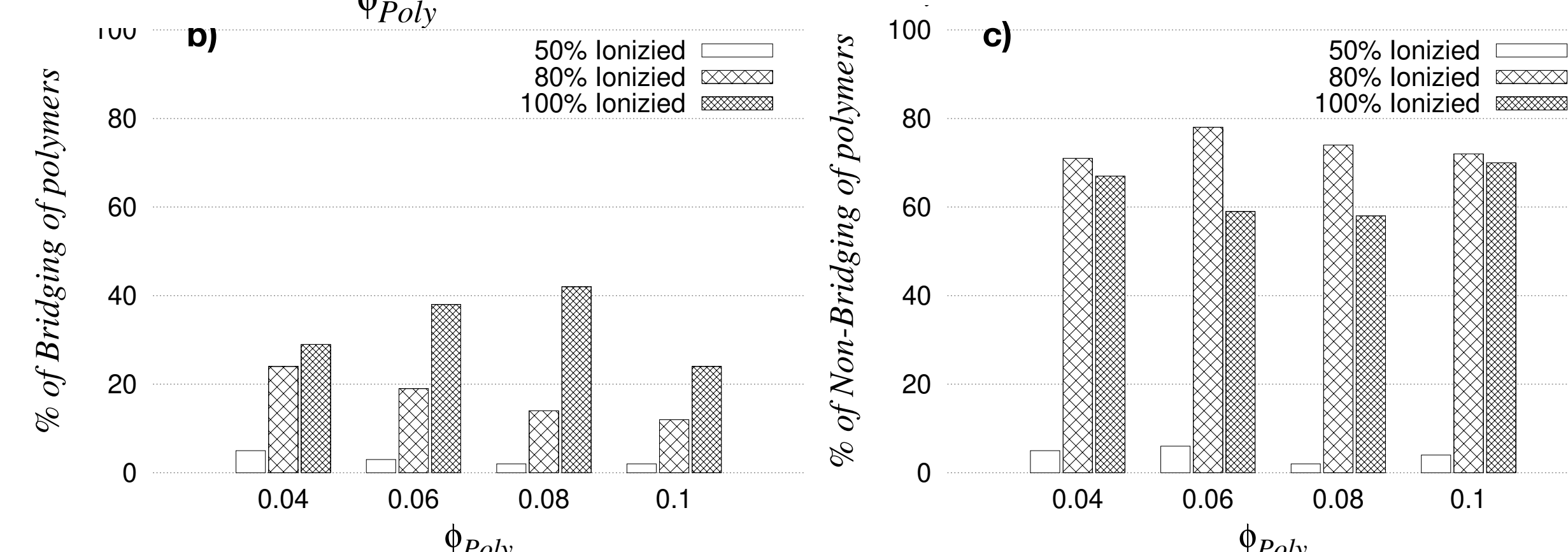


Fig. 6: a) Viscosity as a function of concentration of chain extender. b) Percentage of chain extender that are forming bridging and c) non-bridging between the PENPs

#### b. Effect of stiffness of chain extenders

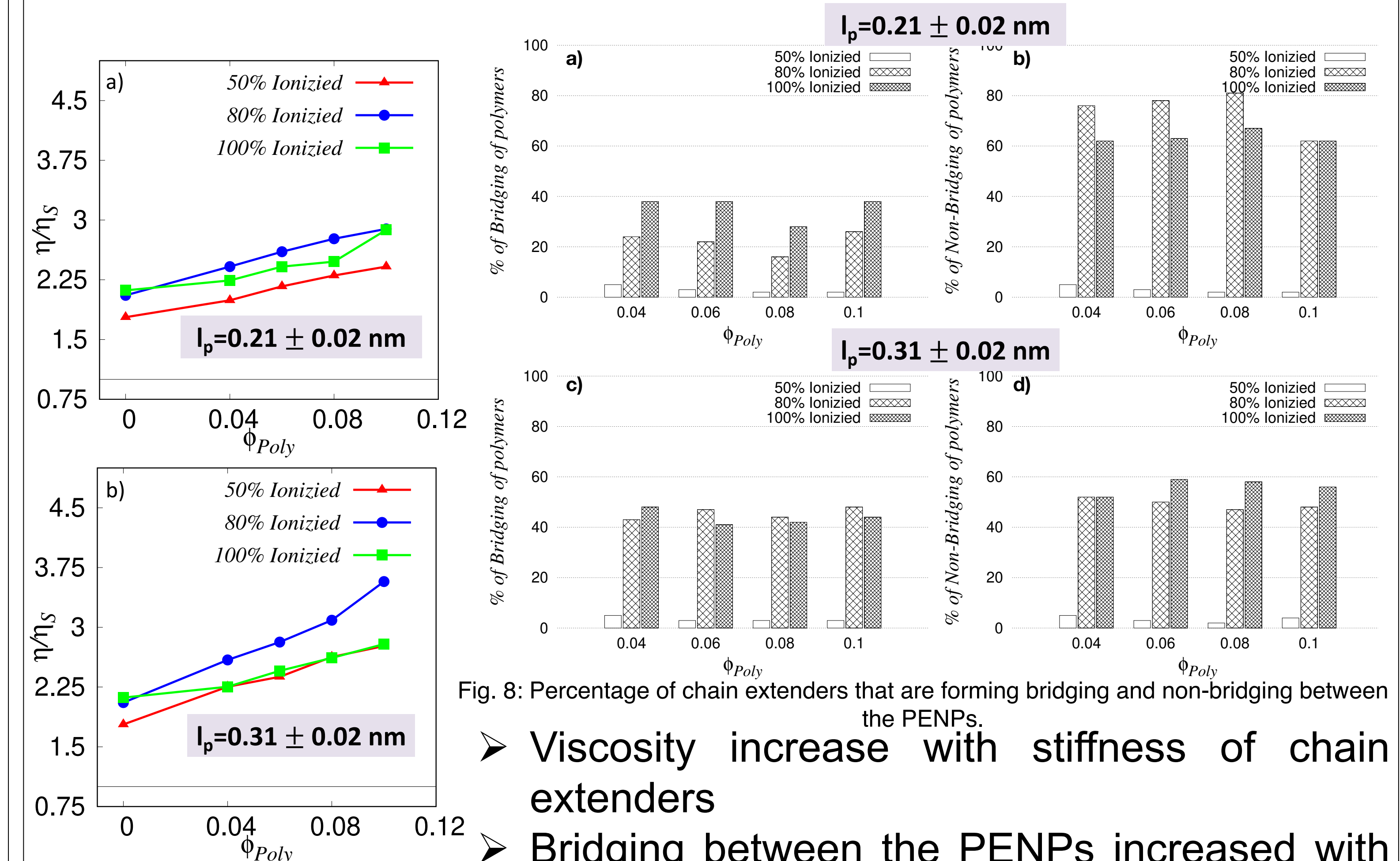


Fig. 7: Viscosity as a function of concentration of polymer. a)  $l_p = 0.21 \pm 0.02$  n and b)  $l_p = 0.31 \pm 0.02$  nm

Fig. 8: Percentage of chain extenders that are forming bridging and non-bridging between the PENPs.

- Viscosity increase with stiffness of chain extenders
- Bridging between the PENPs increased with stiffness of chain extenders

## 5. Conclusions

- Grafting parameter dictates the flow and structural properties of system
- Increase viscosity with degree of ionization but no network formation
- At high concentration with high stiffness of chain extenders results in bridging of nanoparticles and enhance the viscosity of system

## 6. References

- Koteswara Rao Medidhi and Venkat Padmanabhan, The Journal of Chemical Physics, volume 150, no. 4, page 044905, 2019.
- Zhang, Chong Feng, et al. *Macromolecules* (2019).
- Giovino, Marissa, et al. *Macromolecular Chemistry and Physics* 220.7 (2019): 1800543.