

Supporting Material**Dynamic Light Scattering experiments on aqueous solutions of PVP at different concentration**

Solutions of Poly(N-vinyl-pyrrolidone (PVP) at concentration ranging from 0.5 to 8 wt.% were filtered through 0.22 μm filters into cylindrical quartz cuvettes. Dynamic Light Scattering measurements were taken at different scattering angles between 30° and 150° using a Brookhaven BI-9000 correlator and a 100 mW Ar laser (Melles Griot) tuned at $\lambda = 514.5$ nm. Electric field autocorrelation functions at 90° for different PVP concentrations are shown in Fig.1.

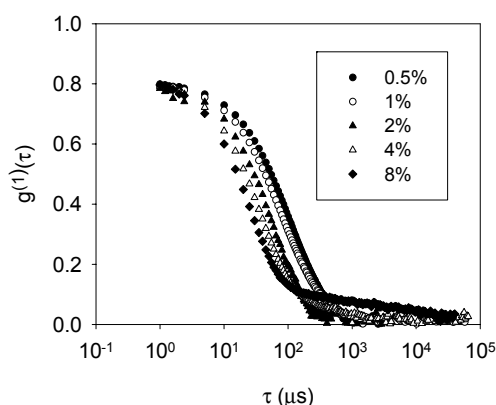


Fig. 1 Electric field autocorrelation function at 90° scattering angle of PVP in water solution at different concentration (wt.%).

At increasing polymer concentration, the correlation function was observed to decay at shorter time while a contribution at much longer time becomes more noticeable. Data at polymer concentration up to wt. 2% were fitted to a double exponential:

$$g^{(1)}(\tau) = A_1 \exp\left(-\frac{\tau}{\tau_1}\right) + A_2 \exp\left(-\frac{\tau}{\tau_2}\right)$$

where A_i and τ_i are the amplitude and decay time of each exponential. The decay at longer time at higher concentration was better described by a stretched exponential, and data were fitted to the following expression:

$$g^{(1)}(\tau) = A_1 \exp\left(-\frac{\tau}{\tau_1}\right) + A_2 \exp\left(-\left(\frac{\tau}{\tau_2}\right)^\beta\right)$$

A stretched exponential ($\beta < 1$) is often used to describe the heterogeneous dynamics of disordered materials such polymeric melts or supercooled liquids close to the glass transition. In this case the dynamics is characterized by a distribution of structural relaxation times, whose mean value $\langle\tau\rangle$ is given by:

$$\langle\tau\rangle = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$

where Γ is the gamma function.

The dependence on the polymer concentration of the two decay times is shown in Fig. 2. Data in the figure are relative to autocorrelation functions measured at 90° scattering angle. Similar results are obtained at different scattering angles. The decay at shorter time (τ_{fast}) decreases at increasing polymer concentration whereas the decay at longer time (τ_{slow}) is quite constant up to 2 wt. % polymer concentration after that it exhibits a strong increase.

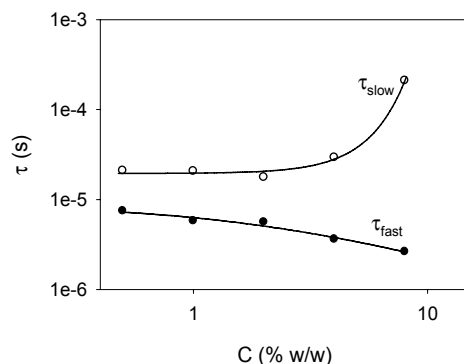


Fig. 2 Double logarithmic plot of fast and slow decay times versus polymer concentration.

Two relaxation modes are frequently observed in semi-dilute solutions of different polymeric systems. Burchard and Eisele¹ reported similar results on aqueous solutions of 560 kDa polyvinyl-pyrrolidone in semi-dilute regime. The fast relaxation was assigned to the irregular motion of centers of mass of chain segments according to De Gennes theory² while the slow relaxation was shown to be due to the reptating motion of individual polymer chains strongly interacting with the rest of the entangled polymeric matrix. According to this frame, our results on solutions of $M_w \approx 400$ kDa polyvinyl-pyrrolidone indicate that at concentration of about 1 or 2 wt.% the polymer solution should be in semidilute regime. For a solution of polymers in theta solvent, the value of the “overlap” concentration can be estimated by the inverse intrinsic viscosity, which practically gives the reciprocal of the volume occupied by the unit mass³. In Fig 3. we plotted some literature values⁴ of the inverse intrinsic viscosity versus the weight average molecular weight of polyvinyl-pyrrolidone with different polymerization degree.

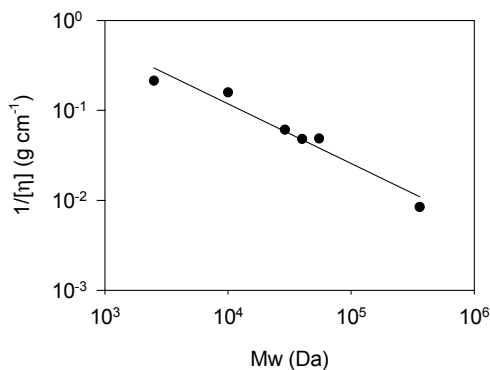


Fig. 3 Double logarithmic of the inverse intrinsic viscosity versus molecular weight of polyvinyl-pyrrolidone with different polymerization degree.

By the linear regression parameters we derived that for a polymer of 400 kDa, the overlap concentration is 0.01 g/ml, in good agreement with the value indicated by DLS results.

References

- 1) Burchard, W., Eisele, M. Cooperative Motion and Self-Diffusion in Polyvinyl-Pyrrolidone Solutions. *Pure & Appl. Chem.* 1984; 56: 1379-1390.
- 2) De Gennes, P.-G. Scaling concepts in Polymer Physics. Cornell University Press, Ithaca (1979).
- 3) Hans-Georg Elias. Macromolecules: Volume 3: Physical Structures and Properties. Macromolecules Series. Wiley-VCH, (2008) Chp. 3.
- 4) Armstrong, J.K., Wenby, R.B., Meiselman, H.J, Fisher, T.C. The hydrodynamic radii of macromolecules and their effects on red blood cell aggregation. *Biophysical Journal* 2004; 87: 4259-4270.