Entanglements

To obtain the packing number P_e and the degree of polymerization between entanglements N_e, we must renormalize for concentrations above φ^{**}. We define two parameters:

$$\lambda_g = \begin{cases} 1, & \varphi^* < \varphi \le \varphi^{**} \\ (\varphi/\varphi^{**})^{-3/2}, & \varphi^{**} < \varphi \end{cases}$$

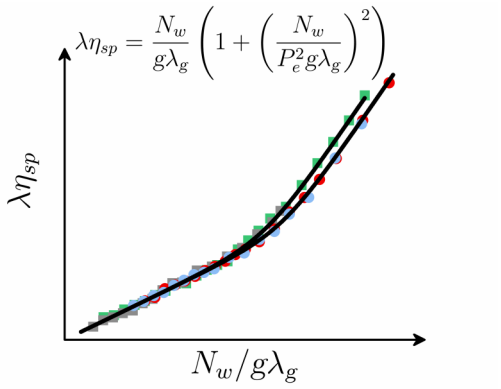
so that

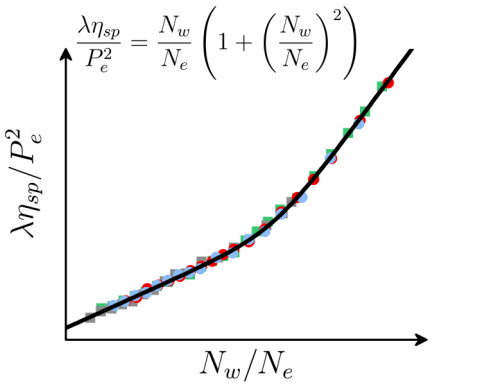
$$N_e = P_e^2 g \lambda_g$$

and

$$\lambda = \begin{cases} 1, & \varphi^* < \varphi \le \varphi^{**} \\ \lambda_g^{-2/3}, & \varphi^{**} < \varphi \end{cases}$$

such that the normalized specific viscosity is a universal function of the normalized number of correlation blobs per chain, $N_w/g\lambda_g$:





References

Derivations

Macromolecules **2021**, *54*, 1859–1869
Macromolecules **2021**, *54*, 2288–2295

Examples

Macromolecules **2021**, *54*, 9577–9586
ACS Polym. Au **2021**, *1*, 196–205
ACS Appl. Polym. Mater. **2022**, ASAP

Kavassalis-Noolandi Conjecture

Phys. Rev. Lett. **1987**, *59*, 2674–2677
Macromolecules **1988**, *21*, 2869–2879
Macromolecules **1989**, *22*, 2709–2720

Rubinstein-Colby Scaling

Macromolecules **1990**, *23*, 2753–2757
Statistical Physics of Macromolecules. AIP Press: 1994
Macromolecules **2008**, *41*, 8903–8915

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How to Analyze Polymer Solutions with Rheology

- Kuhn Length
- Excluded Volume
- Correlation Length
- Thermal Blob Size
- Entanglements

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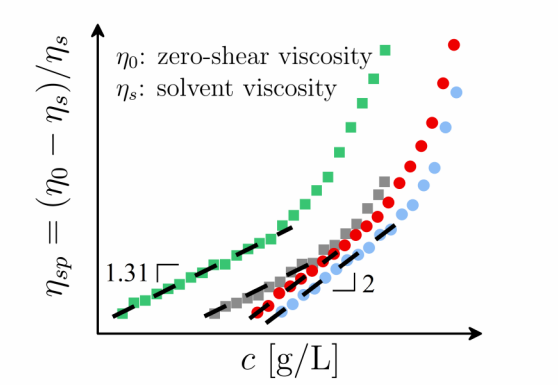
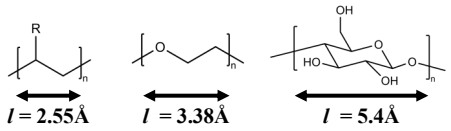
Specific Viscosity

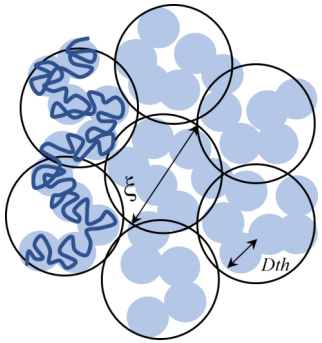


In this example, we demonstrate two polymer/solvent systems (squares and circles), each with two samples of different molecular weights (green > grey, red > blue).

To calculate the structural parameters, we need:

- weight-average degree of polymerization, N_w
- repeat unit projection length, l
- average repeat unit molar mass, M_0



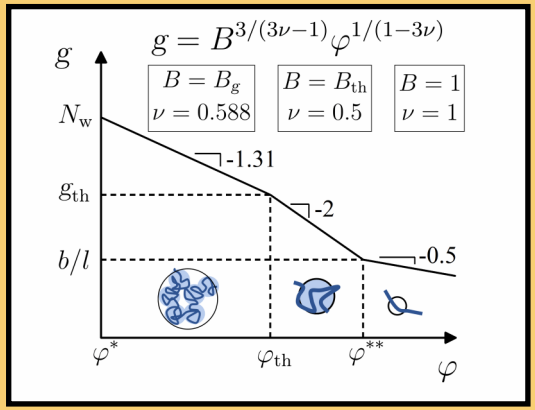


Correlation blobs with size

$\xi = lg^{\nu}/B$

contain g monomers, where exponent $\nu = 0.588$ and $B = B_g$ for good solvents and $\nu = 0.5$ and $B = B_{th}$ at length scales smaller than the thermal blob size D_{th} or for θ solvents.

Scaling Analysis



Intrinsic solution properties

Kuhn length $b = lB_{th}^{-2}$

Excluded volume $v = l^3 B_{th}^{-3}(B_{th}/B_g)^{1/(2\nu-1)}$

Crossover concentrations

Overlap concentration $\varphi^* = B_g^3 N^{1-3\nu}$ for good solvents, $\varphi^* = B_{th}^3 N^{-1/2}$ for θ solvents

Crossover between B_{th} and B_g regimes $\varphi_{th} = B_{th}^3(B_{th}/B_g)^{1/(2\nu-1)}$

Concentration at which $\xi = b$, $\varphi^{**} = B_{th}^4$

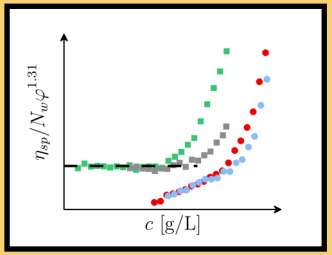
Blob sizes

Thermal blobs with size $D_{th} = l\,B_{th}^2\,\varphi_{th}^{-1}$ contain $g_{th} = B_{th}^6/\varphi_{th}^2$ monomers

Correlation blob size $\xi = l\,B^{1/(3\nu-1)}\varphi^{\nu/(1-3\nu)}$

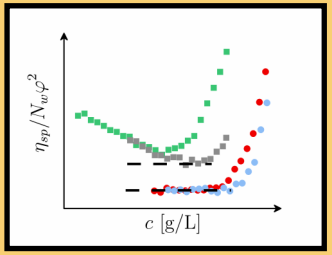
Molecular Parameters

Rouse B_g regime



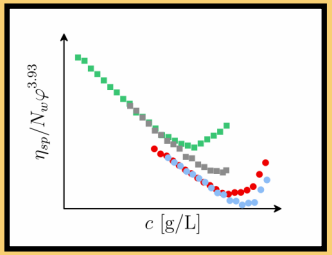
Obtain the value of the plateau, C_p, from the normalized viscosity for good solvent systems. The parameter $B_g = C_p^{1/3-\nu}$ is related to the monomer excluded volume, v.

Rouse B_{th} regime



Good solvent systems with shorter chains can cross over into the thermal blob overlap regime. The parameter $B_{th} = C_p^{-1/6}$ is related to the Kuhn length, b. θ solvents start in this regime.

Entangled regime



If there is a plateau in this plot for good solvent systems, the solution entangles before crossing into the B_{th} regime (green squares). An upturn indicates that the solution is in the entangled B_{th} regime.

Concentration

We define the dimensionless concentration

$\varphi = cl^3N_A/M_0$

where N_A is Avogadro's number and c is the concentration in units of mass per volume.

Copolymers

When calculating M_0 for copolymer solutions (e.g., polyelectrolytes, substituted functional groups) it is important to accurately determine the average monomer molar mass.

Polyelectrolytes (Charged Polymers)

If the initial slope is exactly 0.5, the solution is salt-free. Normalize the viscosity by $N_w\varphi^{0.5}$, and $B_{pe} = C_p^{-2/3}$. If the initial slope is between 0.5 and 1.31, normalize the viscosity by $N_w\varphi_{eff}^{0.5} = N_w\varphi^{0.5}(1+2c_s/f^*c)^{-0.75}$, where c_s is the salt concentration and f^* is the fraction of free counterions.

See *Macromolecules* **1995**, *28*, 1859–1871