A New Model of Polymers in Flow

Dave E. Dunstan

Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Vic., Australia.
e-mail: davided@unimelb.edu.au

doi:10.5618/chem.2011.v1.n1.5 || Received: 01-06-2011, Accepted: 24-07-2011, Available online: 26-07-2011

Abstract

Recent experimental evidence has shown that polymer chains compress in flow at semi-dilute concentrations. It has been assumed in all models of polymer flow behaviour that the chains extend in flow. A new model of polymers in flow in semi-dilute solution is presented where the chains compress. The chains are modeled as simple Hookean dumbbells exposed to compressive hydrodynamic forces. Equating the hydrodynamic and elastic forces predicts chain compression with shear rate. The model predicts both the power law behaviour observed for polymer shear thinning and the measured decrease in radius with shear rate with reasonable accuracy.

Keywords: Polymer chains; dumbbell model; compression and power law.

1. Introduction

Polymers in both solution and melts contribute a significant class of materials in which elasticity is of particular fascination¹. Understanding the flow behaviour of polymeric solutions has long been the quest of soft condensed matter. Polymer science progresses the tradition that single macromolecule dynamics may be used to determine and interpret the macroscopic material behaviour observed for these systems²⁻⁴. The elegant statistical mechanical models of single polymer chains combined with their generalisation using scaling arguments appear to predict the variation of chain solution size with molecular weight and concentration^{4,5}. Furthermore, the *Theory of Rubber Elasticity* that is based on the same physics predicts the elastic behaviour of rubbers over a wide strain range⁶. Importantly, the “*Rubber Theory*” predicts both the compressive and extensional behaviour of rubbers⁵. This agreement between the theory and experiment, albeit at “infinite” molecular weight and high polymer concentration with excluded volume interactions neglected, gives confidence that the fundamental tenets of the theory are correct. However, current models of polymers in flow require considerable effort to reconcile theory and experiment. Classical bead-

spring models qualitatively predict shear thinning behaviour in dilute solution and have been used to model the chains at higher concentrations⁷⁻¹⁰.

A founding assumption of all current models of polymer flow is that the chains extend in flow in response to the hydrodynamic forces⁷⁻¹⁰. Recent experimental evidence shows that synthetic polymer chains compress in Couette flow at semidilute concentrations¹¹⁻¹⁵. Recent studies on semidilute DNA solutions show tumbling occurs^{14, 16, 17}. It appears that the general assumption of chain extension in flow may not be valid for concentrations above critical overlap¹¹⁻¹⁵. Furthermore, recent Brownian dynamics simulations have also predicted chain compression (in dilute solution) where excluded volume effects are neglected and hydrodynamic interactions are accounted for^{18, 19}. While these simulations have been done for dilute chains, the neglect of excluded volume effects and inclusion of hydrodynamic interactions embodies some of the physics of concentrated solutions. Furthermore, it is worth noting that Kuhn originally proposed that both extensive and compressive hydrodynamic forces act on the chains as they tumble in Jeffrey orbits^{20, 21}.

2. Theory

A new model of polymers in flow in which the chains compress in flow in the semi-dilute concentration region is proposed. The polymer molecules are modeled as space filling blobs. The blobs behave as individual random chains that compress into themselves as the concentration is increased above critical overlap, (C^*). A recent study has shown that in the semi-dilute concentration range, mixing and comensurate entanglement is thermodynamically unfavourable²². The lowest free energy state of the chains is compressed into themselves and not interpenetrated and mixed as has been previously assumed¹⁹. The non-entangled chains are then assumed to simply tumble and compress in response to the applied shear stresses as has been observed experimentally^{12, 13}. For the semi-dilute solution, the extensive hydrodynamic force is countered by the surrounding chains (the presence of the neighbouring chains restricts any extension) and the net effect

is that compression occurs in flow. A minimum entropy production argument using steady state irreversible thermodynamics is required to prove if compression is responsible for shear viscoelasticity^{23,24}. Coil compression would however lead to reduced friction in the system and therefore reduced entropy production through viscous losses.

Excluded volume effects are considered isotropic throughout solution and not incorporated in the model as previously discussed³. The macromolecules are treated as ideal chains in concentrated solution as first proposed by Flory³.

In steady state flow the compressive hydrodynamic and elastic forces on the dumbbell are equated:

$$f_{el} = f_{hyd} \quad [1]$$

The elastic force for the ideal chain is a function of the mean square average end-to-end distance, r , as derived previously²⁵:

$$f_{el} = k_B T \left[\frac{3r}{Na^2} - \frac{2}{r} \right] \quad [2]$$

Where k_B is Boltzmann's constant, T the absolute temperature, r , the magnitude of the change in the average end-to-end vector, N the number of freely jointed segments and a the segment length. The equation for the ideal chain is used to describe the Hookean spring connecting the beads of the dumbbell. **Equation 2** is effectively for the chain in a theta solvent with correct form for the elastic response of the random chain²⁶. The generally accepted form uses only the first term in the bracket in **Equation 2**^{2, 4, 5, 7}. Using only the first term for the Hookean force law requires that the force is zero when the end-to-end distance is zero. This is not physically the case as the chains have a finite size at zero force^{6, 25, 26}. The use of the generally accepted form essentially excludes compression from occurring^{25, 27}.

The maximum hydrodynamic force on the dumbbell is a modified Stokes drag:

$$f_{hyd} = 6\pi\eta\dot{\gamma}r^2 \quad [3]$$

Here the viscosity of the polymer solution is η , $\dot{\gamma}$ the shear rate experienced by the chain and r the magnitude of the average end-to-end vector as defined above. The use of r^2 arises from the assumption that the size of the chain determines the effective spring length while the hydrodynamic Stokes drag is also a function of the blob size to

yield an r^2 dependence of the hydrodynamic force on the dumbbell chain^{10, 20}. Both the spring size and the bead size are proportional to r so the approximation is made that the hydrodynamic force varies as r^2 in accord with the original derivation of the hydrodynamic drag by Kuhn²⁰. Equation [3] is then simply the maximum extensive or compressive force as first derived by Kuhn in his 1933 paper²⁰. The direction of the hydrodynamic force on the dumbbell is assumed compressive in nature. **Equation 3** contains no angular dependence and represents the maximum extensive or compressive force. Extension has been assumed in the literature^{2, 4, 7, 8, 10, 28, 29}.

Equating [2] and [3] and using $r = (Na^2)^{1/2}$ yields:

$$r^3 = \frac{k_B T}{6\pi\eta\dot{\gamma}} \quad [4]$$

Which requires that the average end-to-end distance of the chains decrease with increasing shear rate. The viscosity η experienced by the individual chain is not constant, rather is a function of r and will reduce as the chains contract in size. It should be noted that the explicit solution for [4] only exists for chain compression with increasing shear rate.

To first order the viscosity, η , is approximated by a modified version of Einstein's equation:

$$\eta \sim \eta_0 \phi \quad [5]$$

where the η_0 is the effective solvent viscosity and ϕ the volume fraction of the chains. We assume that any change in ϕ is small and that $\phi \sim r^3$. While Einstein's equation is strictly only valid for dilute solutions the approximation used here is that the surrounding chains act as an approximately constant solvent viscosity. This is obviously an approximation and a full calculation would require the use of higher order terms in the so called Batchelor equation^{30, 31}. By substitution into **Equation 4** we obtain the following relationship:

$$\text{So that} \quad \eta \sim \left[\dot{\gamma} \right]^{-\frac{1}{2}} \quad [6]$$

The power law model for shear thinning systems is^{32, 33}:

$$\eta \sim \left[\dot{\gamma} \right]^n \quad [7]$$

Values reported for polymeric systems range between $n \sim -0.2$ to -1 ³²⁻³⁴. Interpretation of the data presented by Stratton indicates that for mono-disperse polystyrene, $n = -0.82$ ³². The value of $n=1/2$ predicted by the model is well within the range of accepted values for shear thinning polymers³⁴.

The radius dependence with shear rate is then:

$$r \sim \left[\dot{\gamma} \right]^{-1/6} \quad [8]$$

3. Discussion

The shear rate dependence of the radius has recently been measured and is plotted on a log-log scale in **Figure 1**¹³.

Figure 1. A log-log plot of the data for the end-to-end distance r versus shear rate for 49kD FRET tagged PMMA in Couette flow¹³. The line of best fit yields an inverse 0.08 power of the radius with shear rate. The fitted equation is: $\log r = -0.08 \ln(\dot{\gamma}) + 0.68$ with $R^2 = 0.81$. The error bars are indicated by the size of the circles.

The data presented in **Figure 1** is for time resolved FRET measurements on end tagged PMMA as a molecular tracer in a matrix of untagged PMMA at $\sim 2C^*$ ¹³. The measured dependence of the decrease in the radius with increasing shear rate (power law of -0.08) is in reasonable agreement with the model prediction of -0.16 derived in Equation 8. Furthermore, the model predicts a power law for the viscosity of -0.5 close to the range observed for polymer solutions which vary from -1.0 to -0.2 ³²⁻³⁴. Given that the model uses a first order approximation for the Einstein equation, and the theta condition the model appears a reasonable fit to the dependence of the radius and viscosity with shear rate. A modified version of the elastic force law

would be required to account for the good solvent condition. This would decrease the rate of decrease in r and η with shear rate to diminish the difference between the predicted and measured values. Also a correction to the Einstein equation for interactions in the higher order terms would yield lower values of the predicted power law as less decrease in r would result in the same change in viscosity. However, the predicted and measured decrease in radius with shear rate are in reasonable agreement given the use of the first order Einstein equation to allow an analytical solution to the equations.

The model presented is where the chains behave as simple blobs, modelled as Hookean dumbbells which compress into themselves with the application of shear. For this approach, the “relaxation time” of the system will increase with increasing shear rate and is therefore consistent with the physics of the problem. Bird and Deaguir have proposed a model for concentrated polymer solutions in which extension of the dumbbells is assumed¹⁰. Extension of the dumbbells would require that the expanded chains interpenetrate in flow or align in the flow direction. The alignment in the flow direction would also lead to a reducing viscosity with increasing shear rate. However, recent experimental evidence has shown that in semi-dilute solutions the chains compress in Couette flow¹¹⁻¹⁵.

4. Conclusions

The model for polymers in flow is presented where the chains behave as elastically deformable dumbbells that compress in simple shear flow at semi-dilute concentrations. Simply equating the elastic and hydrodynamic forces on the dumbbell enables the power law behaviour observed for shear thinning and the reduction in end-to-end distance with shear rate to be predicted with reasonable accuracy. Physically the model is consistent with the observed rheology of polymer solutions which is attributed here to compression of the chains in flow rather than the previously assumed extension. Development of the model using the assumption that the chains compress will enable simple prediction of polymer visco-elastic behaviour including the power law for shear thinning.

References

- [1] L. H. Sperling, *Introduction to Physical Polymer Science*, Wiley Interscience: NJ **1992**.
- [2] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press: Oxford, **1986**.
- [3] P. J. Flory, *Statistical Mechanics of Chain Molecules*, Hanser Publications: New York, **1988**.

- [4] P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press: Ithaca, **1979**.
- [5] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, **1953**.
- [6] L. R. G. Treloar, *The Physics of Rubber Elasticity*, Oxford University Press, Oxford **1975**.
- [7] R. B. Bird, C. F. Curtiss, R. C. Armstrong and O. Hassager, *Dynamics of Polymeric Liquids, Volume II, Kinetic Theory*, Wiley-Interscience: New York, **1987**.
- [8] G. Marrucci and J. J. Hermans, *Macromolecules*, **1980**, 13, 380-387. [doi:10.1021/ma60074a034](https://doi.org/10.1021/ma60074a034)
- [9] G. Marrucci and N. Grizzuti, *Journal of Non-Newtonian Fluid Mechanics*, **1986**, 21, 319-328. [doi:10.1016/0377-0257\(86\)80043-X](https://doi.org/10.1016/0377-0257(86)80043-X)
- [10] R. B. Bird and J. R. Deaguiar, *J. Non-Newtonian Fluid Mechanics*, **1983**, 13, 149-160.
- [11] D. E. Dunstan, E. K. Hill and Y. Wei, *Macromolecules*, **2004**, 37, 1663-1665. [doi:10.1021/ma030413v](https://doi.org/10.1021/ma030413v)
- [12] N. Y. C. Chan, M. Chen and D. E. Dunstan, *European Physical Journal E*, **2009**, 30, 37-41. [doi:10.1140/epje/i2009-10503-x](https://doi.org/10.1140/epje/i2009-10503-x)
- [13] N. Y. C. Chan, M. Chen, X.-T. Hao, T. A. Smith and D. E. Dunstan, *J. Phys. Chem. Lett.*, **2010**, 1, 1912-1916. [doi:10.1021/jz100535b](https://doi.org/10.1021/jz100535b)
- [14] P. LeDuc, C. Haber, G. Bao and D. Wirtz, *Nature*, **1999**, 399, 564-566. [doi:10.1038/21148](https://doi.org/10.1038/21148)
- [15] D. E. Dunstan, *Eur. J. Phys.*, 2008, **29**, 977-985. [doi:10.1088/0143-0807/29/5/011](https://doi.org/10.1088/0143-0807/29/5/011)
- [16] R. E. Teixeira, H. P. Babcock, E. S. G. Shaqfeh and S. Chu, *Macromolecules*, **2004**, 38, 581-592. [doi:10.1021/ma048077l](https://doi.org/10.1021/ma048077l)
- [17] J. S. Lee, E. S. G. Shaqfeh and S. J. Muller, *Phys. Rev. E*, **2007**, 75, 040802-040806. [doi:10.1103/PhysRevE.75.040802](https://doi.org/10.1103/PhysRevE.75.040802)
- [18] C. Sendner and R. R. Netz, *European Physical Journal E*, **2009**, 30, 75-81. [doi:10.1140/epje/i2009-10509-4](https://doi.org/10.1140/epje/i2009-10509-4)
- [19] D. Petera and M. Muthukumar, *Journal of Chemical Physics*, **1999**, 111, 7614-7623. [doi:10.1063/1.480087](https://doi.org/10.1063/1.480087)
- [20] W. Kuhn, *Kolloid Zeitschrift*, **1933**, 62, 269-285. [doi:10.1007/BF01423246](https://doi.org/10.1007/BF01423246)
- [21] G. B. Jeffrey, *Proceedings of the Royal Society of London Series A*, **1922**, 102, 161-179. [doi:10.1098/rspa.1922.0078](https://doi.org/10.1098/rspa.1922.0078)
- [22] N. Y. C. Chan and D. E. Dunstan, *J. Phys. Chem.*, **2010**, 114, 10520-10523. [doi:10.1021/jp101793c](https://doi.org/10.1021/jp101793c)
- [23] K. G. Denbigh, *The Thermodynamics of the Steady State*, John Wiley NY, **1951**.
- [24] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, Charles Thomas, Illinois, **1955**.
- [25] R. M. Neumann, *Phys. Rev. A*, **1986**, 34, 3486-3488. [doi:10.1103/PhysRevA.34.3486](https://doi.org/10.1103/PhysRevA.34.3486)
- [26] R. M. Neumann, *J. Chem. Phys.*, **1999**, 110, 7513-7515. [doi:10.1063/1.478653](https://doi.org/10.1063/1.478653)
- [27] R. M. Neumann, *Biophysical Journal*, **2002**, 82, 3418-3420.
- [28] J. D. Ferry, *Viscoelastic Properties of Polymers*, John Wiley **1980**.
- [29] W. W. Graessley, *Polymeric Liquids & Networks: Structure and Properties*, Garland Science, New York, **2004**.
- [30] G. K. Batchelor, *An Introduction to Fluid Dynamics*, Cambridge University Press, **1967**.
- [31] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press, **2003**.
- [32] R. A. Stratton, *Journal of Colloid and Interface Science*, **1966**, 22, 517-530. [doi:10.1016/0021-9797\(66\)90047-6](https://doi.org/10.1016/0021-9797(66)90047-6)
- [33] H. A. Barnes, J. F. Hutton and K. Walters, *An Introduction to Rheology*, Elsevier, Amsterdam, **1989**.
- [34] D. Song, R. K. Gupta and R. P. Chhabra, *Industrial & Engineering Chemistry Research*, **2011**.