

3. Structure and rheology of polymeric fluids

3.1. Structural properties of polymers

In order to characterize the structure of polymers, different structural parameters need to be taken into account such as the degree of branching, Wiener index, radius of gyration, radial distribution of mass and interpenetration function.

3.1.1. Degree of branching and Wiener index

The topology of a polymer molecule is normally characterized by the degree of polymerization (number of sites), degree of branching and Wiener index. The two latter parameters are of great importance when polymers studied have the same molecular weight. As mentioned in the previous Chapter, the degree of branching, defined as $B = 2D/(2D + L)$ where D and L are the numbers of fully and partially reacted sites respectively, indicates the proportion of perfectly branching units in the molecule. For linear chains, the value of B is always 0. This value reaches the maximum of 1 for the case of dendrimers or fully branched hyperbranched polymers. Randomly branched hyperbranched polymers have the degree of branching falling between 0 and 1. Figure 3.1 illustrates some examples of polymer architecture with the same degree of polymerization but different degree of branching.

In addition to this structural parameter, the Wiener index is also used to distinguish

polymers of different topologies. As previously defined in Chapter 2, $W = \frac{1}{2} \sum_{j=1}^{N_s} \sum_{i=1}^{N_s} d_{ij}$

where d_{ij} is the number of bonds between bead i and j . The Wiener index is important in describing the connectivity within a polymer molecule. Larger Wiener index numbers indicate higher numbers of bonds separating beads in molecules and hence more open structures of polymer molecules. Among non-cyclic polymers of the same molecular weight, linear chains have the largest Wiener index number while star polymers with the core functionality of $N_s - 1$ have the smallest value of W . Figure 3.2 shows the Wiener indices of polymers with different architecture but the same degree of polymerization.

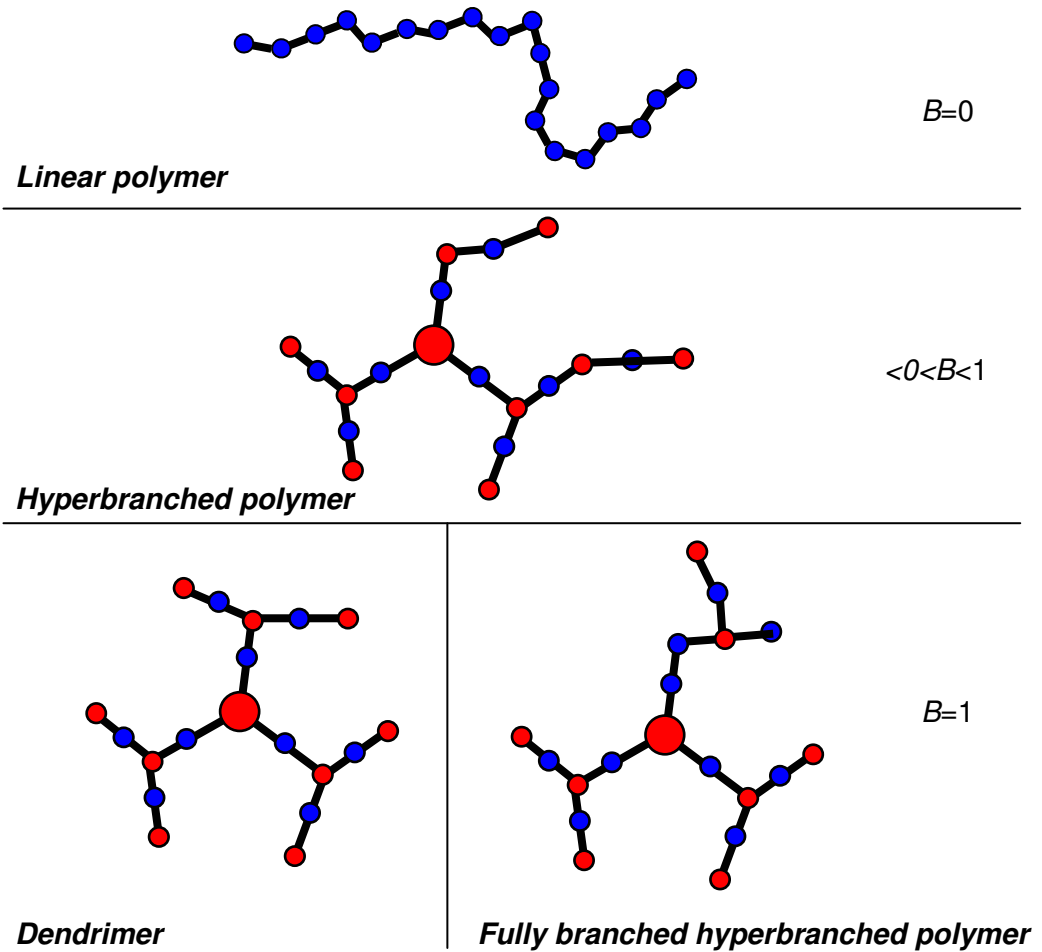


Figure 3.1. Degree of branching for different polymer architectures of the same molecular weight (blue beads representing linear units and red beads representing branching units).

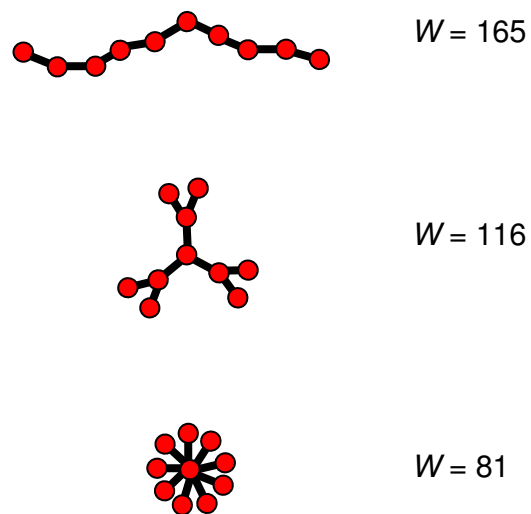


Figure 3.2. Wiener index for different polymer architectures of the same molecular weight (10 monomers).

3.1.2. Radius of gyration

The size of a polymer molecule can be described by the radius of gyration which is the trace of the tensor of gyration given as:

$$\langle \mathbf{R}_g \mathbf{R}_g \rangle \equiv \left\langle \frac{\sum_{\alpha=1}^{N_s} m_{\alpha} (\mathbf{r}_{\alpha} - \mathbf{r}_{CM}) (\mathbf{r}_{\alpha} - \mathbf{r}_{CM})}{\sum_{\alpha=1}^{N_s} m_{\alpha}} \right\rangle \quad (3.1)$$

where \mathbf{r}_{α} is the position of site α , \mathbf{r}_{CM} is the position of the molecular centre of mass, m_{α} is the mass of site α and the angle brackets denote an ensemble average. The radius of gyration is thus the average distance from the centre of gravity to the chain segment. It can be measured experimentally using different techniques and is dependent on molecular weight. Polymers with higher degree of polymerization normally have larger radius of gyration. Furthermore for a given value of molecular weight, depending on the branching topology, the value of the radius of gyration for different branched polymers can vary.

3.1.3. Radial distribution of mass

The radial distribution functions can give an extensive profile of the system structure. The distribution of sites from the molecular centre of mass is given as:

$$g_{CM}(r) = \frac{\left\langle \sum_{i=1}^N \sum_{\alpha=1}^{N_s} \delta(|\mathbf{r} - (\mathbf{r}_{i\alpha} - \mathbf{r}_{CM})|) \right\rangle}{N} \quad (3.2)$$

where N is the total number of molecules, \mathbf{r}_{CM} is the position of the centre of mass and α runs over all other sites belonging to the same molecule. Similarly, the distribution from the central site (the core) can be defined as:

$$g_{core}(r) = \frac{\left\langle \sum_{i=1}^N \sum_{\alpha=2}^{N_s} \delta(|\mathbf{r} - (\mathbf{r}_{i\alpha} - \mathbf{r}_{i1})|) \right\rangle}{N} \quad (3.3)$$

where \mathbf{r}_{i1} is the position of the core. If α only runs over the outermost layer of each molecule, the distribution of terminal groups can be computed. This is important for the analysis of the entanglement and back folding in molecules.

In order to characterize the internal structure and spatial ordering of sites composing the materials, the atomic radial distribution can be computed as:

$$g_A(r) = \frac{\left\langle \frac{1}{2} \sum_{i=1}^{N_{total}} \sum_{j \neq i}^{N_{total}} \delta(|\mathbf{r} - \mathbf{r}_{ij}|) \right\rangle}{4\pi r^2 N_{total} \rho} \quad (3.4)$$

where \mathbf{r}_{ij} is the distance between the sites i and j , $N_{total} = NN_s$ is the total number of sites in the studied system, and ρ is the density. Results can be compared to those of diffraction experiments.

Another useful function that has been used in this work is the interpenetration function which is defined as:

$$g_{inter}(r) = \frac{\left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{\alpha=1}^{N_s} \delta(|\mathbf{r} - (\mathbf{r}_{j\alpha} - \mathbf{r}_{i1})|) \right\rangle}{4\pi r^2 N} \quad (3.5)$$

where $\mathbf{r}_{j\alpha}$ is the position of bead α in molecule j . This function shows the ability of sites of a molecule to penetrate into the volume occupied by other molecules in the system. Polymers with more open structures have higher values of the interpenetration function as interior parts of molecules are more accessible.

3.2. Flow birefringence

Many complex fluids are birefringent because they contain orientable molecules, particles and microstructures that rotate and the index of refraction becomes anisotropic under flow, electric or magnetic fields (Larson, 1999). The birefringence due to the alignment of molecules is called ‘form birefringence’ while that caused by intramolecular bond alignment is called ‘intrinsic birefringence’. For simple polymeric fluids, the birefringence tensor is often proportional to the stress tensor. This relationship is called the ‘stress optical rule’ (SOR).

The form birefringence can be characterized by analysing the molecular alignment tensor given by:

$$\mathbf{S}_m = \sum_{i=1}^N \left\langle \mathbf{u}_i \mathbf{u}_i - \frac{1}{3} \mathbf{I} \right\rangle \quad (3.6)$$

where \mathbf{u}_i is the unit vector denoting the orientation of the single molecules. The direction in which molecules are aligned is indicated by the eigenvectors of this tensor and the eigenvector corresponding to the largest eigenvalue of the tensor of gyration denotes the orientation of the molecule \mathbf{u}_i . The molecular alignment angle is the angle between the flow direction and the molecular alignment direction.

The intrinsic birefringence can be described using the bond alignment tensor which can be computed as:

$$\mathbf{S}_b = \sum_j^N \left\langle \sum_{i=1}^{N_s-1} \mathbf{v}_i \mathbf{v}_i - \frac{1}{3} \mathbf{I} \right\rangle \quad (3.7)$$

where \mathbf{v}_i is the unit vector between neighbouring sites, defined as:

$$\mathbf{v}_i = \frac{\mathbf{r}_{i+1} - \mathbf{r}_i}{|\mathbf{r}_{i+1} - \mathbf{r}_i|}. \quad (3.8)$$

The flow alignment angle and the extent of the bond alignment can be calculated similarly to those of the molecular alignment.

3.3. Rheology of polymeric fluids

Polymeric fluids are the most studied of all complex fluids due to their rich rheological behaviour which determines the ease and expense of processing as well as the final properties of different manufactured products. Polymeric fluids are classic examples of ‘viscoelastic’ fluids (Bird et al., 1987). The use of the word ‘elastic’ is to characterize the ability to return to its original state and shape after the release of the applied stress. Because of this property, polymeric fluids which have the elastic property are also referred to as ‘memory’ fluids.

Polymeric fluids often show strong viscoelastic effects which can include shear thinning, extension shear thickening, viscoelastic normal stresses and time-dependent rheology (Larson, 1999). In order to characterize the rheology of polymer liquids, systems of these materials under shearing or extensional flow are studied. There are many possible deformations that can be imposed on a polymeric fluid. Some of the

simple geometries for imposing a shear flow, including sliding plates, concentric cylinders, parallel disks and the cone and plate (Macosko, 1994), are presented in Figure 3.3.

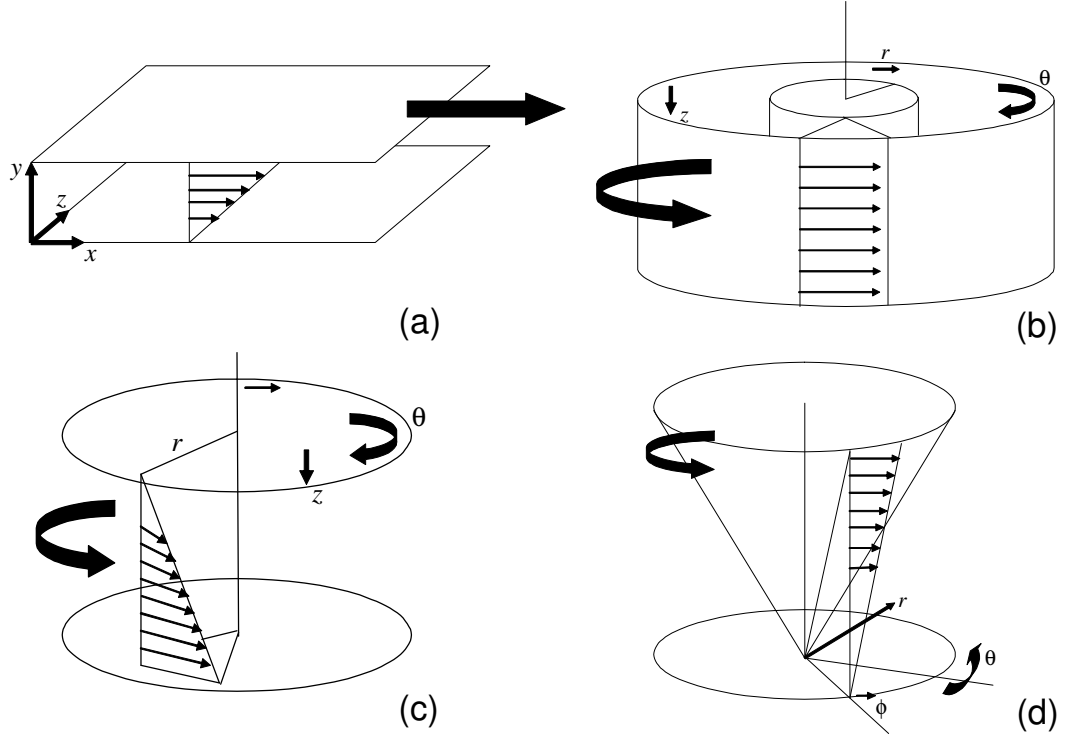


Figure 3.3. Simple geometries for producing shear flows (a) sliding plates (planar Couette geometry), (b) concentric cylinders (cylindrical Couette geometry), (c) parallel disks or plate-and-plate (torsional flow) and (d) the cone-and-plate. (adopted from (Macosko, 1994)).

The simple geometry, sliding plates, experimentally generates planar Couette flow. The polymeric system is placed between two parallel plates moving in opposite directions. The resulting streaming velocity $\mathbf{v} = \mathbf{v}(\mathbf{r}, t)$ of the molecules has a linear profile as can be seen in Figure 3.4. The velocity gradient tensor is calculated as:

$$\nabla \mathbf{v} = \partial \mathbf{v} / \partial \mathbf{r} \quad (3.9)$$

and the strain rate, which is the symmetric part of this tensor, can be computed as:

$$\dot{\gamma} = \sqrt{2I_2} \quad (3.10)$$

where $I_2 = \text{Tr}(\mathbf{D} \cdot \mathbf{D})$ and $\mathbf{D} = \frac{1}{2}(\nabla \mathbf{v} + (\nabla \mathbf{v})^T)$. This planar Couette geometry has been employed in this work with linear streaming velocity profiles for molecules but with the absence of sliding plates.

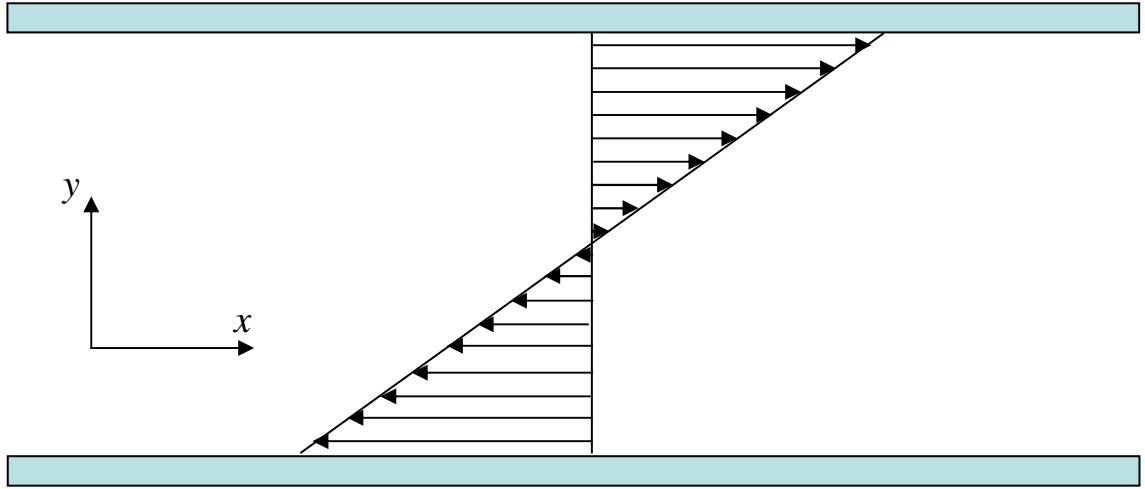


Figure 3.4. Streaming velocity profile of the polymeric fluid undergoing planar Couette flow.

3.3.1. Shear stress

The shear stress is the force that a flowing fluid exerts on a surface in the direction parallel to the flow. The shear stress $\sigma_{xy}(t)$ is the corresponding off-diagonal element of the stress tensor $\boldsymbol{\sigma}(t)$ which is given by:

$$\boldsymbol{\sigma}(t) = -\left[\mathbf{P}(t) - \frac{1}{3} p \mathbf{I} \right] \quad (3.11)$$

where \mathbf{P} is the pressure tensor, p is the hydrostatic pressure and \mathbf{I} is a unit tensor. For Newtonian fluids, only the shear stress is nonzero. However for non-Newtonian liquids, all six independent components of the stress tensor may be nonzero. The general form of the stress tensor in planar shear is given as:

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ \sigma_{yx} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{bmatrix} \quad (3.12)$$

In all polymeric systems, the stress depends on the conformations of the molecules. After a steady shear flow has been imposed on a fluid for a suitable period of time, the shear stress often converges to a steady state value.

3.3.2. *Non-Newtonian viscosity*

The steady-state shear viscosity is defined as:

$$\eta = \frac{\sigma_{xy}}{\dot{\gamma}} \quad (3.13)$$

The dependence of viscosity on shear rate is the most characteristic feature of a macromolecular complex fluid. Unlike Newtonian fluids which have constant viscosity, the viscosity of polymeric fluids reaches a plateau in the low strain rate region and decreases at strain rates above a certain value. In some cases, the viscosity drops rapidly and by many orders of magnitude. The decrease of viscosity is called shear thinning and the materials expressing it are referred to as pseudo-plastic. In fact, most of the polymer solutions and melts which exhibit a shear-rate dependent viscosity are shear thinning (Bird et al., 1987). The critical shear rate at which the transition from Newtonian to non-Newtonian flow occurs is related to a relaxation time τ_0 characteristic for the molecules composing the system through the form:

$$\dot{\gamma}_c = \frac{1}{\tau_0} \quad (3.14)$$

At shear rates above the critical value, the viscosity becomes shear rate dependent.

On the other hand, the shear viscosity for some macromolecular fluids increases with the shear rate. This phenomenon is called shear thickening. Furthermore some fluids can show a region of shear thinning at low shear rates, then shear thickening at higher shear rates and followed by shear thinning again at very high shear rates. This behaviour was found in the flow of dense suspensions (Larson, 1999).

3.3.3. *Normal stress effects*

The viscoelastic effects of polymeric liquids can be represented by the normal stress differences of the liquid in steady flow. The first normal stress difference, which is defined as:

$$N_1(\dot{\gamma}) = \sigma_{xx} - \sigma_{yy} \quad (3.15)$$

where σ_{xx} and σ_{yy} are the xx and yy components of the stress tensor, is always positive.

This implies that there is a higher degree of orientation in the direction of the flow, the x

direction, than in the direction of the velocity gradient, the y direction. In contrast, the second normal stress difference, which is given by:

$$N_2(\dot{\gamma}) = \sigma_{yy} - \sigma_{zz} \quad (3.16)$$

where σ_{zz} is the zz component of the stress tensor, is always negative. This implies that the orientation in the y direction is reduced because of the polymer orientation related to the vorticity z direction (Larson, 1999). Although the second normal stress difference has been studied much less extensively, it was found that the dependence of the second normal stress difference on shear rate is similar to that for the first normal stress difference but smaller by an order of magnitude.

From the first and second normal stress differences, the first and second normal stress coefficients, which are used to describe the behaviour of the molecular fluids, can be calculated using the following equations:

$$\psi_1(\dot{\gamma}) = \frac{N_1}{\dot{\gamma}^2} \quad (3.17)$$

$$\psi_2(\dot{\gamma}) = \frac{N_2}{\dot{\gamma}^2} \quad (3.18)$$

Together with the viscosity, the first and second normal stress coefficients are sometimes collectively referred to as the viscometric functions. The positive value of the first normal stress coefficient means that the polymeric fluids exhibit an extra tension along the streamlines in the x direction in addition to the shear stresses. In contrast, the negative and much smaller value of the second normal stress coefficient means that the fluids exhibit a small extra tension in the z direction. (Bird et al., 1987).

3.3.4. Dimensionless groups in non-Newtonian fluid mechanics

Dimensionless groups are useful for scaling arguments and classifying flow regimes (Bird et al., 1987). In Newtonian fluid mechanics, the Reynolds number, which is interpreted as the ratio of the magnitude of inertial forces to that of viscous forces, is generally the most important dimensionless group. For non-Newtonian fluids, the key dimensionless groups are Deborah number and Weissenberg number.

In this work, only the Weissenberg number has been used with the purpose of establishing master curves for shear viscosity data of different hyperbranched polymers.

The Weissenberg number is defined as:

$$Wi = \lambda\kappa \quad (3.19)$$

where λ is a characteristic time of the fluid and κ is a characteristic strain rate in the flow.