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From reactor to rheology in industrial polymers

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Author Biography

Daniel Read studied Natural Sciences at Cambridge (1991-1994) and has a PhD in Polymer Physics from the University of Leeds (1994-1997). His move to the School of Mathematics in 2000, as a lecturer and subsequently a reader, coincided with his first work on both polymer rheology and on modelling long chain branching in metallocene polymerisations [29]. He is a co-author of the "BoB" code for entangled polymer rheology prediction [72,75,78].

Abstract

This article reviews current efforts towards quantitative prediction of rheological properties of industrial polymer resins, based upon their polydisperse branched molecular structure. This involves both an understanding of how reactor and reaction conditions influence the distribution of chain lengths and branch placement (which is the province of reactor engineering) and an understanding of how the molecular structures in turn give rise to the rheology (the province of polymer physics). Both fields are reviewed at an introductory level, focussing in particular on developments in theoretical prediction of rheology for both entangled model polymers and industrial polymers. Finally, we discuss three classes of reaction for which the fields of reactor engineering and polymer physics have been truly combined to produce predictions from reactor to rheology.

1. Introduction

Controlling the properties of polymeric liquids under processing flows is one of the long standing, and fundamental, challenges of industrial polymer science. It has long been known that even a few branches for every thousand carbons (so-called "long-chain branching") has the potential to confer favourable engineering properties, drastically modifying the viscosity and generating additional elasticity in response to extensional flow [1-4]. For this reason, changes in reactor design, or in the mechanistic pathway of long-chain branch formation (e.g. free radical transfer, or macromonomer incorporation), are able to modify the processing properties of industrial resins via changes in reaction kinetics. A good deal of practical progress can be made on a trial-and-error basis, but there is a natural desire to understand the underlying science, and thereby to open the possibility of control and design within the process.

Multiple academic disciplines feel they have a say in the outcome of this story. Polymer chemists and polymer reaction engineers both have a significant stake. After all, it is chemical processes which determine the mechanisms of long chain branch formation; control via modification of the reaction mechanism is vital. Consideration of the distribution of molecular weight and branching arising from specific reaction kinetics goes back to the earliest days of theoretical polymer chemistry [5]. This being said, reactor design also plays a significant role, since it affects the possible branching events that can occur, via the reagent concentrations, reaction rates and residence times. So, reaction engineers have, for a long time, been developing (largely computational) methods for appropriate solution of chemical rate equations to determine evolution of branching and molecular weight [6-8]. Put simply, the reaction conditions control the distribution of molecular shapes.

On the other hand, polymer physicists will rightly highlight their contribution to this story. A key insight is the near-universality of the configurations and dynamics of polymer chains [9]. Polymers are long, often flexible, connected objects, and the form of their large scale dynamics is, to a good approximation, independent of the detailed local chemistry. The dynamics depend rather on the connectivity of the molecules, and the degree to which they are entangled with each other. Within this picture, the local chain chemistry sets only a few fundamental parameters, such as the timescale of local motions and the molecular weight of polymer chain required to form entanglements [10] (though we may note that real polymers often depart a little from this idealised framework). Important observations result from this dynamical universality. Measurements on one polymer chemistry can inform discussion about the dynamics of other polymer chemistries – so, for example, conclusions drawn from dynamical measurements of a star-shaped polyisoprene [see, e.g. 11] should apply, in principle, to all star-shaped flexible polymers, and can inform discussion about the dynamics of branched polymers in general. Similarly, computational experiments (simulations) on highly idealised bead-spring “chemistries” have direct relevance to the dynamics of real polymers (e.g. [12-16]). This universality has also allowed for the development (over several decades) of a theoretical framework for the dynamics of flexible, entangled, string-like molecules, the so-called “tube-model,” [17] which has been found to be applicable to a wide range of polymer chemistries and architectures [10, 18]. This modelling framework allows for prediction (at a quantitative level) of the flow properties of polymer resins depending upon their detailed shape and branching structure. Put simply, the molecular shape controls the polymer dynamics and rheology.

At all levels, experimental characterisation of polymer resins is vital, through rheology, molecular weight, branching measurements, and more. Such measurements challenge and inform all theoretical developments.

So, significant progress has been made *within* each of the academic disciplines as described above. Nevertheless, it is clear that to understand and control the whole process from reactor and reaction design through to flow properties of the resin requires a joining together of the different disciplines, i.e. a *coupled* investigation both of how reaction conditions affect molecular shapes, and then of how those shapes affect rheology. Ultimately it would be desirable to be able to specify a set of reactor conditions to obtain a required material rheology. There are some investigations along these lines in the literature, as will be described below, but they are (so far) relatively rare. It is partly to inspire such joined-up work that this review article is offered. We begin with a description of the two separate disciplines of polymer reaction engineering (section 2) and the physics of polymer dynamics (section 3). Because of the expertise of the author, section 2 is necessarily shorter than section 3. We then detail, in section 4, a few investigations that have managed, in part, to span the whole problem, before concluding with an outlook in section 5.

2. From reactor to molecules

This section is offered as a brief overview, from the perspective of a polymer physicist, of some of the common methods for prediction of distributions of polymer molecular weight and branching structure. It is therefore not in any sense a comprehensive review of this vast topic. The interested reader may benefit from reviews such as refs [6-8]. In the following, we assume that the polymerisation reactions, the chemical rate equations governing them, and the reaction rate constants, are in principle known or measurable. This is a significant assumption: chemical reactions do not always proceed in an ideal fashion and determination of rate constants is not always straightforward [6].

We also note a specific requirement for connecting the results of reactor simulations to the rheology predictions detailed in section 3: there should be information not simply on the molecular weight and number of branches, but also (vitally) on the positions of branches within the molecular structure. This is required in order to apply the modelling apparatus discussed below in section 3.

Population balance methods

The most straightforward method, in terms of writing down the relevant reactor equations to solve, is the population balance method. This uses the polymerisation rate equations including all of the different chemical processes occurring within a reactor (such as polymerisation, chain termination, long-chain branching, chain scission, comonomer incorporation). This results in a large set of coupled differential equations for variables such as the concentration P_N of chains of degree of polymerisation N, which must then be solved to obtain either the steady state concentrations, or their time-dependence, in the reactor. For example, a simple single site polymerisation forming linear chains gives a dynamical equation for the concentration P_N of form [7]:

$$\frac{dP_N}{dt} = k_p M\left(P_{N-1} - P_N\right) - k_D P_N - sP_N \tag{2.1}$$

where k_p is a polymerisation rate constant, M is monomer concentration, k_D is the rate constant for a chain termination reaction and (assuming this is a stirred tank reactor) s is the rate at which material leaves the reactor. In principle this gives an infinite set of coupled differential equations which must be solved, but these can be immediately simplified by treating N as a continuous variable so that the difference $\left(P_N - P_{N-1}\right)$ becomes a derivative. At steady-state, equation (2.1) becomes:

$$0 = -k_p M \frac{dP_N}{dN} - \left(k_D + s\right)P_N\,. \tag{2.2}$$

The result is a single differential equation, and in this simple case analytical solution is possible, giving the “most probable” (exponential) distribution [19]. When a greater number of different chemical processes (such as branching) are included, the set of equations become significantly more complicated, and it becomes necessary to resort to numerical methods for solution, for example using the PREDICI© finite element software package (see, e.g. [20-23]), with parallel developments elsewhere, for example [24].

From the point of view of connecting to rheology modelling, the population balance method suffers from the shortcoming that whilst it predicts distributions of molecular weight and number of branches, it does not provide explicit information concerning the distribution of branches within the polymer molecules (there are many different possible shapes of molecule with the same number of branches and molecular weight). Attempts have been made to infer the distribution of polymer shapes for a given molecular weight and degree of branching, using a conditional Monte-Carlo sampling method [25, 26] but this requires assumptions to be made about sequence of chemical steps to produce the molecules. This lack of knowledge of the precise distribution of molecular topologies also produces uncertainties within the population balance equations themselves, specifically when polymer scission occurs (e.g. in free-radical polymerisation of low density polyethylene) where the distribution of scission fragments depends on the polymer structure. In linear polymers the scission point could be anywhere along the polymer length, giving a uniform distribution of scission fragments. In contrast, for branched polymers, the majority of the polymer length is contained within the outermost branches, so random scission would be expected to produce predominantly large and small scission fragments, depending upon the precise branched structure [27].

On the other hand, a positive aspect of population balance methods is that they interface naturally with larger scale simulations of realistic and complex reactors. In this more general case, chemical concentrations of reagents, catalysts and polymer product become dependent on both spatial position and time. Similarly, reaction rate constants may also vary, because of temperature changes, dependence on chemical concentration, or physical changes such as viscosity of the reaction mixture. Fluid flow, or material transport, may need to be accounted for. In this case, the population balance equations become more complicated, including (for example) both spatial derivatives and temporal derivatives. Steady-state assumptions may not apply. Nevertheless, the resulting partial differential equations can in principle still be solved using numerical techniques such as finite element or finite difference methods.

A yet simpler method of dealing with population balance equations is the method of moments [7], which proceeds by solving for the leading moments of the chain length distribution (directly related to the number average, weight average, and higher order averages of molecular weight). Often, for simple rate equations such as (2.1), this produces a closed set of equations which can be used to determine the evolution of quantities such as average molecular weight or average degree of branching. More complicated reaction schemes usually require the use of closure approximations to obtain a closed set of equations. From the point of view of connecting to rheology modelling, this method (unfortunately) produces less information on molecular branching structures than full solution of the population balance equations.

Analytical statistical methods

For some classes of polymerisation reaction, simple statistical methods can be used to obtain the distribution of molecular weight, branching, or topology. Such methods go back to the early days of theoretical polymer chemistry – for example Flory [5, 28] was able to investigate the molecular weight distribution of polycondensation reactions (e.g. AB_{f-1} monomers in which A groups react to B). These methods rely on the assumption that the likelihood of a given chemical group reacting is independent of that group's position within a molecule (so, for example, in the AB_{f-1} reaction one can define a fixed probability, p, that any given B group has reacted).

A further property of such reactions is a statistical self-similarity of the molecules. In the AB_{f-1} reaction, the probability distribution of what is attached to the reacted B groups of a given monomer is assumed to be independent of whether the A group on that monomer is reacted or not. Thus the statistical distribution of the molecule side-branches is identical to the statistical distribution of the molecules as a whole. For some polyolefin reactions, notably single-site metallocene catalysis, arguments can be made for an equivalent statistical self-similarity to the molecules [29, 30] permitting the same range of statistical techniques to be utilised as for polycondensation processes. One elegant method, relying on the self-similarity of molecules, is that of generating functions [9]. As an example of this, one can define a generating function $F(z)$ which is a power series in an arbitrary variable z:

$$F(z)=\sum_{N} p_N z^N \ . \tag{2.3}$$

The coefficients of the power series are the probabilities, p_N, that a molecule selected at random has degree of polymerisation *N*. The self-similarity of the molecules permits a closed formula to be written for $F(z)$. For example, for polycondensation of AB_2 monomers, the closed formula would be:

$$F(z)=z(1-p)^2+2p(1-p)zF+p^2zF^2 \tag{2.4}$$

where the three terms on the right correspond to the situation that a randomly chosen monomer has no reacted *B* groups, one reacted *B* group or two reacted *B* groups respectively. Implicit differentiation of closed formulae such as (2.4) yields averages of molecular weight. On the other hand, equations such as (2.4) can be rearranged so that $F(z)$ may be expanded in powers of the variable z, so that the probabilities, p_N, can be computed from the coefficients of the series expansion. Examples of this approach can be found in [9] for polycondensation reactions, and [29, 30] for metallocene reactions. Figure 1 shows the results from such an analytical calculation, in comparison to the population balance approach, for a mixed metallocene catalyst polymerisation [30].

With regard to supplying information for rheology calculations, the advantage of analytical statistical methods is that, in principle, everything about the molecules is statistically known, including the local probabilities of branching and the whole distribution of molecules. Thus it is very straightforward to generate a representative sample of molecules using Monte Carlo methods (see immediately below) or to calculate distributions, or averages, of rheologically relevant quantities such as *seniority* and *priority* (see section 3.2 below). Unfortunately, the range of polymerisation reactions and reactor conditions exhibiting the self-similarity property is extremely limited. As a result these methods, while elegant, are not of general applicability.

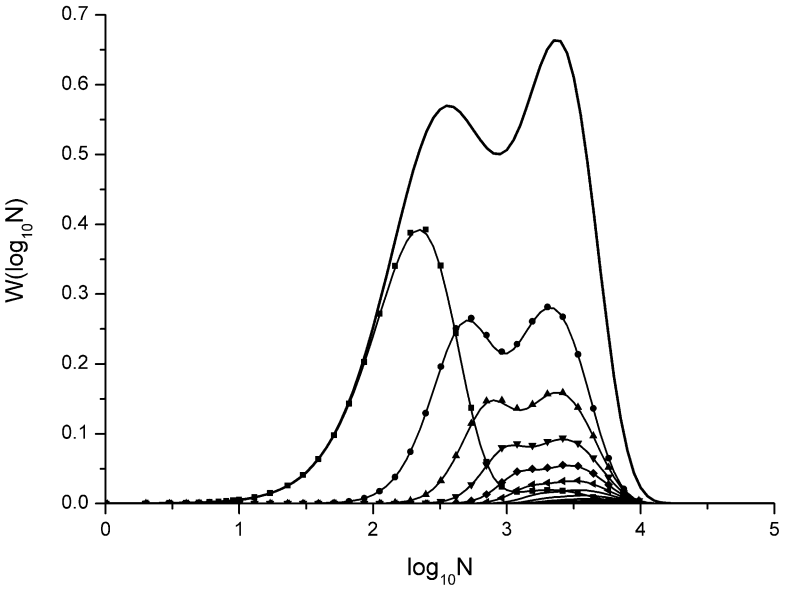

Figure 1: Prediction of the molecular weight distribution for a polymerisation involving two metallocene catalysts, one producing long linear chains, and the other producing shorter chains which admit branches. Lines are predictions using analytical methods, symbols are results of numerical solution of population balance equations. Reprinted with permission from *Macromolecules* **2003**, 36, 10037-10051. Copyright (2003) American Chemical Society.

Monte Carlo methods

The goal of a Monte Carlo method [6, 8] is to generate, by means of computation using random numbers, a representative sample of polymer shapes (in terms of size and location of branches). Since this is precisely the information required for subsequent prediction of the rheology of an entangled polymer resin, Monte Carlo methods have, to date, provided the principle means of connecting reactor simulations to rheology prediction.

Central to any Monte Carlo method is a consideration of the different chemical reactions occurring, in terms of their contribution to the chemical structure along a particular polymer chain strand. For example, in a metallocene polyolefin polymerisation [7, 29, 30], the rate of chain growth is the product $\mathrm{k_p M}$ of the polymerisation rate constant and monomer concentration. On the other hand, macromonomers, present in the reactor at concentration $\mathrm{D}^{=}$, are incorporated into the chain at an average rate of $\mathrm{k_{pLCB}D}^{=}$, forming long chain branches. The average number of monomers between long chain branches is obtained as the ratio of the two rates:

$$\frac{k_p M}{k_{pLCB} D^{=}} . \qquad (2.5)$$

These branches will be randomly distributed along the growing chain, and so within a computer algorithm can be placed statistically. Thus, the statistics of branch incorporation along a chain are obtained from the chemical rates, and might depend on the time at which the chain was formed, since monomer and macromonomer concentrations may be time-dependent quantities. A macromonomer, incorporated to form a long chain branch, will itself have been polymerised at some earlier time. The distribution for this time can also be determined from the rate equations of formation and reaction of macromonomers. So, having dealt with the branch distribution along a particular chain, one can then consider each side-branch in turn, and their branching structure. By these and similar considerations, it is possible to generate randomly, and recursively, a “representative” molecule based upon the reaction chemistry and rates. A typical Monte Carlo routine will generate many thousands of representative molecules in this manner, allowing the full distribution of molecular weight and branching to be approximated accurately.

The above description, for the metallocene reaction, was the basis of a Monte Carlo scheme to calculate the distribution of molecular topologies for batch polymerisations involving a mixture of metallocene catalysts [31], as shown in Figure 2. The method, however, is widely applicable [8], and has (for example) been applied to low density polyethylene (LDPE) polymerisation [32, 33] and vinyl-acetate polymerisation [34,35].

Application of the Monte Carlo sampling method is straightforward in idealised reactor engineering scenarios, such as an ideal batch, semi-batch, or continuous stirred tank reactor. In such cases, it is usually possible to calculate the statistical distribution of the lifetime of reactive species analytically: this is the type of information required in determining the local statistics of events such as branching during formation of a chain strand [6, 8]. Such calculations are less straightforward for industrial reactors where there are (for example) multiple injections points in a tubular reactor. In such cases, the population balance method is the more natural one. Nevertheless, progress can be made via numerical solution of lifetimes of reactor species [36, 37].

In summary, Monte Carlo methods appear (presently) to offer the best means of connecting reactor engineering to the polymer dynamics community, via a prediction of the distribution of molecular topologies. We now turn to that field of polymer dynamics.

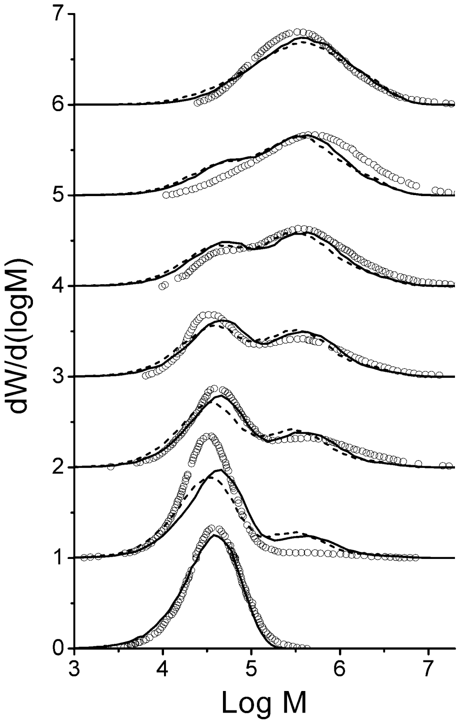

Figure 2: Experimental and computational molecular weight distributions for a batch polymerisations with different ratios of two metallocene catalysts, one producing linear macromonomers, and a second constrained geometry catalyst (CGC) allowing formation of long chain branches. Curves are shifted vertically, for clarity, and represent (from bottom to top) 0%, 20%, 35%, 50%, 65%, 80%, and 100% CGC catalyst. The solid line and dashed line give results from two different model parameterisations. Reprinted with permission from *Macromolecules* **2006**, 39, 4920-4931. Copyright (2006) American Chemical Society.

3. From molecules to rheology

3.1 The “standard” theoretical framework

In order to understand the rheology of a polymeric resin, and in particular the effect of molecular architecture, we need to describe the dynamics of the molecules and how they respond to the imposition of flow. The study of the dynamics of large macromolecules is now a relatively mature field, going back at least to the middle of the last century. Although there remains much room for research and debate about the details and foundations of models, a “standard” theoretical picture has emerged, to which the majority of work in this area refers. Substantial reviews and summaries of this field have been presented elsewhere [10, 18] and the interested reader is referred to these for details. Here, we shall summarise the main results and present the basic underlying picture.

Within this field, much research has focussed on the study of model polymers, nearly-monodisperse molecules with well-defined architecture in terms of their branching shape. Such materials give much sharper features in rheological experiments than their polydisperse industrial counterparts, and so are better suited to interrogation of the underlying physics of their motion. We begin by focussing on results for model systems, before discussing the efforts that have been made towards applying the lessons learnt to more practical industrial situations.

The Rouse model

For polymer melts, the local dynamics of chains are usually described using the Rouse model [38], which is the simplest existing model for polymer dynamics; all theoretical descriptions for polymer melt dynamics build on this. The polymer is modelled as a string of beads, each bead representing a short chain subsection, with typical distance b between beads. The chain configuration obeys random walk statistics, so a linear chain (sub)section of N beads, has mean square end-to-end distance $\left\langle \mathrm{R}^2 \right\rangle = \mathrm{Nb}^2$ at equilibrium. Chain dynamics are introduced in the Rouse model by giving each bead a local friction constant with a corresponding fluctuating thermal force. The detailed construction and solution can be found in [10]; for simplicity, the modal structure of the dynamics can be considered in terms of a hierarchy of relaxations. A chain subsection containing N beads relaxes its internal configurations on timescale given by its Rouse time:

$$\tau_{\mathrm{R}}(\mathrm{N}) = \tau_{\mathrm{bead}} \mathrm{N}^2 \qquad (3.1)$$

where τ_{bead} is a local monomer relaxation time.

Within this model, stress arises from deformation of chains, with spring forces arising due to chain configurational entropy. The shear modulus associated with deformations at the bead scale is $\mathrm{G}_{\mathrm{bead}} = \mathrm{C}_{\mathrm{bead}} \mathrm{k}_{\mathrm{B}} \mathrm{T}$ where $\mathrm{C}_{\mathrm{bead}}$ is the concentration of beads (naturally this is related to the concentration of monomers in a real physical resin). The modal structure of the dynamics within the Rouse model encourages *coarse-graining*. If we consider deformations on a longer timescale than the relaxation time $\tau_{\mathrm{R}}(\mathrm{N})$ of subchains of N beads, then these will have relaxed their internal configurations over the deformation timescale. We can coarse-grain to the scale of these chain subsections; the corresponding shear modulus at this coarse-grained scale is $\mathrm{G}_{\mathrm{N}} = \mathrm{C}_{\mathrm{N}} \mathrm{k}_{\mathrm{B}} \mathrm{T}$ where $\mathrm{C}_{\mathrm{N}} = \mathrm{C}_{\mathrm{bead}} / \mathrm{N}$ is the concentration of chain sections of length N.

Entanglements

If polymer chains in the melt are sufficiently long, then inter-chain entanglements become important. As regards the polymer dynamics, the main contribution of entanglements is to restrict motion of a given chain perpendicular to its contour, but to allow motion along the chain contour. This insight suggests that the chain is confined to a tube-like region of space (see Figure 3), leading to the “tube model” for entangled polymers, first applied to polymer dynamics by de Gennes [17].

We consider that there are, typically, N_e beads per entanglement strand, corresponding to a tube diameter a given by $a^2 = N_e b^2$ (the chain is a random walk within the tube; the tube diameter sets the typical confinement scale of the chain, and also the persistence length of the tube). A chain strand of N beads contains $Z = N/N_e$ entanglement strands. The tube provides a natural lengthscale for coarse-graining: the total concentration of entanglement strands is $C_e = C_{\mathrm{bead}} / N_e$ and the entanglement modulus is $G_e = C_e k_B T$. Using the recommended definitions in ref. [39] the so-called plateau modulus is then $G_0 = \frac{4}{5} G_e$. We also obtain a fundamental timescale, which is the Rouse time of an entanglement strand:

$$\tau_e = \tau_R(N_e) = \tau_{\mathrm{bead}} N_e^2 . \tag{3.2}$$

The set of parameters N_e, G_e and τ_e are the fundamental parameters for any tube-model description of a polymer melt, since they set a degree of entanglement, and the scales of stress and time respectively. In principle, N_e and G_e are related by $G_e = C_e k_B T$, but this constraint is sometimes relaxed a little for the purposes of fitting data.

de Gennes recognised that the fundamental motion of an entangled linear chain involves diffusion back and forth along its tube contour (see Figure 3). He termed this motion *reptation* [17] and noted that pure reptation motion gives rise to a tube escape time which can be written as

$$\tau_d = 3Z^3 \tau_{\mathbf{e}} = 3Z\tau_R . \tag{3.3}$$

Within the tube model, tube escape is considered to be the primary mode of stress relaxation: a deformed chain will hold memory of its deformation for as long as it is trapped

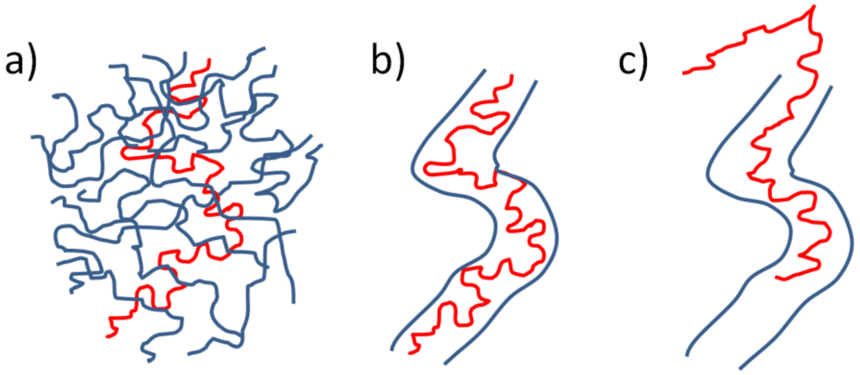

Figure 3: (a) a polymer chain in the melt is entangled with other chains, (b) this confines the motion of a the test-chain to a tube like region of space, (c) diffusive motion of the chain along the tube contour is known as reptation.

within the originally deformed tube, but cannot hold stress for longer than this. Hence, the tube escape time is also the terminal time for stress relaxation.

More recent models of entangled linear chains have improved substantially upon the original predictions of de Gennes, largely by adding two fundamental mechanisms to the original reptation picture:

- *Contour length fluctuations.* [13, 40-42] The "pure" reptation picture assumes that a fixed contour length of the chain in its tube. However, polymer chains are flexible objects, and their contour length fluctuates due to Rouse modes along the tube (with longest fluctuation timescale given by the Rouse time). This fluctuation is able to relax a fraction of the chain of order $Z^{-1/2}$, and correspondingly reduces the distance required to reptate for tube escape and the terminal time.
- *Constraint release*. [41, 43] The original reptation picture considers the tube to be a fixed object. However, the tube represents entanglements with other chains which are also in motion, so the entanglement constraints themselves can relax. For near-monodisperse linear chains, this provides a relatively small perturbation to the original reptation picture, giving small local rearrangements of the entanglement structure on the timescale of reptation of the chains. Thus, it results in a small change in the terminal relaxation behaviour [41]. For polymer melts with a broader distribution of relaxation times, such as binary blends [44, 45], and branched polymers (see below) the effect of constraint release on chain relaxation is much more drastic.

These two additional mechanisms, together with internal Rouse modes of the chain, were incorporated by Likhtman and McLeish [41] to predict the full viscoelastic spectrum of entangled linear chains (though more recent work suggests they marginally overestimated the contour length fluctuation effects [13, 42]).

Branched polymers

Long chain branching is extremely common in industrial resins; its introduction affects both linear and non-linear rheology. The simplest model polymer to incorporate a long chain branch is the symmetric star polymer. The presence of just a single branchpoint in this polymer completely changes the mode of tube escape and stress relaxation. Reptation (free diffusion of the chain along the tube) is no longer possible, since this would involve motion of the branchpoint into one of the tubes occupied by the star arms. This necessarily pulls the other arms into the same tube, for which there is a substantial entropic penalty due to the reduction of degrees of freedom available to the chain. Such "diving modes" have been suggested to be potentially significant for three-functional branchpoints [28] and have recently been visualised in simulation [46] but they are expected to be insignificant for higher branchpoint functionalities.

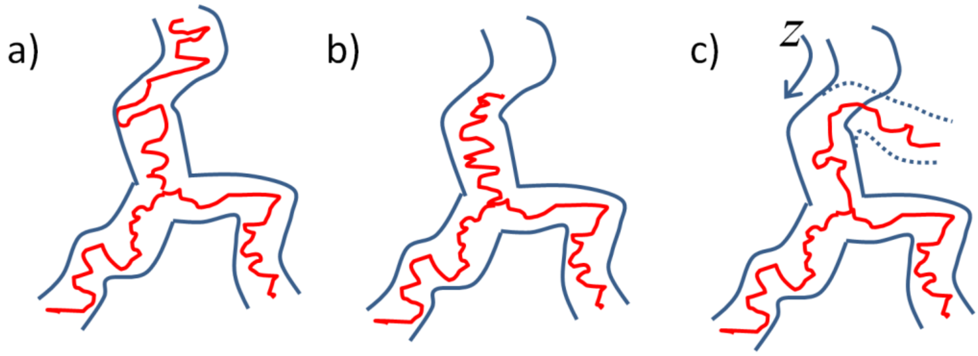

Figure 4: (a) Schematic of a star polymer trapped in its entanglement “tube”.
(b) A deep contour length fluctuation of the upper arm allows (c) the chain end to explore a new region of the entanglement mesh. The relaxation co-ordinate *z* indicates the amount of the original tube relaxed in this manner.

How, then, can a star polymer relax? Deep fluctuations in the contour length of the star arms along their tube are possible, and allow tube escape and stress relaxation because after a fluctuation in which the contour length of the arm is reduced, that arm is then free to explore a new path through the entanglement mesh [18, 47] (see Figure 4 for a schematic representation). These fluctuations involve a substantial entropic penalty, becoming progressively more difficult for larger fluctuations that allow tube escape (and stress relaxation) for portions of the chain closer to the branchpoint. For a star arm of length Z entanglements, in a fixed entanglement network, the free energy for contour length fluctuations a distance z (measured in entanglement units) is given by:

$$\mathrm{U}(\mathrm{z})=\frac{3\mathrm{k_B T z^2}}{2\mathrm{Z}}. \tag{3.4}$$

For well entangled star polymers, $\mathrm{U}(\mathrm{z}) >> \mathrm{k_B T}$, suggesting that arm relaxation is an activated process. The timescale to relax z entanglements from the outside of a star arm should, to leading approximation, behave as

$$\tau(\mathrm{z})=\tau_0 \exp\left(\frac{\mathrm{U}(\mathrm{z})}{\mathrm{k_B T}}\right)=\tau_0 \exp\left(\frac{3\mathrm{z}^2}{2\mathrm{Z}}\right) \tag{3.5}$$

where τ_0 is a typical attempt time [47]. This simple expression captures two experimental facts, observed in linear rheology of star polymer melts [47, 48], that (i) there is a broad distribution of relaxation times, and (ii) the terminal relaxation time, $\tau(\mathrm{z}=\mathrm{Z})$, depends exponentially on the overall degree of entanglement of the arms Z but not on the number of arms. However, detailed comparison with experimental data revealed that the relaxation times predicted by equation (3.5) varied too strongly with increasing arm molecular weight. Ball and McLeish [49] recognised that this was due to the fact that polymer chains do not move in a fixed entanglement network, but instead the network is made up of other chains that are simultaneously relaxing. In a branched polymer melt, where there is a broad distribution of relaxation times, chain sections that relax on fast timescales can be thought of as solvent-like as regards their constraints on more slowly relaxing chain sections. Hence, as a function of relaxation time, the effective entanglement strand length increases as

$$N_e = N_{e0}\phi^{-\alpha}(t) \tag{3.6}$$

where $\phi(t)$ is the fraction of unrelaxed material at time *t* and α is a dilution exponent, whose value is usually taken between 1 and 4/3 [18]. Equation (3.6) is a means of parameterising *constraint release* in branched polymer systems. It corresponds to an increase in tube diameter as $a^2 = a_0^2\phi^{\alpha}(t)$ so that chains become less localised as the relaxation continues – as was recently confirmed in computer simulations [46].

Equation (3.6) also corresponds to a decrease in the effective entanglement of the branched polymer arms, and so to a speeding up of relaxation. Ball and McLeish [49] expressed this, mathematically, by casting the retraction potential $U(z)$ in differential form:

$$\frac{dU}{dz} = \frac{3k_BTz}{Z}\phi^{\alpha}(z). \tag{3.7}$$

This was justified by noting that small increases in the distance of relaxation z occur within a progressively larger tube, given by $\phi(z)$. For star polymers in which all arms are the same length, we expect $\phi(z) = 1 - z/Z$ so that, for dilution exponent $\alpha = 1$, equation (3.7) integrates to

$$U(z) = 3k_BTZ\left(\frac{z^2}{2Z^2} - \frac{z^3}{3Z^3}\right) \tag{3.8}$$

corresponding to a substantial reduction in the retraction potential and a speeding up of polymer relaxation.

Equation (3.7) is referred to as the “dynamic dilution hypothesis” and includes two separate ideas: (i) the effective decrease in entanglement with relaxation of the surrounding chains, and (ii) the *ansatz* of casting the retraction potential in differential form. As noted above, the first idea has found support in recent computer simulation [46]. However, the modification of the relaxation potential via equation 3.7 is not so obvious, and remains open to question (see for example ref [50], which notes, among other things, a problem in describing dielectric relaxation data for star polyisoprenes [11]). Nevertheless, it is by no means an understatement to say that virtually all subsequent modelling of branched polymer relaxation and rheology is based upon the dynamic dilution hypothesis as expressed in equation (3.7).

The theory was made fully quantitative for star polymers by McLeish and Milner [51] by using Kramers' theory [52] for activated diffusion to fix the pre-exponential factor τ_0, and also by using a crossover formula to account for early time arm fluctuations (which do not require activated diffusion).

Subsequent work has aimed to generalise this apparently successful theory for star polymers towards more complicated model polymer systems, including H-shaped polymers [53] asymmetric star polymers [54], blends of stars and linears [55], comb polymers [56-58], and Cayley trees [59, 60]. Due to the restrictions on motion due to branchpoints and entanglements, branched polymers relax from the outside inwards, a process known as hierarchical relaxation. So, for example, in an H-shaped polymer, the arms relax first, in a manner analogous to the contour length fluctuations of star polymers. The dilution function $\phi(z)$ must be appropriately modified so as to allow for the fact that the arms remain entangled with the central backbone for the entirety of their relaxation. The complete relaxation of an arm permits it to explore a new path through the entanglement mesh, which allows the branchpoint freedom to take a hop forward or backward along the path of the backbone (and other arm). Over a longer timescale, such hops of the branchpoint permit the backbone to escape its tube in a process analogous to reptation, but with friction effectively concentrated at the branchpoints (see Figure 5 for a representation of these two

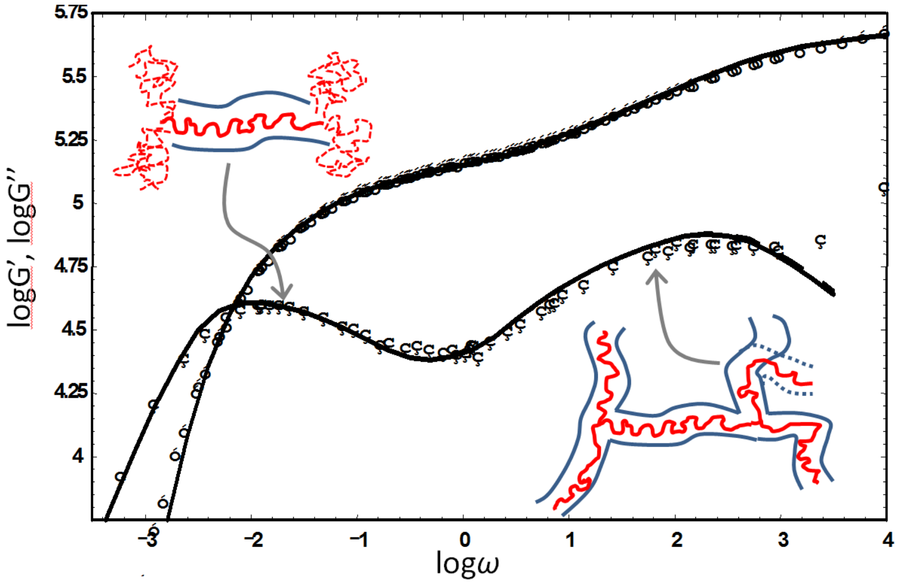

Figure 5: Relaxation of an H-polymer is via two discrete processes. At short times (high frequency) the arms relax, giving a broad shoulder in the loss modulus. At longer times (low frequency) the backbones relaxes via reptation along its tube, subject to friction from the arms. Data and theoretical fit for polyisoprene H-polymer from ref. [53]. Adapted with permission from *Macromolecules* **1999**, 32, 6734-6758. Copyright (1999) American Chemical Society.

processes). So, the relaxation spectrum of a melt of H-shaped polymers exhibits two separate bands of relaxation, one corresponding to the arms and a second to the backbone. Similar considerations are required for other polymer architectures. Two key issues are:

- *Branchpoint hopping.* A branchpoint is considered to "hop" a distance of order the tube diameter when a side arm relaxes. One question is whether the hops should be considered to be in the original, undiluted tube, or in the diluted tube? Also, how far is the hop as compared to the tube diameter? This is parameterised by a parameter p^2 such that the hop length is of order pa [53, 54]. Values for p^2 used in the literature range by a surprisingly large amount, from 1 [61] to 1/60 [54]. There are some indications that the hop length may be smaller for shorter arms though this may be due to assuming that all friction comes from the relaxing side-arms, and neglecting the extra friction from the chain itself [58]. It may also be due to the difficulty of defining a well defined relaxation time for short side arms. Recent work [62] has examined the branchpoint diffusion using computer simulation and experiments on comb polymers, concluding that hopping in the diluted tube gives the most consistent picture over a range of different chain architectures.
- *Tube dilution function*. As noted above, there remains some debate as the correct dilution exponent α for polymer melts. An additional consideration, which becomes important for example in blends of star and linear polymers [55], is how to handle the situation where a large amount of material relaxes suddenly (e.g. when a large number of linear chains reptate). It is common to introduce a so-called "supertube relaxation" [55, 63] which limits the rate at which chains explore space through constraint release. This exploration cannot proceed faster than would be allowed by Rouse motion of the chain, which implies a limiting scaling such that the effective dilution cannot decrease faster than:

  $$\phi_{ST} \sim t^{-1/2\alpha} \qquad (3.9)$$

  Although this gives a clear prediction as to how the entanglement modulus should decrease during the supertube phase, there remains some uncertainty as to the correct $\phi(t)$ to include in equation 3.7 for the renormalised retraction potential. Different options could be the value of $\phi(t)$ at the beginning of the supertube regime (this is the option used in ref [55]), or $\phi_{ST} \sim t^{-1/2\alpha}$, or the fraction of unrelaxed material (which, we recall, had decreased suddenly).

Non-linear flow behaviour and modelling

Non-linear deformation of polymer entangled polymer melts results in strong orientation of the polymer chains and their confining tubes, and also stretching of the chains within the tube. In addition to relaxation of chain orientation (through tube escape), it is necessary also to consider the dynamics of chain stretch, which (in principle) relaxes on a different timescale to that of orientation. In extensional flows, tubes orient in the flow direction, and if the deformation rate is sufficiently rapid the chains stretch in their tubes, leading to the phenomenon of *extension hardenning* (in which the extensional stress exceeds the value that would be predicted by linear viscoelasticity). Extension hardening is particularly important in stabilising processing flows such as film blowing, where strong extension of the resin occurs. In shear flow, orientation of tubes in the flow direction leads to *shear thinning*, because chains are oriented beyond the direction required for to produce a shear component of the stress.

A number of constitutive equations are available for describing the non-linear flow behaviour of branched polymer resins. Several build on the integral constitutive equations of the K-BKZ type [64] and include, for example, the molecular stress function formalism of Wagner and co-workers (see e.g. [65, 66]).

Taking a different approach, McLeish and Larson developed the “pom-pom” constitutive model [67]. This considers the dynamics of an idealised “pom-pom” molecule consisting of a central backbone segment with a branch-point at each end, connected to q arms for each branch-point. The model focuses on the dynamics and stress arising from the backbone. Like the H-shaped polymer discussed above, once the arms have relaxed, the branchpoints can hop back and forth, and the backbone is free to move along its tube via a reptation-like motion (subject to friction coming from branch-point hops). This defines an orientation relaxation time, τ_{b}, for the backbone. In non-linear flow, the backbone is stretched within its tube, and relaxation of that stretch occurs via the backbone tension pulling against the friction from the branch-points – this defines a stretch relaxation time, τ_{s}. If the flow is sufficiently fast, however, the backbone will continue to stretch. McLeish and Larson identified that the limit of stretch occurs when the chain tension along the backbone tube balances the summed chain tension within the arms. At this point, it becomes entropically favourable for the branchpoint to be pulled inside the backbone tube, a process known as “branch-point withdrawal”. Thus the maximum stretch available to the backbone is equal to the number of arms, q, at the end of the backbone, a quantity which McLeish and Larson called the *priority*. This process of branchpoint withdrawal was claimed to set the limit of extension hardening in branched polymer melts.

The pom-pom model was designed to capture the essential features of branched polymer melt rheology: the existence of separate relaxation times for orientation and stretch, and the existence of a maximum stretch set by the priority. So, in a multimode form [68, 69] the model is very successful at matching the rheology of branched resins. This is essentially a data-fitting exercise: the linear response is matched with a set of Maxwell modes, and then each Maxwell mode is associated with a pom-pom equation. The non-linear parameters τ_{s} and q are adjusted to fit extensional rheology experiments.

However, the pom-pom model is built upon consideration of the dynamics of a particular molecule, and it may be hoped that a link could be made from more general branched polymer structures to equations, similar to the pom-pom form. This was attempted, for a Cayley-tree shaped polymer, by Blackwell [60]. For more randomly branched industrial resins, it is necessary either to take more approximate approach, or to codify the relevant physics in a computer algorithm. It is to these two approaches that we now turn.

3.2 Approximate schemes – seniority and priority

As is clear from the preceding section, model polymers have proved a useful tool in elucidating much of the physics of entangled polymer rheology. However, practical industrial resins are very far from being model polymers – they are typically polydisperse both in terms of strand length and branching topology. Application of the lessons learnt from model polymers to branched industrial resins, in a quantitative and predictive manner, remains a significant task.

One possibility is to attempt to capture the essential features of branched polymer relaxation in an approximate way. One may reasonably hope that the significant averaging occurring due to the extreme dispersity of most resins will mask any slight inaccuracies in the approximate approach. To describe linear rheology, we note that the main feature of branched polymer relaxation is that *branched polymers relax from the outside segments first*. To capture this feature, Rubinstein *et al.* [70] introduced the quantity *seniority*, initially as a means of describing relaxation of entangled polymers close to the classical gel point. The seniority of a chain segment within a particular branched molecule may be evaluated by counting the number of strands (inclusive of the current strand) to the furthest free end in each chain direction. The seniority is then the smaller of the two values obtained. A branched polymer chain, decorated with the seniority values of the strands, is shown in Figure 6(a). The idea, then, is that the outermost chain strands have seniority 1, and relax first. The next strands in have seniority 2, and relax next, and so on. Thus, it is anticipated that an approximate mapping from seniority to relaxation time of the chain strand may be possible, so that a description of the distribution of strand seniorities in the molecule allows prediction of the relaxation time distribution. Such a mapping would be exact for a regular structure such as a Cayley tree, but can only be approximate where there is polydispersity of strand length and branching structure.

For modelling non-linear flow, the concept of *priority* introduced above for pom-pom molecules can be generalised to general branched structures in order to calculate, in principle, the maximum stretch of a given chain strand (which determines the limit of extensional stress). This was first done by Bick and McLeish [71] for the classical gelation ensemble, and used to calculate the damping function for a melt of such polymers. Since each free end caries a strand tension of 1, and this tension is propagated through the branchpoints towards the interior of the molecule, the priority of a given strand is obtained by counting the number of free ends attached in each chain direction, and then taking the

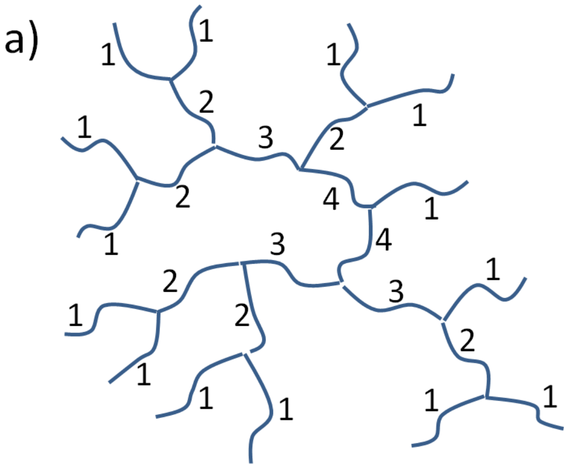

Figure 6: (a) Schematic branched polymer decorated with the "seniority" values of the polymer strands. (b) The same polymer decorated with the "priority" values.

smaller of the two values (we call this calculation where all free ends are included the *geometric priority* – see below). A branched polymer chain, decorated with the priority values of the strands, is shown in Figure 6(b).

The advantages of the seniority and priority measures are that they are simple to calculate for a given polymer molecule. Thus, a set of representative molecules generated in a Monte-Carlo simulation of polymerisation can straightforwardly be decorated with their seniority and priority values, as has been done in LDPE simulations (for example [36]) and simulations of mixed metallocene catalysts [31]. It is also, in some instances, possible to obtain the probability distribution for these quantities analytically, or via recursion relations. This was the approach taken in the original papers defining seniority [70] and priority [71] and also in metallocene systems [29, 30].

As noted above, one potential problem with this approach is that any mapping between seniority and relaxation time is approximate. Read and McLeish [29] identified a potential problem with the priority variable: some sections of the molecules may relax much faster than the current flow timescale, and so be unable to transfer chain tension from the outside of the molecule towards the inside. Thus the maximum stretch (the "priority") of a given segment should depend on the flow rate, and the geometric priority defined above gives an absolute maximum value of the stretch, applicable only at high flow rates. Read and McLeish suggested that, at lower flow rates, any chain sections relaxing faster than the flow timescale should be effectively "snipped" from the molecules when evaluating the priorities; the "snipped" priority values were typically much smaller than the geometric priority. More recently, Read and co-workers [72, 73] have proposed an alternative scheme in which stretch relaxation times of different chain segments are used to determine whether they are able to transfer chain tension from the outside of a molecule towards the inside.

3.3 Computational schemes for linear rheology

The "Hierarchical" and "BoB" algorithms

As noted above, relaxation of entangled branched polymers is a hierarchical process (from the outside inwards) and it is possible to generalise, analytically, the dynamic dilution scheme of Ball and McLeish to quite complicated model polymer systems (H-shaped polymers, comb polymers, Cayley trees, etc). Still, any attempt to write down and analytically solve such equations for polydisperse industrial resins would be an impossible task. However, in a landmark paper, Larson [63] noted that the dynamic dilution equations could be cast as an iterative computational scheme, to follow the relaxation of all arms in a polydisperse mixture of branched polymers in steps of time. Taking the logarithm of equation (3.5) we note that if logarithmic time is increased by an amount $\Delta \ln \tau$, then a given polymer arm relaxes a little more, such that the change in relaxation potential $\Delta U(z)$ is obtained from:

$$\Delta \ln \tau = \frac{\Delta U(z)}{k_B T}. \tag{3.10}$$

But, according to the dynamic dilution equation (3.7), the increment in arm co-ordinate Δz corresponding to $\Delta U(z)$ is found from:

$$\Delta z = \frac{Z}{3 k_B T z \phi^{\alpha}(z)} \Delta U(z). \tag{3.11}$$

Combining equations (3.10) and (3.11), we find that if logarithmic time changes by an increment $\Delta \ln \tau$, then a given branched polymer arm relaxes an increment in arm co-ordinate Δz given by:

$$\Delta z = \frac{Z}{3 z \phi^{\alpha}(z)} \Delta \ln \tau . \tag{3.12}$$

This is the basis of the iterative scheme proposed by Larson [63]. The scheme operates by storing a representative set of polymer architectures in computer memory. As with the approximate seniority scheme above, the branched polymers relax from the outside segments first. For each increment $\Delta \ln \tau$ in logarithmic time, the relaxed portion of each free polymer arm is updated according to equation (3.12), and the unrelaxed fraction ϕ updated before taking the next step in logarithmic time. In this way, the relaxation time of all sections of the polymer chains can, in principle, be obtained, and thus the linear relaxation modulus as a function of time can be predicted.

In order to implement such a scheme for complex polymer architectures, and to produce quantitative predictions, a number of additional physical processes, outlined above for model polymers, need to be included:

- Early time relaxation due to sub-tube diameter motion of the chains, and local Rouse motion of chains along tube contour, can be included in the same manner as Likhtman and McLeish [41] implemented for linear polymers.
- The numerical pre-factor in equation (3.5) should be adjusted according to the arm length, and early time fluctuations of the arms should be included via a cross-over formula, in line with the theory of star polymers of Milner and McLeish [51]. It is possible to adjust the iterative numerical scheme to accomplish this [74, 75].
- During the relaxation of most branched polymer architectures, "compound arms" are formed: side arms fully relax, so that their branchpoints are now able to move, and this in turn affects the relaxation of the main polymer arm. In the original algorithm, Larson [63] introduced the concept of a "waiting time" to handle this situation. Later developments gave alternative proposals, either involving modification of the effective pre-factor in equation (3.5) to account for extra friction of the side arms [74, 76], or modifying the scheme to update the retraction potential [75].
- Supertube relaxation (equation (3.9) above, and related discussion) needs to be included.
- The terminal relaxation of most branched polymers is via a reptation-like process, but subject to extra friction arising from relaxed side-arms. In Larson's algorithm, polymer chains relax by fluctuation until the time when reptation is possible (and the distance required to reptate is adjusted to account for relaxation of the chain ends by the fluctuation modes). At the reptation time, any remaining unrelaxed portions of the chain are assumed to relax with that timescale.

Larson and co-workers made further developments to the original algorithm so as to include or improve upon the description of all the above processes [74, 76]; this series of models is collectively known as the "Hierarchical" algorithm. In a parallel development, Das *et al.* [75] also modified the Larson algorithm, producing the so-called "BoB" (Branch-on-Branch) algorithm. One specific computational difference between the two is that the data structure used in the Hierarchical algorithm permits only comb-like polymer topologies to be included in the set of polymer architectures considered, whilst the BoB algorithm makes use of a flexible data structure that permits any branched structure to be included, including "Branch-on-Branch" topologies such as Cayley trees and hyperbranched structures. Thus, the BoB algorithm is more suited towards the modelling of highly branched industrial resins. Both algorithms can be freely downloaded [77, 78].

Although both the Hierarchical and BoB algorithms share the same foundation and basic methodology, there are numerous differences between them in detailed implementation, partly related to numerical methods, but also partly related to assumptions regarding the detailed physics of branched polymer relaxation (e.g. whether branchpoint hopping is in the undiluted or diluted tube). Thus, the quantitative predictions of the two algorithms are often different, and the optimal set of parameters required to fit data (e.g. branchpoint hopping parameter p^2) are different for each algorithm. For the interested reader, a detailed comparison of the two algorithms, including a description of the latest "Hierarchical-3.0" algorithm, can be found in Ref. [76]. There is not yet a consensus regarding details of all physical mechanisms in branched polymer relaxation, and the Hierarchical and BoB models each encode a reasonable, if different, set of assumptions.

A particular advantage of these algorithms is that they allow predictions to be made for relaxation of mixtures of a large number of different molecular shapes and sizes. This is relevant even for the so-called "model" polymer architectures. At the very least, such resins are polydisperse in terms of the lengths of the individual chain strands. However, there has been a growing realisation in recent years that, despite the best efforts of chemists, a typical "model" polymer melt will not purely consist of the target polymer architecture, but rather there is a mixture of architectures (some with arms missing, some with side reactions producing larger polymers). In this context, a relatively new characterisation technique, temperature gradient interaction chromatography (TGIC) is proving invaluable at quantifying the actual mixture of architectures present [79 - 85]; a presence of the target architecture in above 90% of the molecules would appear a good result. The family of algorithms based on the Larson algorithm provide a means to predict the effect of these impurities on linear rheology.

So, for example, Chambon *et al.* [79] used TGIC to quantify the distribution of side arm number in a pair of polystyrene comb melts, using the BoB model to make predictions of linear rheology (see Figure 7). Hutchings *et al.* [84] synthesised a Cayley-tree shaped polybutadiene according to a design provided by the BoB algorithm, quantified the

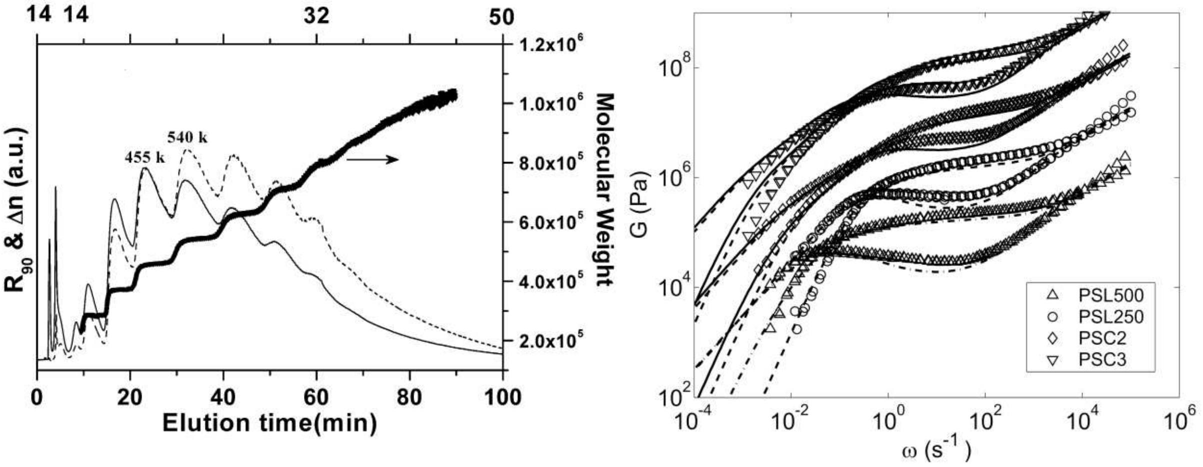

Figure 7: Left: A polysyrene comb sample separated by TGIC according to the number of arms. Right: Experimental data and predictions of linear rheology using the BoB code for two linear polystyrene samples (PSL) and two comb samples analysed using TGIC (PSC). Data are vertically shifted for clarity. Adapted with permission from *Macromolecules* **2008**, 41, 5869-5875. Copyright (2008) American Chemical Society.

impurities by TGIC, and used BoB (again) to compare with the resin rheology, investigating the impurity effect.

Nevertheless, the real motivation behind developing the Hierarchical and BoB algorithms was to address the complexity of industrial polymer melts. In section 4, we describe some examples of their application in this area.

The "Time-marching" algorithm

Whilst the Hierarchical and BoB algorithms very much belong to the same immediate family (descended directly from Larson's work [63]), the time-marching algorithm of van Ruymbeke [61, 86] is more distantly related. Within this model, the relaxation function $\phi(t)$ is written as:

$$\phi(t) = \int p_{\text{rept}}(x,t)\, p_{\text{fluc}}(x,t)\, dx\,. \tag{3.13}$$

where $p_{\text{rept}}(x,t)$ is the probability that a given segment (labelled with x) has not relaxed by reptation, and $p_{\text{fluc}}(x,t)$ is the probability that it has not relaxed by arm fluctuations. These two probabilities are updated as a function of time by set of iterative steps over time, accounting for the current value of $\phi(t)$ at each iterative step (hence the term "time-marching"). The integral represents a sum over all chain sections. A significant difference compared to the algorithms based on the work of Larson [63] is that within the time-marching algorithm the reptation and fluctuation processes are considered independent processes (though they can indirectly affect one another through $\phi(t)$). In contrast, within the Larson family of algorithms, reptation is considered to be the terminal process of relaxation for a molecule, occurring sequentially *after* arm fluctuation. As a result, in the Larson algorithm, arm fluctuation speeds up the terminal reptation relaxation by shortening the distance required to reptate (this is in qualitative agreement with the Likhtman-McLeish [41] and similar models for linear rheology of linear chains). Within the time-marching algorithm, no such shortening of the distance required to reptate is included. Thus, reptation is often a slower process within the time-marching algorithm, and this may be one reason why it is possible to use $p^2 = 1$ to describe branch-point hopping within the algorithm [61].

A second feature of the time-marching algorithm is that it enforces continuity of the fluctuation relaxation time for segments on either side of a branchpoint, by introducing an effective chain length for fluctuations of inner segments [61]. This chain length is adjusted at each branchpoint so as to enforce continuity of relaxation times, a process which becomes complicated for large molecules with multiple branches [58]. For multiply branched molecules, the algorithm also considers multiple retraction pathways. These may be the reasons why the algorithm has not yet been applied to arbitrarily branched polymers; the automation of such detailed considerations within a computer algorithm is likely to be difficult. Nevertheless, the time marching algorithm has been applied to a number of different model architectures such as stars [86], pom-poms [61], Cayley trees [59, 87] and combs [58], and also to mixtures of these inspired by TGIC results on a “model” polymer melt [82].

In summary, there are some clear differences between the time marching algorithm and the hierarchical algorithms based on the work of Larson, and there remains scope for discussion about which (if either) is the better approximation to the underlying physics. At present, the time marching algorithm does not have the flexibility to deal with the huge complexity and polydispersity of industrial polymer resins.

3.4 Computational schemes for non-linear rheology

If prediction of linear rheology of industrially complex branched polymers is a daunting task, *ab initio* prediction of their non-linear rheology given their molecular structure would seem a distant dream. In principle, coupled tube-model equations, along the lines of Blackwell *et al*. [60] (but most likely more complex), should be solved for every chain strand within the representative molecular distribution. In principle, such an algorithm is possible to construct, but no one has done it yet.

A simpler possibility was considered by Read *et al.* [72, 73]. Recognising that the multi-mode pom pom is very successful at matching the rheology of branched polymers (once the non-linear parameters have been determined by data-fitting to extensional rheology data), they attempted to predict a numerical ensemble of pom-pom modes, for a given resin, based upon the numerical solution of the linear rheology within the BoB algorithm [75] . Their method was to split the predicted linear relaxation spectrum into a set of Maxwell modes with different relaxation times, and then in turn split each Maxwell mode into a distribution of pom-pom modes based upon the chain segments relaxing stress at that timescale. For consistency with the linear rheology predictions, stress relaxation was noted to have two separate contributions, each with a corresponding set of pom-pom modes: stress relaxation by entanglement escape of strands, and stress relaxation by release of constraints on neighbouring strands.

A single pom-pom mode requires two non-linear parameters: a stretch relaxation time and a maximum stretch (the priority, as described in section 3.2 above). These two parameters must be determined for each strand in the numerical mixture of polymers. Read *et al.* found that there was sufficient information within the BoB algorithm to achieve this: the stretch relaxation time could be determined from an internal solution variable, and the priority could be obtained based on the branched topological structure of the stored molecules. The segment priority was proposed to depend on the applied flow-rate and was calculated by propagating segmental tension onto the segment from its connected free ends, noting that a segment can only stretch (and thus propagate tension) if the flow rate exceeds the inverse of its stretch relaxation time.

As we will describe in more detail below, Read *et al.* successfully applied this algorithm to predict the non-linear response of a series of LDPE resins [72, 73]. However, their algorithm must, still, be considered an approximate, if practical, solution to the prediction of non-linear rheology. Their method for assignment of segment priorities is expected to break down for model polymers such as combs, where side arms all have similar relaxation times. In mapping on to a set of pom-pom molecules, they ignore possible dynamical coupling along polymer chains, and it is not clear that the physics of constraint release is properly represented. More work in this area is certainly required.

4. Literature case studies

We restrict ourselves to the limited number of studies which have attempted to *both* predict the molecular shapes of randomly branched molecules from reactor conditions, and also to use these to predict rheology.

Metallocene-catalyzed polyolefins

In this context, perhaps the most studied industrial polymer type is polyolefins produced using constrained geometry metallocene catalysts. The generally accepted mechanism for formation of long-chain branches in these systems is via macromonomer formation and reincorporation. Using population balance methods, Soares and Hamielec [88] were able to obtain the bivariate distribution of molecular weight and branching number for single site reactions in idealised continuous stirred tank reactor conditions. A Monte Carlo simulation scheme was also proposed [89] and improved upon by Costeux *et al.* [90], which allowed the distribution of molecular topologies to be sampled – this proceeded by saving generated macromonomers from the past, and incorporating the previously saved macromonomers randomly into the new chains. By repeatedly generating molecules in this manner, a representative set of molecules can be obtained.

Read and McLeish [29] demonstrated that the reaction scheme used by Soares and Hamielec led to a statistically self-similar distribution of branched molecules characterised by just two parameters: the average degree of polymerisation of chains between branches, and a branching probability (defined by Read and McLeish as the probability of encountering a branch, rather than a chain termination, upon following the chain in the reverse direction to the polymerisation direction). They used this to rederive the Soares and Hamielec result for branching and molecular weight distribution, but also to obtain the bivariate distribution of the priority and seniority variables for chain strands within a metallocene catalysed resin. By making an approximate correspondence between seniority and relaxation time, they (ambitiously) mapped their derived seniority and priority distribution onto a set of pom-pom modes, and thus made predictions of extensional viscosity as a function of their model parameters. No direct comparisons with experimental data were attempted, since the scheme was evidently too approximate. Nevertheless, this work represented the first attempt at using tube theory to predict non-linear flow behaviour on the basis of a quantitative description of branching structure for a class of industrial polymer resins.

Read and McLeish [29] concluded by suggesting “careful rheological experiments on well-characterized ensembles” of polymers was needed. Fortunately, many industrial scientists were already alive to this need. In particular, researchers at the Dow Chemical Company produced a series of resins (known in the literature as HDB1-7, with higher numbers representing an increased amount of branching [75, 91, 92]) which have been a gift to the academic community in this field. The great advantage of these resins was that, since they were all synthesised without co-monomer, NMR could in principle be used as a direct measure of the long-chain branching content. This, together with a measurement of overall molecular weight via GPC, provides sufficient information to fix the two parameters noted by Read and McLeish to govern the distribution of molecular shapes. So, this series of resins provide a testing ground for schemes of quantitative rheology prediction.

Thus, Park and Larson [93] used their version of the Hierarchical model to predict linear rheology of the resins HDB1, 2 and 3, making use of the Costeux Monte Carlo algorithm [90] to generate representative molecular structures. In order to apply the Hierarchical code

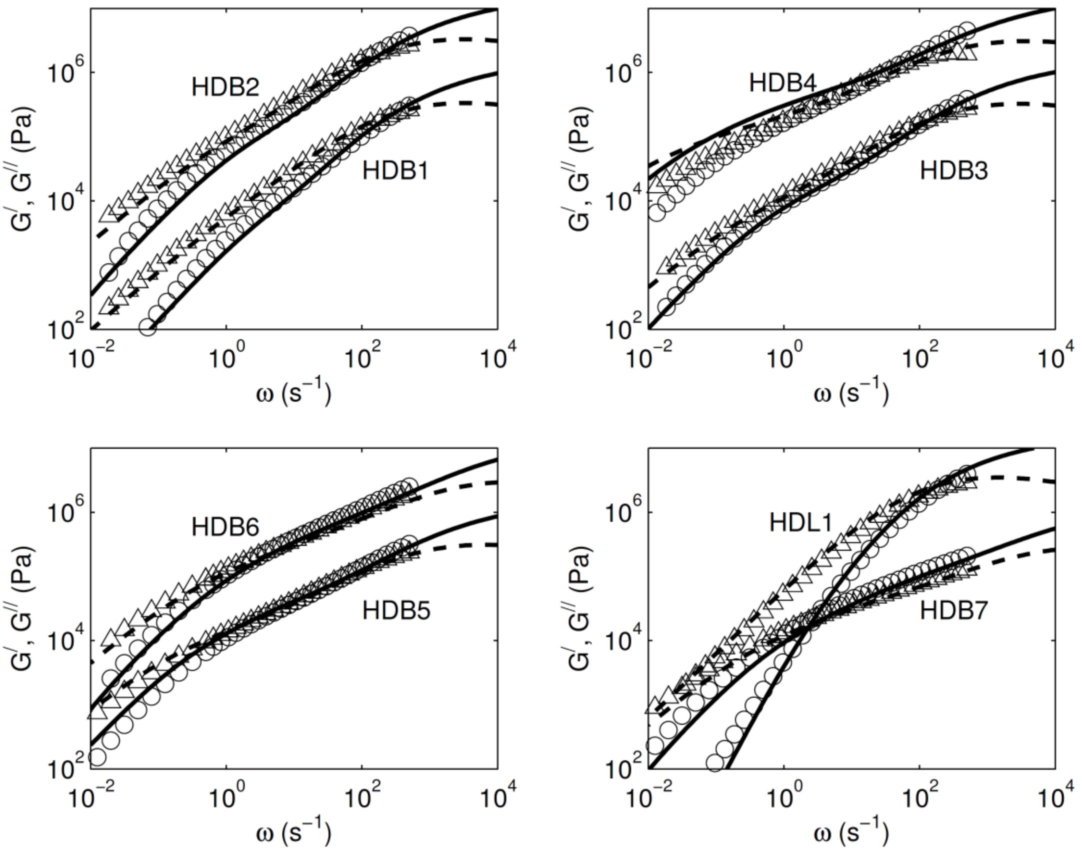

Figure 8: Linear rheology (triangles: loss modulus, circles: storage modulus) of the HDB series of resins and one polydisperse linear sample (HDL), together with predictions using the BoB algorithm. Reprinted with permission from *J. Rheol.* **2006**, 50, 207–234. Copyright 2006, The Society of Rheology.

(which permits only comb-like topologies to be considered) they constrained the Monte Carlo algorithm so that it would not produce structures with a "branch-on-branch" architecture. More recently the same group [76] noted, and corrected, some problems with the iterative timestep used by Park and Larson.

In their original paper on the "BoB" algorithm , Das *et al.* [75] used their method to predict , successfully, the linear rheology of the full set of HDB resins, using the same set of rheological parameters for the whole series (see Figure 8). In doing this, they proposed a new Monte Carlo routine for producing a representative set of molecules, based on the statistical description of Read and McLeish, which did not require the storage of previously-generated macromonomers. Significantly, Das *et al.* also estimated the statistical weight of polymers with a "branch-on-branch" architecture in the HDB series of resins, demonstrating that these were negligible for the more lightly branched resins HDB1, 2 and 3, but that there was an increasing fraction of such molecules with increased branching. The branch-on-branch molecules are large, and have a significant effect on the terminal relaxation of the resin: for the most highly-branched resin in the HDB series, Das *et al.* showed that neglect of branch-on-branch architectures could lead to underestimate of the terminal viscosity by more than a factor of 6.

More recently, Chen *et al.* [94] successfully used the hierarchical model to explore the rheology of a series of blends between branched and unbranched metallocene resins. Since the resins were only lightly branched, they were able to show that the effect of branch-on-branch molecules on the resin were negligible.

Polycondensation reactions

The production of randomly branched polymers via polycondensation reactions is a topic with a long history. Theoretical description of the distribution of branching and molecular weight goes back to the early pioneers of polymer science (see e.g. ref [5]). Within a polycondensation process, branching may be introduced by the inclusion of multifunctional monomers (with three or more reactive groups).

It has been long known that the distribution of size and shape of the molecules is strongly affected by the types of reactive groups on the branching units. If these reactive groups are all of the same chemical type (i.e. the branching units are of the A_f type, where f is the functionality) then this typically gives rise to the *gelation* ensemble of molecules. In this case, there is no directionality to the molecule introduced by the reactive groups (the reaction is statistically isotropic) and it is possible for gelation to occur (i.e. formation of an infinite network). The initial calculations for both the *seniority* [70] and *priority* [71] variables were both performed on the gelation ensemble.

In contrast, if the reactive groups on the branching units are of different type (i.e. AB_{f-1} monomers in which A groups react to B) then the branching units introduce a directionality to the molecule and (if these are the only type of monomer) gelation cannot occur because of a lack of *A* groups to react. The molecular weight distribution is quite different to the gelation ensemble (see ref [5], or ref [28] for a recent treatment of this). In this case, there are similarities to the ensemble of molecules generated by single site metallocene catalysis. This fact was exploited by Kunamaneni *et al.* [95], who studied the ensemble of molecules generated from reaction of $AB_2 + AB$ monomers. Their theoretical description of the molecular weight and branching distribution was achieved by mapping the reaction parameters directly onto the single site metallocene distribution [29, 88, 90]. Increasing the fraction of *AB* monomers results in longer chain strands between branch points, and so a transition towards entangled polymer dynamics; this transition was the main focus of their theoretical work. Specifically, they demonstrated that, for this statistical ensemble of molecular shape and size, the transition from unentangled to entangled dynamics occurs when the typical length of chain between branchpoints exceeds the entanglement spacing (as opposed to the point when the average *total* molecular weight exceeds the entanglement molecular weight). It is possible to create highly branched samples with large total molecular weight, which nevertheless exhibit unentangled dynamics. Experimentally, they synthesised and investigated two separate families of samples (based on polyester chemistry), one in the unentangled regime, and one in the entangled regime. The reaction parameters were determined from the fraction of species in the initial reaction mixture, but complemented by NMR measurements to determine the degree of branching. The entangled samples were not highly branched, and included mostly linear and star-like molecules (zero or one branchpoint). Consequently, they aimed to describe the linear rheology of their samples through a generalisation of the Milner-McLeish theory for star-linear blends [51], with some corrections for more deeply embedded (higher seniority) chain sections. As can be seen from their results (Figure 9) this theory provided a good description of the high and intermediate frequency regimes of linear rheology, but did not give a very good description of the terminal (low frequency) behaviour. This is likely to be due to not fully accounting for polydispersity in chain length, or the full distribution of deeply embedded chain sections.

A better approach to the rheology prediction can be found in the recent work of van Ruymbeke *et al.* [96] who study a series of randomly branched polyamide polymers, this time of the *gelation* type. They use a Monte-Carlo algorithm to sample the polymer

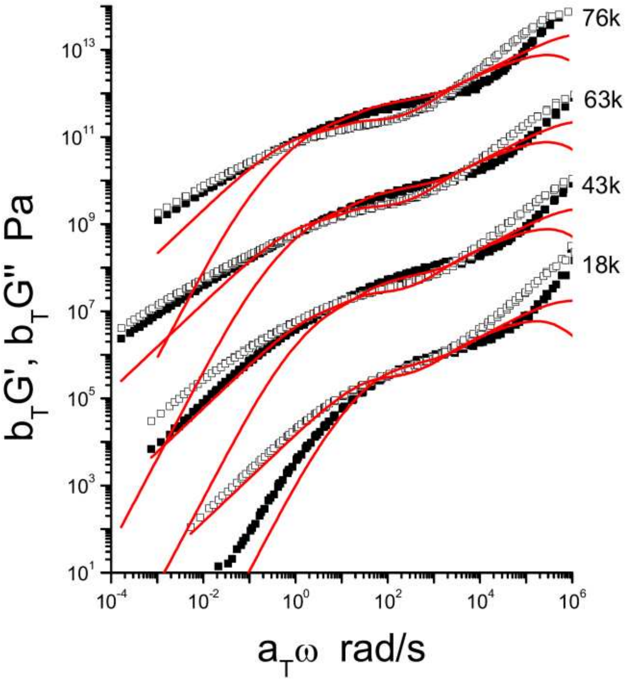

Figure 9: Linear rheology of a series of polyester resins formed from AB_2 + AB type monomers (with approximately 1 mole % AB_2). Increasing degree of conversion gives higher molecular weights. Data are vertically shifted for clarity. Also shown is a fit to the data using a simple extension of Milner-McLeish theory; the fit is less successful at lower frequencies where higher branching structures become important. Adapted with permission from *Macromolecules* **2006**, 39, 6720-6736. Copyright 2006 American Chemical Society.

distribution (this algorithm is made more efficient by noting that all chain strands between branched or terminal groups are known *a priori* to conform to the same Flory distribution). In confronting the experimental molecular weight distributions, they needed to treat the degree of reaction of some species as an adjustable parameter. This contrasts with the previously discussed work of Kunamaneni *et al.* [95], who were able to use NMR to measure some reaction parameters independently of the molecular weight distribution; such independent measures are to be encouraged, where possible, since they reduce uncertainty in the description of the statistical ensemble of polymers.

Having determined, as well as possible, the distribution of molecular shapes in the reaction ensemble, van Ruymbeke *et al.* used their time marching algorithm [61, 86] for rheology prediction. Since (as noted above) this is not yet developed to a stage of automatically predicting rheology for an arbitrary distribution of molecular shapes, they took an intermediate approach. They divided the chain strands in their ensemble according to their seniority. However, they recognised that, due to strand polydispersity, this quantity is only an approximate proxy for relaxation time, and so they further divided their chain strands according to length. Since the sample was only lightly branched, the volume fraction of strands with seniority of 3 or more was extremely small; such strands were considered to have an effectively unentangled terminal relaxation. The final result of this method was a very satisfactory prediction of the linear rheology of this family of samples.

It is, however, less clear whether such an approach will work for samples with a higher degree of branching as the gelation limit is approached. Using polyester chemistry, Lusignan *et al.* [97] created a series of entangled gelation class polymer melts, in which they approached the gelation threshold. Their study included a careful measurement of intrinsic viscosity as a function of molecular weight for different elution volumes in the gel permeation chromatogram; this displayed two separate scaling regimes corresponding to linear-like chains at small molecular weight, and highly branched chains at higher molecular weight. The crossover molecular weight between these two regimes is obviously inversely proportional to the branching density, but it is not clear what the proportionality constant is. Das *et al.* [98] investigated this same series of resins, using a Monte-Carlo algorithm based on reaction rate equations to generate a representative set of molecules. As a proxy for intrinsic viscosity (which they could not calculate) they examined the scaling behaviour of the ideal radius of gyration as a function of molecular weight, concluding that the crossover molecular weight between scaling regimes may be ten times larger than the typical strand length between cross-links. They then used the BoB algorithm to predict linear rheology for the resins – this was successful for all but the most highly branched resin, where it was possible that the mean field description of the reaction rate equations became an inaccurate approximation. A further issue may be that the terminal relaxation of highly branched resins, close to the gel point, involves a disentanglement transition which is not accurately handled within the BoB formalism.

Low density polyethylene

As a final case study, we turn to low-density polyethylene (LDPE), a ubiquitous resin formed through free-radical polymerisation. There are many literature studies of the development of molecular weight and branching distribution in industrial reactor conditions, predominantly using either population balance approaches (see e.g. [21]) or Monte-Carlo schemes (see e.g. [36, 32, 33]) . Practically all such studies focus on the formation of branches via transfer of the reactive radical to the middle of another polymer chain, which is then followed either by chain scission, or polymerisation to form a long-chain branch; this, in combination with processes such as initiation, propagation, and termination via disproportionation or combination give rise to the studied reaction rate equations.

Given the large number of publications on the reaction engineering of LDPE, it is disappointing that there is, to our knowledge, only one study which explicitly uses the molecular topologies from a reaction engineering simulation to predict rheology of these resins. One reason for this might be that a significant proportion of the LDPE molecules are highly branched, requiring consideration of branch-on-branch topologies. Read *et al.* [72, 73] studied a series of tubular reactor LDPE resins, characterised according to molecular weight distribution, and radius of gyration contraction factor (g-factor) as a function of elution volume in the gel permeation chromatogram. This latter quantity is a measure of branching density, because more highly branched molecules have smaller radius of gyration (we caution against using the common Zimm-Stockmayer formula [99] to calculate branching density, since this assumes ideal random branching of the molecules). The linear rheology of the resins was also measured, and for three of the resins the transient viscosity was measured in non-linear shear and extension. The goal of the study was to use simulated molecular topologies to predict the rheology.

A further disappointment to some might be that the study, at the level of reaction engineering, was quite crude. Recognising that an *ideal* tubular reactor is equivalent to a batch reaction, Read *et al.* made use of a previously published Monte-Carlo scheme [32] in order to predict a representative set of molecular topologies. They found, however, that the predicted output from a single, ideal batch reaction could not match the measured molecular weight and g-factor distribution of the resins. To account for this discrepancy, they used a superposition of two, or three, batch reactions, keeping most of the reactor variables constant but varying the final conversion between the three modes. Possible justifications for this approach include the fact that a tubular reactor is rarely an ideal batch reaction; there is a boundary layer which takes more time to travel through the tube, and there are usually multiple injection points for reagents. In the absence of detailed information about the industrial reactors, it was felt (or perhaps hoped) that using a superposition of batch modes (constrained by molecular weight distribution and g-factor) might give a reasonable representation of the mixture of molecules in the resins. Nevertheless it is clear that there is scope for using a more detailed and accurate reactor model in conjunction with their methodology for predicting non-linear rheology.

Read *et al.* found that, having matched the molecular weight and g-factor distribution of the resins, and using the same rheological parameters for all resins (entanglement time, entanglement molecular weight, plateau modulus) their BoB algorithm was able to make a reasonably close prediction of their linear rheology. So, for example, the terminal viscosity of each resin was predicted to within roughly a factor of two, which was accurate enough to rank the resins in order of increasing viscosity. Small adjustments to the reaction parameters (whilst maintaining the fit of the molecular weight and g-factor distribution) allowed the linear rheology of the resins to be accurately matched (see Figure 10). This indicates that, due to the exponential dependence of relaxation time on strand molecular weight in an entangled branched polymer, rheology is more sensitive than either molecular weight or g-factor to the reaction parameters.

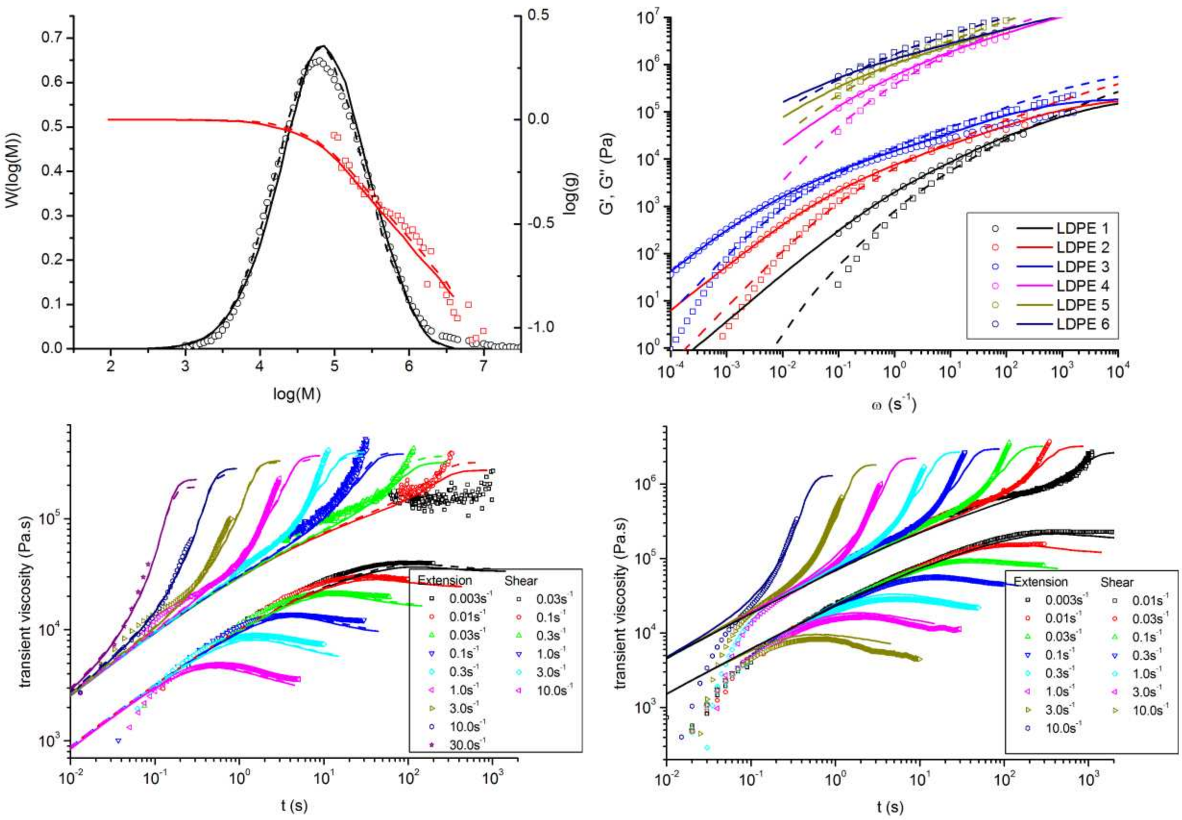

Figure 10: [Top left] Matching the molecular weight distribution and radius of gyration g-factor for a tubular LDPE (LDPE2). Dashed and solid lines represent two different fits. [Top right] predictions of linear rheology for a series of six tubular LDPEs (using identical rheological parameters). Predictions of non-linear rheology (start up shear and extension at different rates) for [Bottom left] LDPE2 and [Bottom right] LDPE3. Data and theoretical predictions from ref. [72]. Non-linear predictions corrected as described in ref. [73]. From *Science* **2011**, 333, 1871-1874. Reprinted with permission from AAAS.

Having matched the linear rheology, there were no further free parameters to adjust in their model, and so Read *et al.* used their approximate scheme (outlined in section 3.4 above) to predict with reasonable accuracy the transient viscosity of the resins in start-up shear and extension, as illustrated in Figure 10. One might note that the predictions were not perfect: for example whilst the onset of extension hardening was well predicted, the final stress under extension was typically underpredicted, especially at lower extension rates. The non-linear rheology predictions in Figure 10 are slightly different from the original article [72] due to a small error in the original code, as described recently [73].

It will be readily apparent that there are approximations made at each level of the scheme of Read *et al.* [72, 73]. Their reactor simulation was quite simplistic. As noted in section 3.3 above, there remains an active debate as to the best approximate computational method for predicting linear rheology of randomly branched resins, with different suggestions as to the correct description of various physical mechanisms. Following on from this, their scheme for predicting non-linear rheology (section 3.4) relies on an approximate parameter mapping onto a multi-mode pom-pom constitutive model; here there are approximations and assumptions in both the idealised constitutive model and in the parameter mapping. All this being noted, their predictions are (perhaps surprisingly) reasonable, though not perfect. In this sense, the work of Read *et al.* might simply provide a pragmatic and practical method for prediction of non-linear rheology from reactor variables. We consider it to be an ambitious marker as to what may be possible, rather than the final word on the topic.

5. Outlook

In this review, we have aimed to give an overview of techniques for prediction of branched molecular topologies from reaction engineering models, and of developments in "molecular rheology" of entangled polymers. The various case studies in the final section indicate that it is now possible, in principle, to marry these two fields so as to make quantitative rheological predictions based on reactor and reaction conditions. It is, nevertheless, apparent that such work is still in its infancy, and approximations made at each level of such schemes require further testing, and refinement. In this context, we note the following challenges.

Characterisation

It is clear from the case studies above that developments in characterisation methods from randomly branched polymers are still needed. In the case studies of section 4, we note that additional methods to measure even the average amount of branching in the resins (e.g. using NMR, light scattering, or intrinsic viscosity) give additional confidence in the predicted distribution of molecular topologies. It is not always possible to obtain such measurements, but we would certainly recommend their use. We would also hope for continued development in multiple separation methods, e.g. making use of TGIC [79-84] to further constrain the modelling efforts.

It might be hoped that, ultimately, rheology itself will be the best characterisation tool for branched resins. This, however, relies on modelling methods to deduce the degree of branching from rheology measurements. At present, there remain uncertainties in these modelling methods.

Molecular rheology

Molecular modelling for the rheology of branched resins has now reached a point where there are several algorithms "on the market" for automatic computational prediction of linear rheology. Despite the successes of the Hierarchical [63, 74, 76], BoB [73, 75], and time-marching [61, 86] algorithms, it is clear that a certain amount of data-fitting has taken place in all cases. In each case, parameters in the model are fixed for good prediction of some resins, and it is then found that similar resins, or blends of such resins, are often well-predicted by the models. This is evidently very useful in a practical industrial context, since it allows for predictive capabilities– but it is not wholly satisfactory from an academic standpoint. The models make different assumptions about some of the underlying physics (probably all are wrong to some extent!) and so require different parameters to match the same resin. It is clear that further work is required before we can claim that the problem is fully understood and solved. There is a place here for further experiments on model materials. There is also an increasing possibility of probing the underlying physical mechanisms, and indeed the basis for the tube modelling framework, via computer simulation [12-16, 46, 62].

Reactor engineering

Presently, it seems that the Monte Carlo approach offers the best means for connecting the reaction engineering community to the polymer rheology community. In order to make industrially relevant predictions, it will be necessary to develop Monte Carlo methods that are applicable within larger scale simulations of realistic and complex reactors, in which chemical concentrations become dependent on both spatial position and time. Efforts in this direction (e.g. refs [36, 37]) are already being made, and should be encouraged.

Whilst there remain serious scientific questions to be addressed, there appear to be good grounds for optimism. Despite the remaining questions, practical predictions of the rheology of industrial resins are now, evidently, possible. It is to be hoped that with further developments they will become still more accurate and dependable. This, of course, relies on increased communication between the normally separate fields of reactor engineering and polymer physics. This being the case, we anticipate that the field can begin to move from science towards technology, from investigation towards design.

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Possible TOC graphic

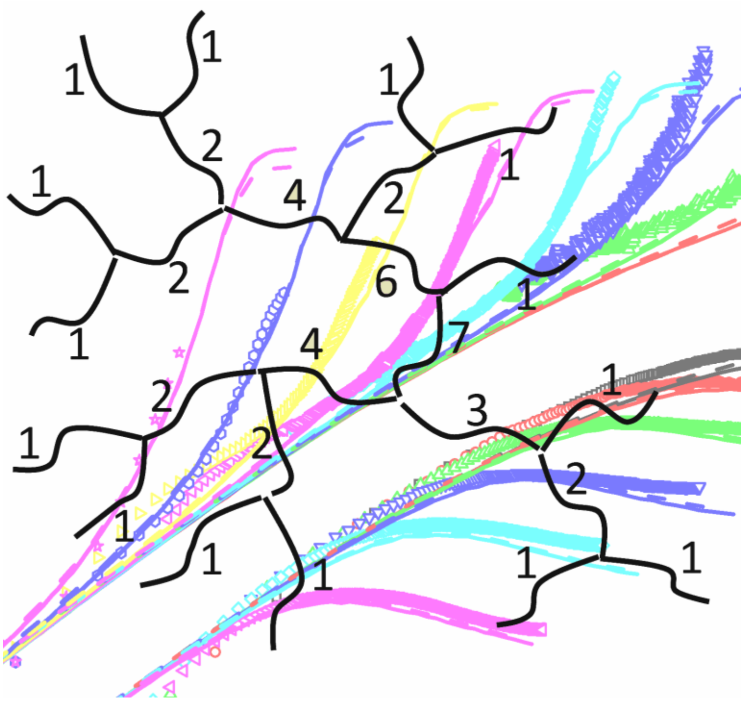

Table of contents text

This article reviews current efforts towards practical, quantitative methods for prediction of flow properties of industrial polymer resins, based upon their branched molecular structure. Such work spans the fields of polymer reaction engineering and polymer physics, and requires researchers from both to work together to achieve the goal of design of polymeric resins with required processing properties. In this article, both fields are reviewed at an introductory level, with illustrations from several case studies.