

An Overview of the Basic Rheological Behavior of Polymer Fluids with an Emphasis on Polymer Melts

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This series of "educationally oriented" papers has the purpose of assisting the academician who is planning to introduce a basic course in polymer science to chemistry students. One might wonder, then, just why the subject of polymer melt or fluid rheology¹ is a part of this series since the flow or fluid mechanics behavior is generally viewed as the domain of the engineer. In fact, often times the subject is so dominated by complex mathematical expressions that the average chemist (even the mathematically oriented physical chemist) often has severe difficulty in transforming these expressions into physical reality for the student. While some may think this mathematical clothing is for providing a barrier to the chemist, this is certainly not meant to be the case. Indeed, the mathematical framework applied to rheological studies has many benefits. Our goal here, however, is to attempt to take a molecular and a nonmathematical approach to explain many of the basics of the rheological behavior of polymer melts or fluids.

Just why should the student interested in polymer science become exposed to this subject? From the author's point of view based on several years of teaching and industrial consulting, there is a very important need for both the chemist and the engineer to recognize that very often the final marketability of a polymer material is dependent both on (1) the inherent chain structure and associated molecular weight distribution that are generally controlled by the chemist through polymerization; and (2) the way these molecules are packed together to make the final material—the latter of which is very often dictated by the rheological behavior induced through some given engineering fabrication method, e.g., spinning, melt drawing, film blowing, etc. Hence, this author believes it is extremely important for the polymer chemist and polymer engineer to join hands and learn some of each other's terminology and basic concepts so that a more thorough understanding of the "total system" will be obtained. In this way, better means of achieving a useful end product will be obtained. Hence, the format of this paper is to introduce basic terminology and concepts regarding the flow (rheological behavior) of polymer melts and fluids. Due to the length restrictions of this paper and the relative industrial utility of polymer melts, emphasis will be placed on describing the flow behavior of melts as compared to that of solutions; however, many of the fundamentals discussed here apply to both. Rheological or flow behavior of solids is also important but we will not concern ourselves with the area directly; however, indirectly many of the concepts discussed here apply.

Some Basic Terminology

First, let us recognize the basic aspects of material deformation that may be involved with melt flow and hence polymer processing. As in solids one can deform a melt or a polymer solution via shear, tensile (elongation), hydrostatic bulk deformation or some combination of these three principal means. For purposes of our discussion, we will emphasize shear behavior; thus, let us inspect this means of deformation. Figure 1 shows a cube or volume element that is undergoing a shear deformation due to a force, F , that is applied as shown

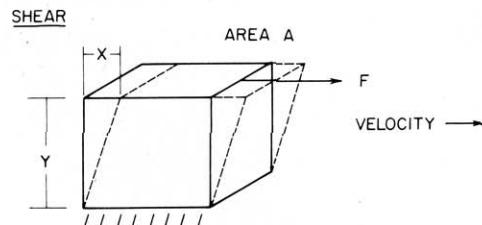


Figure 1. Schematic of an element undergoing deformation by shear.

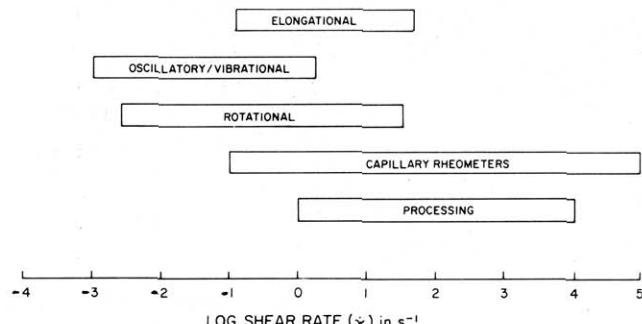


Figure 2. Ranges of shear rate that typically are involved with the general types of rheometers and are also observed in polymer processing.

to the upper surface which has a cross-sectional area of A . The resulting shear stress, τ , that results is defined as

$$\tau = F/A \quad (1)$$

Assuming this degree of deformation is not great, one can define the associated shear strain, γ , as

$$\gamma = \frac{X}{Y} \quad (2)$$

Relative to Figure 1 one can view this process as a sliding of layers of material (fluid) across one another as in shearing a deck of cards.

Another very important parameter that will be utilized extensively in our discussions is that of shear rate, $\dot{\gamma}$ which is also known as the velocity gradient. This is given as

$$\dot{\gamma} = \frac{dx}{ydt} = \frac{d\gamma}{dt} = \dot{\gamma} \quad (s^{-1} = \text{reciprocal seconds}) \quad (3)$$

The significance of this term to our molecular considerations of flow will be to relate to how fast is the shearing process, i.e., how high is the shear rate, (or how high is the velocity gradient) relative to the speed or rate at which molecular motions can occur for a given set of conditions. Just what is the realistic range for the values of $\dot{\gamma}$ for such polymer processes as injection molding, fiber spinning, etc? Figure 2 attempts to illustrate this and it is observed that the range is rather large, i.e., values from $1-10^4 s^{-1}$ are allowed for different polymer pro-

¹ Rheology—This term originates from the Greek word *rheo* meaning to flow. Hence rheology is the science concerned with the flow behavior of systems.

cesses. Note that high speed injection molding tends to be the upper shear rate values while compression molding is an example of a low shear rate process. Also included in this figure are the general shear rate ranges for various types of instruments used for measuring rheological properties of fluids.

While it is somewhat outside the scope of the paper, it should be realized that besides shear deformation of a melt or a solution, the same fluid could undergo a tensile or uniaxial deformation as jetting of a fluid. The effect of this type of deformation gives rise to a *tensile elongational viscosity* which will be different from that of a shear viscosity for the same fluid and at the same rate of deformation. While it is not to be considered here, the tensile or elongational viscosity will exceed that of the shear viscosity by at least a factor of three and often higher at higher shear rates.

In expressing the resistance of a material to flow, the term *viscosity* (symbolized by η) is the common indicator used. This parameter relates the observed shear stress to the imposed shear rate (or visa versa). One of the basic laws of flow extends from *Newton's law of viscosity* which is

$$\tau = \eta \dot{\gamma} \quad (4)$$

where it assumes η to be independent of $\dot{\gamma}$; hence the law is linear in nature. Also it is noted that $\eta = \tau/\dot{\gamma} = (\text{Force}/\text{Area}) \cdot \text{time} = \text{Pa}\cdot\text{s}$ where $\text{Pa}\cdot\text{s}$ is *Pascal seconds* and represents the accepted SI units. (The older units still often used would be poise where 1 poise equals 1 (dyne/cm²)(s). Some representative values of the viscosity for various systems are given in Table 1. Indeed, many low molecular weight systems display flow behavior in laminar flow (see Fig. 3a) that is describable by eqn. (4) and hence are called *Newtonian fluids*. As we shall see shortly, polymer melts and solutions often deviate from this linear behavior. With Newton's law of shear viscosity (eqn. (4)) we realize that a plot of shear stress, τ , versus shear rate, $\dot{\gamma}$, will provide a straight line whose slope will be the viscosity—see Figure 4—line A. One clearly notes what is meant by this linear viscous law, i.e., the shear stress goes in direct proportion to the shear rate. An analogy to this behavior would be the raising or lowering of a tire pump handle when the pump is not connected to a tire. Specifically, if you push

Table 1. Viscosity Values of Some Fluids (From Cogswell (1)).

Material	η (Pa·s)	Consistency
Air	10^{-5}	gaseous
Water	10^{-3}	fluid
Olive Oil	10^{-1}	liquid
Glycerine	10^0	liquid
Syrup	10^2	thick liquid
Polymer Melts	10^2 – 10^6	viscous fluids
Pitch	10^9	stiff
Glass	10^{21}	rigid

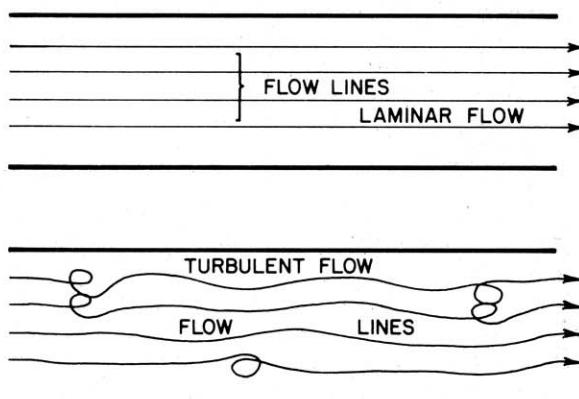


Figure 3. a, Schematic of streamline or laminar flow. b, Schematic of turbulent flow.

or pull harder (faster) the resulting resisting force you feel also increases. If it increases directly in proportion to your increased rate, then we might call it analogous to Newtonian behavior. A second example might be the stirring of one of several low molecular weight fluids such as water, toluene, etc. If one stirs at twice the speed (doubles the shear rate), the resulting resisting force or, more appropriately the shear stress, also doubles as predicted from Newton's law. (This latter experiment will not work when turbulent flow ("unstreamlined" flow) is encountered, see Figure 3b). For our discussion, which is principally focused on polymer melts, turbulent flow is seldom encountered in polymer processing although it may more easily occur for polymer solutions.

Also shown in Figure 4, line B, is another type of flow behavior that appears Newtonian *once* the system begins to flow, i.e. when $\dot{\gamma}$ is nonzero. However, we note that it intersects the shear stress axis at a nonzero value rather than at the origin as did line A. This type of behavior can be described as a *Bingham Newtonian fluid* whose shear stress-shear rate relationship is given by

$$\tau = \tau_c + \eta \dot{\gamma} \quad (5)$$

where τ_c represents the necessary or "critical" shear stress that must exist before flow will begin, see Figure 4. Fluids which display a critical shear stress of this type classify as

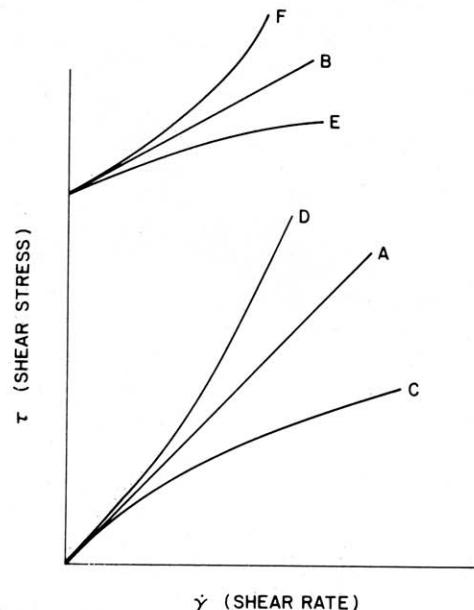


Figure 4. General plot of six different types of shear stress-shear rate behavior: A, Newtonian; B, Bingham Newtonian; C, Shear thinning (pseudoplastic); D, Shear thickening (dilatant); E, Bingham shear thinning; F, Bingham shear thickening.

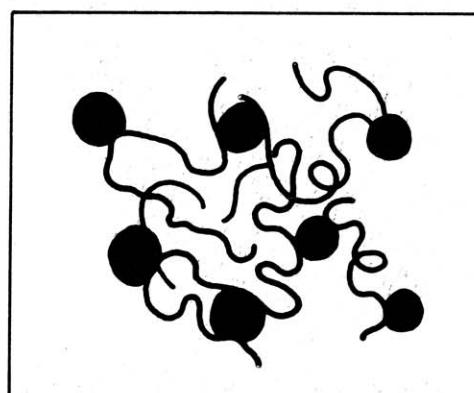


Figure 5. Schematic of one type of structured fluid. In this case the polymer chains are entangled and also partially sorbed on the particles.

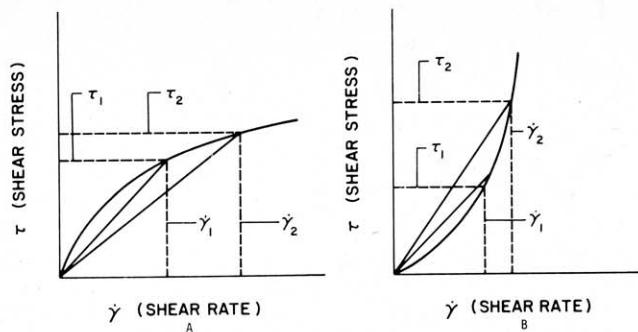


Figure 6. Schematic of how the apparent viscosity is calculated at different shear rates for two different non-Newtonian fluids; A, Shear thinning; B, Shear thickening.

Bingham fluids. (Sometimes a fluid that displays a critical shear stress is also referred to as a "plastic" fluid. In this paper, use of the Bingham description will be used.) Do such Bingham fluids exist and what is the origin of τ_c ? Indeed, this behavior is sometimes observed, three examples being a concentrated clay suspension (mud-like material), butter, and blood, although for the latter fluid τ_c is quite small. Basically, the presence of the τ_c values suggests that the fluid may be "structured" to some degree, see Figure 5. Hence, one must apply an initial critical stress in order to "break down" this structure and initiate flow behavior. At this point it is worth noting that intuitively one can realize that following the cessation of flow, the initial structure may or may not recover. If it does, it may depend on both *external (nonmolecular) variables* as time and temperature, as well as upon *internal or system variables* such as molecular weight, filler content, etc. Some of these considerations will be given later and indeed are important with regard to polymer rheology.

Two other important types of flow behavior are shown by lines C and D of Figure 4. Here we clearly denote *non-Newtonian behavior*, as is clear from the nonlinear shear stress dependence upon shear rate. Each of these latter behavioral patterns are commonly referred to by one of two fluid types. Line C, which shows that shear stress *does not* increase in proportion to shear rate is called a *pseudoplastic* or *shear thinning* fluid. Line D, however, shows that shear stress rises faster than in proportion to shear rate and is called a *dilatant* or *shear thickening* fluid. Before discussing each of these let us add that lines E and F indicate the last two important types of shear stress-shear rate behavior. These being denoted as a *Bingham shear thinning* (Bingham pseudoplastic) fluid for line E and a *Bingham shear thickening* (Bingham dilatant) fluid for line F. The difference in lines E and F from those, respectively, of C and D is the occurrence of a critical shear stress value.

Focusing back on lines C and D we ask just how do we relate shear stress to shear rate since a single proportionality constant as in Newton's law (eqn. (3)) is not applicable? One of the common approaches is to force this law to apply in the following way as illustrated in Figure 6A and B. Here it is shown that by constructing secants from the origin to any point on the shear stress curve, the slope of this linear line provides what is denoted as the "apparent viscosity" and sometimes given by the symbol η_{app} . However, it is more common to drop this subscript and still refer to the varying respective slopes as the viscosity, η , but at the specified shear rate. Indeed, we will also drop the subscript for later usage. Thus, if one now plots this calculated viscosity against shear rate for these two non-Newtonian cases (Lines B and C), Figure 7 is obtained. Here we see that as expected the Newtonian behavior provides a constant viscosity value with shear rate while the shear thinning (pseudoplastic) fluid behavior shows a decreasing viscosity with shear rate. Finally, the shear thickening (dilatant) fluid indicates an increasing viscosity with increasing shear rate.² The reader can now better understand the origin of the terms shear thinning and shear

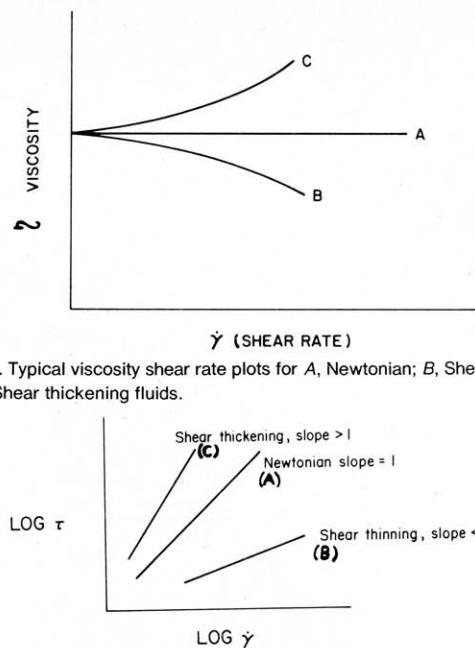


Figure 7. Typical viscosity shear rate plots for A, Newtonian; B, Shear thinning; and C, Shear thickening fluids.

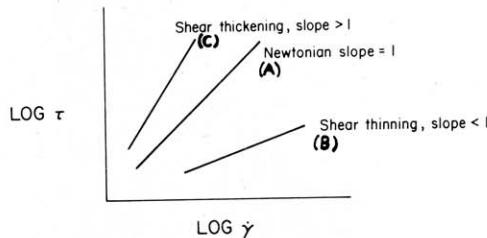


Figure 8. Power law plots for three types of fluids: A, Newtonian; B, Shear thinning; and C, Shear thickening.

thickening by the simple fact that the newly defined viscosity values show that for the former, the resistance of flow decreases as shear rate increases (appears to get "thinner" as adding paint thinner to give easier flow to a paint) while for the latter, the resistance (viscosity) increases with rate for the latter thus implying a thickening behavior.

Another useful form of expressing flow behavior is to utilize what is called the power law equation given by

$$\tau = A \dot{\gamma}^B \quad (6)$$

Clearly if B is unity, then "A" has the identical form to η and eqn. (6) appears as Newton's law. To maintain dimensions of "A" equivalent to η , eqn. (6) may be written as

$$\tau = A \dot{\gamma} |\dot{\gamma}^{B-1}| \quad (7)$$

where the bars denote that no dimensions are used. For our discussion we will use eqn. (6) but written in logarithm form thereby giving

$$\log \tau = \log A + B \log \dot{\gamma} \quad (8)$$

From this relationship we see that plotting $\log \tau$ versus $\log \dot{\gamma}$ should provide a line whose slope is "B"—the exponent of the power law fluid, and an intercept whose value should be "A". It is the former that is the most important for as one can see from the three lines in Figure 8, i.e., the slopes would be unity, less than unity, and greater than unity for a Newtonian, shear thinning, and shear thickening fluid, respectively. Indeed a plot of $\log \tau$ versus $\log \dot{\gamma}$ is called a power law plot, and the slope provides an indicator of Newtonian or non-Newtonian behavior. It should be stated here that a fluid may show *both* Newtonian and non-Newtonian behavior as a function of $\dot{\gamma}$. Examples of this will follow shortly.

Before discussing the origin of these different flow behaviors, let us also briefly consider some of the basic means of measuring the viscosity (resistance to flow). It will not be our purpose to derive the equations relating the observed flow rate to shear stress in these flow geometries but rather to bring to mind some of the important experimental and instrumental

² The Society of Rheology suggests the use of the terms shear thinning and shear thickening in contrast to using pseudoplastic and dilatant. However, all are common terms used in the literature. To promote the suggestion of the Society, all future statements in this paper will refer to shear thinning and shear thickening.

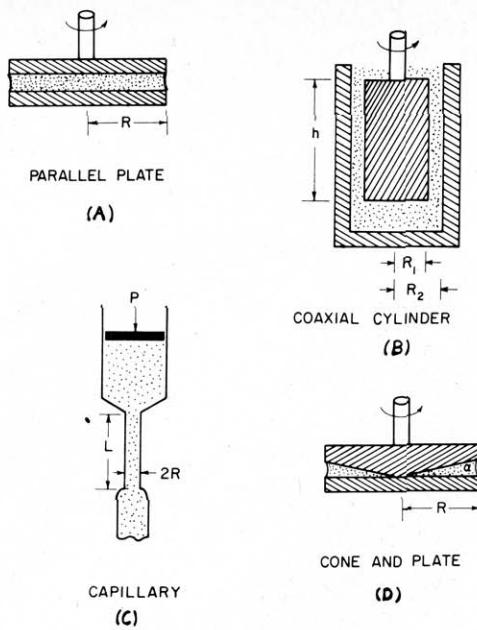


Figure 9. Generalized sketches of four different types of instrumental geometries used for measuring rheological properties: A, Parallel plates; B, Couette or coaxial cylinders; C, Capillary flow; D, Cone and plate.

variables. Further details of the exact methodology can be found elsewhere (2).

Figure 9 shows four simple schematics of four geometries that one might utilize to measure the shear stress-shear rate behavior. Figure 9A shows that if one shears a fluid between parallel plates, (by rotational or torsional motion) the flow process could be viewed somewhat like a sliding of layers of fluid over one another as if shearing a deck of cards parallel to the surface of the deck as was the case for Figure 1. By measuring the force it takes to do this at some given shear rate (rotational speed) and plate separation distance will provide the flow behavior of the given fluid. Figure 9B shows another common approach in that a cylinder of a smaller size is placed inside of a somewhat larger one providing what is called a *couette* or *concentric cylinder* viscometer. When either the outer or inner cylinder is rotated, at a given speed, the concentric fluid layers slide over one another in the defined fluid gap providing the resistance to flow. To determine the shear stress requires one to connect a torque transducer to the stationary cylinder. The flow is therefore of a torsional type. Again, one connects a torque transducer to the stationary plate while rotating the other at a fixed speed. Figure 9C shows the schematic behavior encountered in pipe flow—sometimes referred to capillary, poiseuille or telescopic flow. The latter term applies in that the centermost “tube” of fluid moves faster than the others with the layer at the pipe wall moving at zero velocity caused by the presence of the “wall.” For this system the shear stress is calculated from the pressure (a stress) to produce a given volumetric throughput in a pipe of a given length and diameter. A fourth and final type of flow system is shown in Figure 9D. This device is called a cone and plate viscometer. It is similar to the rotating parallel plate viscometer except the uppermost plate is conical but possesses only a small angle, α .

Now just what device should one use for measuring the flow behavior? This will depend on both external and internal factors. An important point to recognize, however, is the nature of the shear rate pattern provided by each of these devices. Specifically we have learned from Figure 4 that for non-Newtonian fluids, the resistance to flow is dependent upon the shear rate experienced by a given volume element of fluid. Now, if we briefly inspect the shear rate profile generated by the three devices above, we find what is shown in Figures 10A–C where the instrumentation variables of interest

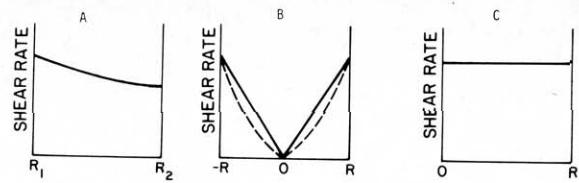


Figure 10. Shear rate profile as might occur for three of the instruments shown in Figure 9A–D. A, Coaxial cylinders; B, Capillary flow; C, Cone and plate.

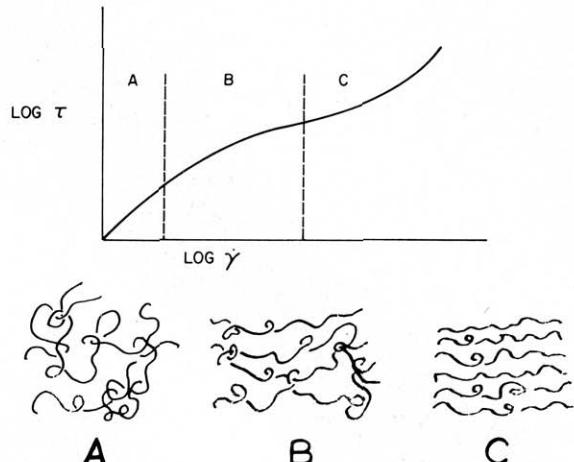


Figure 11. Hypothetical power law plot of a typical high molecular weight polymer melt. Note the three regions of behavior (A–C) and the generalized sketches below that attempt to relate these three regions to the fluid structure.

are coupled to the drawings in Figure 9. The significant factor to observe is that all of the flow devices, with the exception of the cone and plate viscometer, do not provide a constant shear rate. (While not shown, the shear rate profile for the parallel plate system also is not constant.) Rather it varies and, in the case of Figure 10A and B, the values range from zero upward. Hence, this means if one is using other than a cone and plate viscometer, the observed shear stress is in response to some form of an average of the shear rate range experienced by the non-Newtonian fluid elements. Clearly for a Newtonian fluid, one need not be concerned about the varying shear rate with position since the viscosity is independent of this variable (recall Figure 4). This suggests for non-Newtonian fluids possibly one should always use a cone and plate device. Typically this is not done in many cases. Two principal reasons are that at (1) high shear or (2) low viscosities, the fluid may well be “thrown” from between the cone and plate due to centrifugal forces. In these two cases, a capillary viscometer is likely to be the preferred instrument to use. (Generally when a capillary system is used, the shear stress and shear rate reported is that at the walls of the capillary.)

Now, let us return to the molecular considerations that can help provide an understanding of the non-Newtonian behavior commonly observed for polymer melts (and solutions). In particular let us focus on Figure 11 which shows a power law plot ($\log \tau$ versus $\log \dot{\gamma}$) for the flow behavior of what will be considered to represent a *hypothetical* polymer melt. In this simplified sketch, three (A–C) distinct regions can be noted. Region A, which might occur at low to extremely low shear rates, is actually Newtonian in behavior since a slope of unity is observed. Region B, however, shows that the slope decreases from unity with increasing shear rate thereby displaying shear thinning non-Newtonian behavior. Interestingly at high shear rates this plot again shows that in Region C the flow takes on Newtonian behavior for once more a slope of unity is observed. It should be pointed out, however, that region C is not likely to be attained in real systems for reasons that will soon become apparent.

It is now time to consider the flow behavior on a molecular basis if we wish to account for the behavior in Figure 11. We first recall that pure low molecular weight fluids would display

only Region A behavior (Newtonian) that simply arises from a tumbling or sliding of the molecules over one another (molecular frictional forces) as the system is sheared. Increasing the shear rate on such a system simply imposes a shorter time scale (per unit of shear strain) on the system which means that for a given fluid structure, the system will clearly display a higher shear stress since the molecules will not have had the same time scale to relax (flow or tumble) as they did at a lower shear rate. Indeed, one would expect a linear relationship between shear stress and shear rate for such a fluid where the "structure" is not changing during laminar flow conditions. Clearly on the basis of the above argument then Figure 11 implies a changing fluid structure with shear rate. Is this reasonable for our macromolecular fluid? It is here that the author wishes to introduce the "worm concept" into our discussion.

Specifically the macromolecular fluids we are discussing can be crudely viewed as a mass of entangled earthworms—particularly if the chains possess a flexible backbone. The similarity with earthworms is quite reasonable in some ways and not in others. One particular advantage is the fact that "long" worms entangle and display coiling as to flexible macromolecular chains. In addition, this degree of motion or mobility (and hence "response" or "relaxation" time) will depend on the temperature and degree of entanglement (e.g., number of entanglements/chain). One difference that generally exists between worms and macromolecules is their difference in aspect ratio, i.e. length to diameter ratio. Clearly, for most high molecular weight chains, the aspect ratio could be considerably greater than that of an earthworm. In fact the useful polymer systems as materials may possess an aspect ratio of 1000 or often greater, thereby demonstrating the *very long* nature of the macromolecular worms. This consideration, which is clearly molecular weight dependent suggests that macromolecules often may be much more entangled than a ball of earthworms. As crude as the analogy may sound, this concept will find its way into the interpretations of many of the examples which we will now begin to consider.

In view of this worm model let us return to its correlation between the sketches shown below Figure 11 that relate to the three regions of shear rate.

In region A, there is only a low rate of shear (as slow rate of rotation in a cone and plate viscometer). Hence, the melt or fluid "structure" has a much better ability to be retained. Specifically, if the rate of molecular response or relaxation (worm motions) are fast relative to the rate of shear (time frame imposed on the "worms") the fluid structure will continue to be maintained. Sure, some entanglements may be lost or altered, but others will be generated at the same time so as a first approximation, the same entanglement density will be maintained. Indeed as we will later see, it is the occurrence of molecular overlap or entanglements that is highly responsible for much of the unique flow behavior of macromolecular fluids. In view of our worm model analogy, consider yourself shearing a handful of worms at *low* rates. Certainly, the worms will try to *maintain* their coiled entangled structure by moving quicker than the time frame of the shearing.

Now let us raise the shear rate but maintain other factors constant. In Figure 11 this increase may lead to region B where we see a less than proportional increase in shear stress with an increase in $\dot{\gamma}$; hence, a lower viscosity will result. In view of sketch B, given below Figure 11 and in light of our worm model, we can picture that at a higher $\dot{\gamma}$, the response time of the molecules or "worms" no longer permits the original structure to be maintained. Rather, one can imagine, just as shearing real worms, the entanglement density will likely be decreased. This loss of entanglements, however, serves to clearly lower the resistance of flow and thus the shear stress does not increase at the same rate as when in region A. Hence in region B, shear thinning is observed—as is the general behavior for polymers. If $\dot{\gamma}$ is again increased the entanglement density may be decreased further or, in other words,

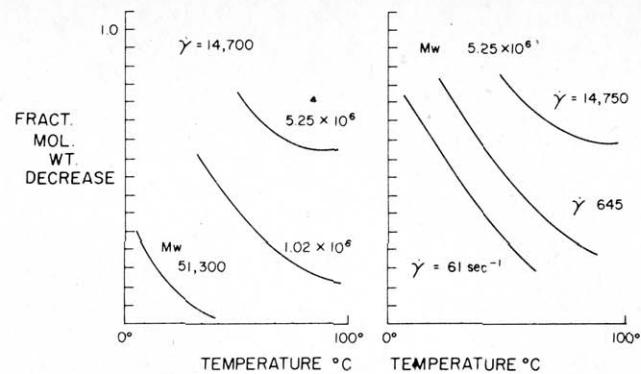


Figure 12. Plot of fractional molecular weight change that occurred for polyisobutylene samples undergoing specific shear rates at specific temperatures. Actual data points are not shown, but each point on a given curve would represent a single sample. (As redrawn from Pohl et al. (3)).

additional loss of initial fluid structure occurs. Indeed at high $\dot{\gamma}$, one might in principle approach Newtonian behavior again as depicted by Region C. The cause of this second Newtonian region is due to the simple fact that all fluid structure is lost in terms of molecular entanglements. Hence, only segmental frictional forces now resist flow just as in low molecular weight systems, thereby causing a Newtonian response (see Sketch C). If one observes the general shear rate response of polymer melts, one generally does not see the onset of a second Newtonian region. Why is this so? One very good reason for this is due to the same result that would happen if you very rapidly sheared (or stretched) a handful of worms. In short, they cannot move fast enough to rearrange and relieve the incurred shear stress (or tensile stress if stretched) and thus chain scission occurs! Does this really happen? If it does, our molecular intuition suggests that the longest molecules (or worms) will be the ones to break first since these will more highly entangle and have the longest relaxation or response time. Similarly, from our earlier comment that temperature will affect molecular motion, as well as the mobility of real worms, we would also intuitively expect, that for a given molecular weight, lowering the temperature would lead to more chain scission (*mechanical shear degradation*) at a given $\dot{\gamma}$ than for a higher temperature. This of course follows from the simple fact that at a lower temperature, the Brownian motion of the molecules (worms) is less (the relaxation or response time is increased with a decrease in temperature) and thus the chain backbone may reach a critical stress at a lower $\dot{\gamma}$ so as to cause rupture. The experimental data of Figures 12A and 12B clearly confirms all of the above expectations. In short, Figure 12A shows that for three different narrow molecular weight fractions of polyisobutylene ($-\text{CH}_2-\text{C}(\text{CH}_3)_2-$), as the temperature is increased while keeping $\dot{\gamma}$ at $14,700 \text{ s}^{-1}$, the fractional molecular weight decrease is less.³

Clearly one notes from Figure 12A that the fractional decrease in molecular weight also increases as molecular weight goes up. [Certainly a macromolecular "worm" of five million molecular weight has a high aspect ratio!] In Figure 12B, the effect of $\dot{\gamma}$ on shear degradation is given and is expected i.e., raising $\dot{\gamma}$ at a given temperature, increases shear degradation yet the decrease is less for higher temperatures due to the faster response time of the molecules.

It now is appropriate to introduce the concept of the dimensionless term known as the Deborah number, N_D . We will define this as

$$N_D = \frac{\text{response time of the material}}{\text{experimental or observation time}} \quad (9)$$

³ Fractional molecular weight decrease refers to how much the molecular weight decreased after shearing the material for a specified time. For example, a value of 0.5 means a 50% decrease in molecular weight due to shearing.

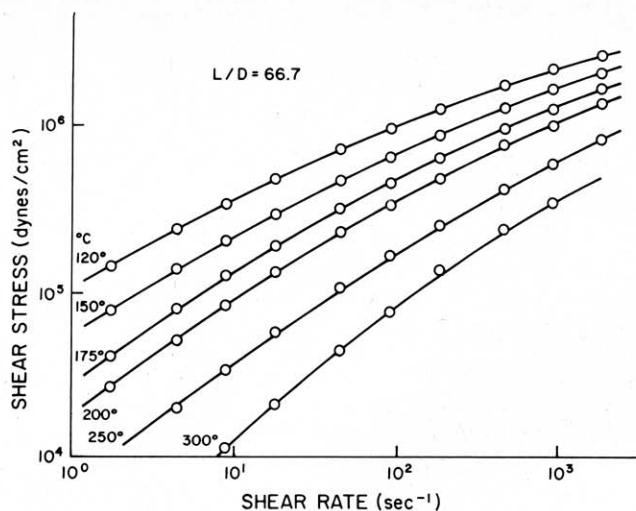


Figure 13. Power law plot at various temperatures for a low density polyethylene. (Reproduced from R Mendelson, (4) 1.

From our discussion we can easily see that for a given shear rate (fixed experimental or observation time), then N_D will increase with an increase in molecular weight or a decrease in temperature. In essence then, anything that tends to increase N_D implies that it is becoming more difficult for the molecular system to maintain its structure under the experimental conditions of a given deformation. With respect to Figure 11, the reader should also now realize that N_D is increasing as $\dot{\gamma}$ is increased. We will make use of the concept of the Deborah number in several of our later discussions so let us attempt to reinforce the importance of this concept by referring to a system that most students are familiar with—silly putty. This polymeric system is one that can behave as a viscous fluid if deformed at low rates (lower Deborah numbers) since the molecules have sufficient time to flow relative to the experimental time imposed on them (deformation rate). However, as the student is also aware, if this material is rapidly stretched (or hit with a hammer) it behaves very much as a brittle solid. The cause is that the response time of the molecules (worms) is too great relative to the experimental time window that no smooth flow takes place and the system ruptures—a result of a much higher Deborah number than unity.

Now let us inspect a real example of shear stress behavior with shear rate. Figure 13 provides this information in a power law plot for a specific low density polyethylene as taken from Mendelson and determined by capillary rheometry. It is noted that data are given for several temperatures—an external variable we will be considering shortly. For now it is only important to recognize that at low $\dot{\gamma}$, the slopes tend to be near unity (particularly for the highest temperatures) but become less than unity and, thus display shear thinning, as $\dot{\gamma}$ increases. This behavior is directly in line with our earlier discussions regarding the behavior of the “earthworms” and the concept of the Deborah number. It is finally noted in this same figure that the data go to values of $\dot{\gamma}$ above 10^3 s^{-1} . Recalling that real processing of polymers seldom exceeds 10^4 s^{-1} then it is clear that these data do not suggest any sign of ever reaching Newtonian behavior at the higher useful shear rates. Indeed this data is quite representative of most flexible macromolecular melts.

Effect of the External Variables of Temperature, Pressure and Time on Viscous Behavior

Temperature

The temperature dependence of viscosity is indeed quite significant in macromolecular systems. A means of noting this is by using the expression often employed for low molecular weight systems and which extends from the kinetic theory of fluid flow. Specifically

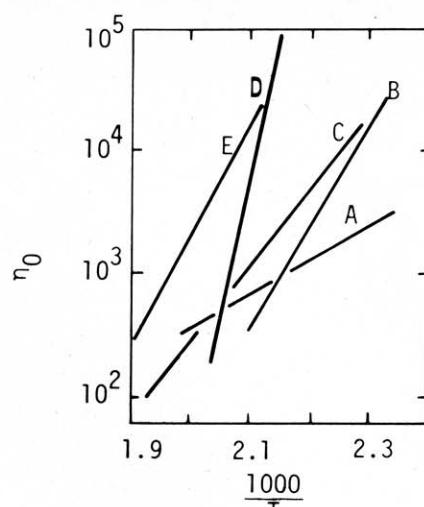


Figure 14. General temperature dependence of the zero shear viscosity for various polymers. Note that molecular weight and chain branching would affect the absolute values. (As redrawn from Severs (5)). (A) Polyethylene; (B) Cellulose acetate; (C) Polystyrene; (D) Ethyl cellulose; and (E) Polymethyl methacrylate.

$$\eta(T) = A_0 \cdot e^{Ea/RT} \quad (10)$$

where $\eta(T)$ represents the zero shear viscosity⁴ at temperature T , A_0 is a constant, Ea a flow activation energy (energy for segmental movement), and R is the gas constant. Taking the logarithm of eqn. (10) gives

$$\log \eta(T) = A_0 + Ea/RT \quad (11)$$

Hence, plotting $\log \eta(T)$ versus $1/T$ should provide a straight line whose slope is Ea/R if this Arrhenius type law applies. As shown in Figure 14, this equation does apply over a reasonable range of temperature and it is noted that the slopes vary for different chain chemistry.⁵ It should also be stated that the slope is not dependent on molecular weight thereby implying that it is only the *local segmental character* that determines Ea . Is there a correlation of Ea with chain chemistry? In general there is and it has to do with the “bumpiness” of the chain backbone. In fact, then, Figure 14 is a bit misleading for the “polyethylene” plot in this figure is not specified as to whether it is low density (branched) or linear high density. Indeed these two types of polyethylene display different values of Ea . Linear (non bumpy) polyethylene has a value of Ea of about 7 Kcal/mol while branched polyethylene may approach 11 K cal/mole depending on the degree of branching and whether it is long or short chain branching. Doesn't this make some sense that segmental motion will be more difficult as the chain becomes less “smooth”? In fact it has been found by various workers that Ea will systematically increase as one goes from “smooth” linear polyethylene to polypropylene to polybutene-1 to polypentene-1. In light of this a chain like polystyrene that has a large phenyl group, which is not only a large bump but also produces steric rotation effects, would be expected to have a higher Ea than the other chains we have discussed. Indeed Ea for polystyrene is the order of 18 Kcal/mole. In general then, any change in chemistry that tends to stiffen the chain or make it a bit bumpy will often lead to a higher Ea and hence a *stronger* dependence of viscosity on temperature. A distinct exception to this general statement occurs when the chain is *very stiff or rodlike*. In this case the special case of liquid crystal behavior *may be* induced which will be addressed briefly later in this paper.

⁴ By zero shear viscosity, it is meant that one is at a low enough shear rate such that the behavior is Newtonian, i.e., shear rate independent. This makes sense since otherwise the *structure of the fluid* would be varied if data were obtained in the non-Newtonian region.

⁵ The reader should be informed that eqn. (10 or 11) is not valid as the glass transition region is approached. Specifically, the WLF relationship for viscosity is much better in the range of T_g . See the lecture by Prof. Aklonis or reference (6).

To illustrate the strong temperature dependence of viscosity, Table 2 is given below as modified from Cogswell's recent introductory book on polymer rheology (1). Note the large decrease in viscosity with only a ten-degree temperature change from the reference temperature for most of the polymers shown.

Before leaving the variable of temperature, the reader should not forget that raising the temperature will typically lower the Deborah number, N_D , for a given shear rate since the increase in kT will speed up the motion of worms and hence decrease their response time. Thus a generalized plot of how log viscosity depends upon temperature and $\dot{\gamma}$ is given in Figure 15. As is noted, the degree of Newtonian behavior is increased as temperature is increased due to the decrease in the Deborah number. Another feature about this general plot is the fact that at the higher shear rates the viscosity behavior shows less difference for the different temperatures than at the lower shear rates. This of course arises from the fact that the fluid structures are more similar at the higher $\dot{\gamma}$ due to overriding the response times of the molecules by the higher velocity gradient, i.e., deformation rate. However, the lowest temperature still provides the highest viscosity as expected.

A passing comment but one of importance is that regarding temperature changes *induced* by the deformation process; this is known as *viscous heating effects*. Specifically, it is clear that segmental motion (molecular sliding) leads to the loss of input energy i.e., the work done on the system. Where does this energy go? The dissipative or viscous loss is expended in the form of heat which, of course, could increase the temperature of the system undergoing the deformation. Indeed such viscous heating effects are even desirable in some processes, for this thermal energy is utilized to help heat the material and hence may reduce the direct thermal input by conductive heaters. The fact that organic polymers are of relatively poor thermal conductivity promotes the possibility of viscous heating and the generation of "hot spots" or "hot layers" in real processes. Hence, recognition of this phenomenon must be made. In the actual rheological measurements of polymer systems, care must be taken either to correct for or eliminate viscous heating. This of course can be eliminated by using good thermal conductive rheometer surfaces (such as metal) and making the fluid thickness or "gap" small so as to minimize thermal gradients.

Pressure

As one might expect there is a viscosity dependence on pressure, P . Since flow requires some free volume for molecular motion then it is only reasonable that an increase in overall hydrostatic pressure (from all sides) would squeeze or compress the available free volume thereby restricting molecular motion and raising viscosity. Indeed this is the common behavior. The general form of the pressure dependence is often given as

$$\eta(P) = Ae^{BP} \quad (12)$$

where A and B are constants for a given polymer at a given temperature and shear rate. In brief, the pressure effects become more important at lower temperature—particularly if at all in the range of T_g . However, if well above T_g , the pressure dependence is less. To give some indication of the effect of pressure Table 3 is provided as taken from Cogswell (1).

Time

Suppose we now conduct the following experiment—a polymer melt is placed within a cone and plate viscometer (recall Figure 9D) and the experiment is *instantaneously started* at a fixed temperature and shear rate. Just how would the viscosity behave with *time* at this fixed shear rate? Once again using the worm model, we realize that prior to beginning the experiment, the worms had a given equilibrium fluid structure of some entanglement density. However, once the

experiment is started, and assuming that the shear rate is high enough to place the fluid into the non-Newtonian region, then a new equilibrium fluid structure must develop, i.e., a new entanglement density at the specific shear rate. This change in structure, however, is not by any means instantaneous in nature. Rather, it will take a finite amount of time to reach the second equilibrium state. This *transient* time will clearly not only be dependent upon such external factors as temperature, $\dot{\gamma}$, and pressure but likely upon the internal variables of molecular weight, its distribution, branching, etc.

With most flexible chain polymers, the general behavior of this *time dependent* experiment will be as curve A in Figure 16 below. That is, the viscosity will decrease *with time* as the entanglement density decreases *with time*. This behavior common to most shear thinning systems is known as *thixotropy*. (At this point the reader should be sure they do not confuse thixotropy with shear thinning. The former is *time dependent at a fixed shear rate* while the latter refers to the *steady state (equilibrium) dependence of viscosity on shear rate*.) Also shown in Figure 16 is the expected time independent behavior for a Newtonian fluid (curve B) as well as for what is known as a *rheoplectic fluid* (rheopexy behavior) as given by curve C. While the Newtonian behavior is time de-

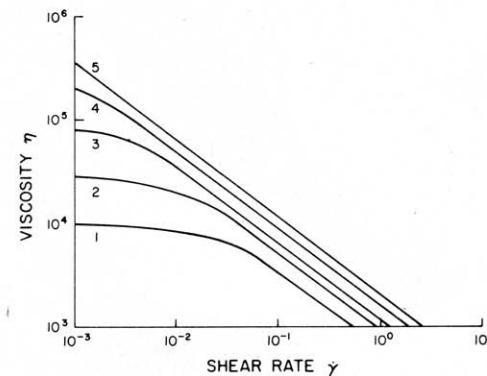


Figure 15. Typical log viscosity-log shear rate curves at five different temperatures. Curve 1 is for the highest temperature, and curve 5 is for the lowest temperature. For a typical polymer, the temperature difference between each curve is approximately 10°C. (Taken from (7)).

Table 2. Viscosity Dependence on Temperature (From Cogswell (2)).

Polymer	Test Temp = T	$\eta(T)/\eta(T + 10^\circ\text{C})$
Branched PE	150	1.35
	200	1.30
	250	1.25
Linear PE	200	1.20
Polystyrene	200	1.70
PMMA	200	2.50
	250	1.90
Polycarbonate	250	1.50
PET	275	1.35
PVC	300	3.00

Table 3. Relative Increase of Viscosity (above its value at atmospheric pressure) at a Fixed Shear Stress by an Imposed Hydrostatic Pressure of 1000 atm. (From Cogswell (1)).

	Polystyrene ≈ 150°C	200°C	Low-density polyethylene ≈ 150°C
...	50		4.8
1000	40		3.9-5.3
270	...		4.0
250
200	30		4.0

Each line in the table represents data from a different worker.

pendent as expected, the *rheoplectic* fluid shows an increase in viscosity with time at a fixed shear rate. How could this be? This latter behavior implies that the occurrence of shear is changing the structure of the fluid so as to increase the apparent entanglements. This sounds at first unreasonable. While indeed this behavior is uncommon, it can occur and one possible cause for this behavior as shown below in Figure 17. This figure depicts the effect of packing upon the viscosity of particulate solutions or suspensions. The orderly packing at low shear rates allows for minimum interference between particles during flow. At higher shear rates, the particles take a more random arrangement which leads to interparticle interference and thus higher viscosities. A second well-known case is the rheoplectic behavior of polyvinyl alcohol (PVA) in an aqueous solution containing a borate salt. The effect of shear results in the formation of "bridges" between the hydroxyl groups of the PVA molecules with the salt ions thereby giving a higher apparent entanglement density thereby raising the viscosity. The same polymer solution without the salt will show thixotropic behavior (8)!

Another variable which can be viewed as an external variable is that of the *type of deformation*. Specifically for our brief discussion here, the two principal types as stated very early are those of shear or extensional flow. Clearly in real processes, there may be a combination of these. Just what are the principal differences in the two? The one feature that clearly stands out is that shear promotes rotation of the flow

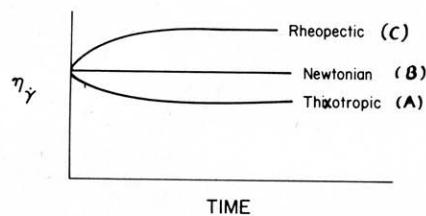


Figure 16. Plot of the viscosity at a fixed shear rate against time for three different types of fluids: A, Thixotropic; B, Newtonian; C, Rheoplectic.

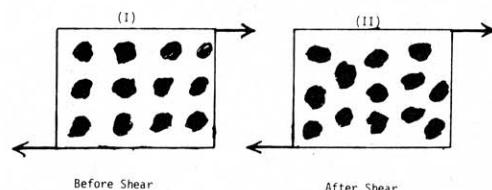


Figure 17. Sketch of a possible fluid structure that, when undergoing shear, would lead to a structure change that would increase the viscosity (rheoplectic fluid).

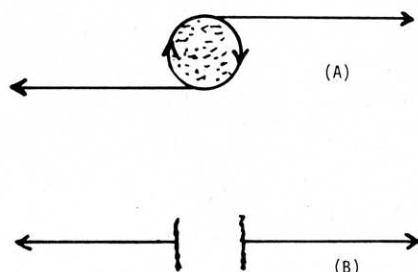


Figure 18. Schematic showing A, Rotation induced by a shear flow; B, Extension with no rotation caused by extensional flow.

elements whereas no rotation occurs for extension thereby being referred to as *irrotational flow*—see Figure 18. In brief the effect is that extensional flows display higher viscosities than shear flows—the difference being three or greater. Possibly the reader can relate to this by the worm experiment—consider shearing (stirring) a group of worms versus extending them by a simple uniaxial drawing. Certainly one can picture that the response (or resistance to flow) will not be the same! Due to the fact that extensional viscosities are higher than that for shear flow at the same shear rate, it is very important to recognize the occurrence of extensional flows in actual processing for these flow regimes may have a more pronounced influence on the processability.

Effect of Internal Variables on Viscous Behavior

Clearly there are many such variables, that we could consider, some of these being molecular weight, its distribution, chain chemistry, chain architecture, additive concentration as filler or plasticizer polymer concentration (as in polymer solutions, etc). We will attempt to touch on most of these although in view of space limitation much detail will be lacking at times.

Molecular Weight

If one plots the log of zero shear viscosity versus $\log \bar{M}_w$, where \bar{M}_w is the weight average molecular weight, Figure 19 will be the general result for flexible chain polymers.⁶ Up until some critical value of \bar{M}_w , the slope is unity but above this critical value denoted as \bar{M}_{w_c} , the slope is of the order 3.4. In other words above \bar{M}_{w_c} viscosity increases with \bar{M}_w raised to the 3.4 power. Just what are the values for \bar{M}_{w_c} ? Generally they fall in the range of 4000–15,000 g/mol. In fact, it is generally values of molecular weight above \bar{M}_{w_c} that the corresponding polymer provides useful materials. Does this suggest a hint as to the origin of \bar{M}_{w_c} ? The general belief is that at \bar{M}_{w_c} the molecular weight is sufficient enough to create or induce entanglements which of course are unique only to macromolecular systems. Certainly one can easily visualize this by thinking about a mass of short worms versus a mass of long worms. The former can be pulled apart easily while the latter cannot due to the entanglement structure! Just why then does \bar{M}_{w_c} vary for different systems? In brief, if one considers the backbone length (number of repeat units) to be the critical factor, then one must ask what is the number of repeat links to achieve \bar{M}_{w_c} ? Since the molecular weight of different repeat units vary *per unit length*, e.g. $-\text{CH}_2-\text{CH}_2-$ versus $-\text{CH}_2-\text{CHCl}-$ then it is not surprising to find a variation in \bar{M}_{w_c} . In fact if one normalizes the viscosity behavior on the backbone atoms the behavior shown in Figure 20 is obtained. Without full detail, this data from *many different polymers of different chemistry* show nearly universal behavior. These data are indeed highly convincing of the entanglement con-

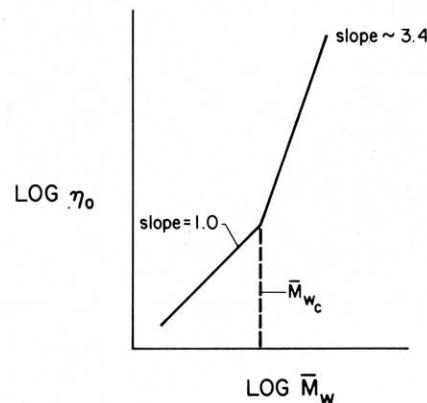


Figure 19. General plot of the log of the zero shear viscosity versus the log of the weight average molecular weight for flexible chain polymers.

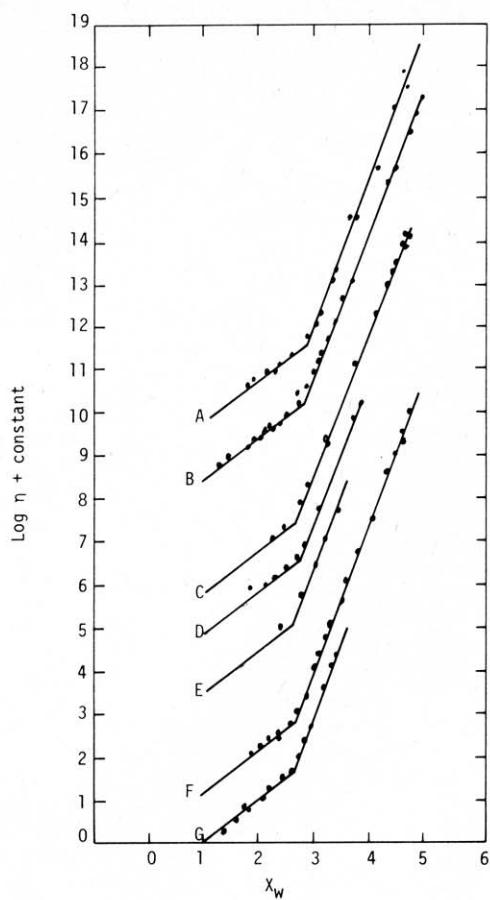


Figure 20. Plot of the log of the zero shear viscosity for several polymers against a variable X_w that is related to a parameter that normalizes the behavior on the basis of backbone atoms or chain links. A constant was used for vertical shifting of the data in order to avoid superposition. A, Poly(di-methyl siloxane); B, Poly(isobutylene); C, Poly(butadiene); D, Poly(tetramethyl *p*-silphenyl siloxane); E, Poly(methyl methacrylate); F, Poly(vinyl acetate); G, Poly(styrene). (From (10)).

cept. Hence we realize that viscosity is made up of a localized frictional effect of sliding a segment (or just a small molecule) over one another as well as an entanglement or structural component that is common to polymer systems of sufficient molecular weight.

At this point it should be realized that since viscosity (resistance to flow) will clearly influence the processibility and horsepower requirements, there is a bit of a trade off between final solid state properties and processibility. Specifically, it is necessary to acquire a sufficient molecular weight so as to promote acceptable bulk properties in the final solid, however, it must be processible so that molecular weight can not be too high.

Another aspect of molecular weight is its effect on the shear thinning behavior. Figure 21 shows this behavior as determined from an oscillatory or dynamic experiment.⁷ At this time, the reader may for simplicity view this set of data as $\log \eta$ versus $\log \dot{\gamma}$. It is noted that an increase in molecular weight causes a higher zero shear viscosity (higher η in the Newtonian region). In addition and, as expected in view of the worm concept, the onset of non-Newtonian shear thinning behavior

⁶ Stiff rodlike polymers will show a similar behavior to Figure 19, except the slope of the higher molecular weight regions may be somewhat greater (9).

⁷ In this lecture, dynamic or oscillatory measurements will not be treated in detail. Suffice to say, however, that this experiment amounts to oscillating the melt at a small shear strain at a given shear rate. From this, both viscosity (viscous) and elasticity or elastic effects can be determined. Later on elastic effects will be discussed.

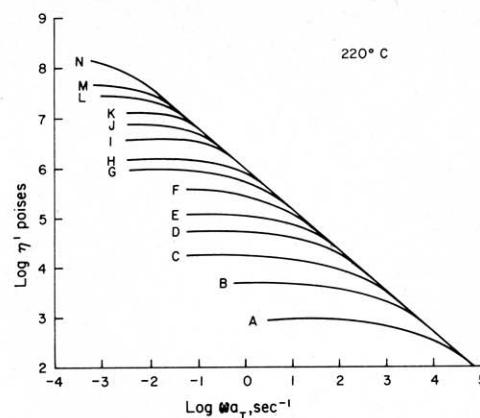


Figure 21. Plot of the log viscosity versus $\log \omega a_T$. The latter variable is related to shear rate. The data are for polymethyl methacrylate of different weight average molecular weight as follows: A, 18,400; B, 29,100; C, 40,800; D, 52,100; E, 65,800; F, 80,100; G, 101,000; H, 114,000; I, 143,000; J, 174,000; K, 191,000; L, 229,000; M, 278,000; N, 408,000. (From (7)).

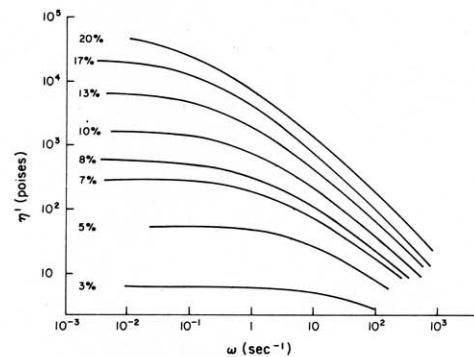


Figure 22. Dynamic viscosities of polyisobutylene solutions in decalin as a function of concentration and frequency. $M_n = 370,000$; $M_w = 1.06 \times 10^6$. (From (7)).

occurs at a lower $\dot{\gamma}$ as molecular weight increases. That is, the Deborah number, N_D , increases with molecular weight due to increased relaxation times of the bigger more entangled worms.

Molecular Concentration (Solution Behavior)

Suppose the polymer is diluted with a small compatible solvent molecule—how will the viscosity be affected? Certainly the general answer is that it will likely decrease. In general this is certainly true. One example is shown in Figure 22. Here high molecular weight polyisobutylene (PIB) is placed in the solvent decalin and the $\log \eta$ versus $\log \dot{\gamma}$ behavior determined. (Again the data are from a dynamic or oscillatory experiment, but we will, for simplicity, view the data as $\log \eta$ versus $\log \dot{\gamma}$.) The important points to recognize are that (1) viscosity decreases as polymer concentration decreases; (2) the decrease in η with decreasing polymer concentration is considerable for the data are on a log scale, and (3) the degree of Newtonian character is maintained to higher frequency ($\dot{\gamma}$) for lower concentrations than those which exist for higher concentrations. All of these observations are hardly surprising in view of the worm concept. While the first two are quite obvious, the third arises because of the lower degree of chain overlap and hence few chain entanglements per molecule. Thus, the response times or relaxation times are shortened and Newtonian character is maintained to a higher frequency. In other words, a lower concentration system displays a low value of the Deborah number.

Molecular Weight Distribution

As discussed in other lectures in this series, polymer systems (particularly synthetic) are not monodisperse but rather have a considerable range of molecular weight species in a given sample. Because the overall distribution has a significant effect on melt and solid state properties it is important to characterize the distribution. (Professor T. C. Ward has discussed this means of characterization in his lecture on molecular weight.) Our point of importance here is to point out that the distribution has important consequences on the processibility of a system and in particular, the shear thinning response. In general for a given value of \bar{M}_w , a broader distribution tends to show the onset of shear thinning behavior at a lower shear rate, yet the shear thinning behavior is not as dependent upon shear rate as in a narrow distribution. That is, the narrower distribution may well display Newtonian behavior to a higher shear rate, yet upon entering the shear thinning region its fall off in η with shear rate may well be more pronounced than for the broader distribution. A sketch of this very general behavior is shown in Figure 23. Again, the molecular reasoning for this effect of breadth is not surprising in view of the worm concept in conjunction with the Deborah number, i.e., a broader distribution possesses a broader range of response times than does a narrow distribution of the same \bar{M}_w . In brief then, recognition of molecular weight distribution effects are very significant in the processing of a given polymer.

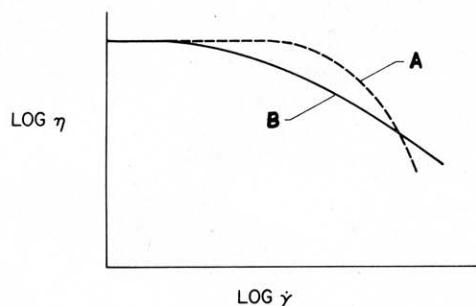


Figure 23. Generalized plot of $\log \eta$ versus $\log \dot{\gamma}$ for A), Narrow molecular weight distribution; B), Branch molecular weight distribution. It is assumed that the weight average molecular weights of the two distributions are nearly the same.

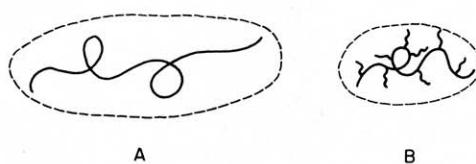


Figure 24. Oversimplified view of how the hydrodynamic volume varies for (A), Linear and (B), Branched polymer of the same molecular weight.

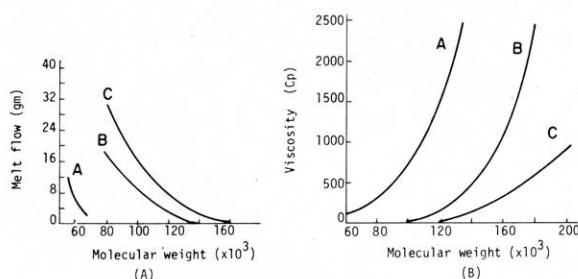


Figure 25. Two plots showing the effect of chain architecture on viscosity. (From McGrath et al. [13]). A, Melt flow (inversely related to viscosity) versus molecular weight for (A) Linear, (B), Trichain, and (C), Tetrachain block copolymers. B, Solutions viscosity (17% solids in toluene-naphtha) versus molecular weight for (A) Linear; (B) Trichain, and (C) Tetrachain styrene butadiene block copolymers.

Molecular Architecture

In view of the fact that the viscous behavior is dependent upon a structural variable (entanglements) as well as just a frictional factor (segment-segment friction) then it is not surprising to find that molecular architecture influences the viscous response. As might be intuitively anticipated, a branched system behaves differently from its linear counterpart. Yes, earlier we discussed the flow activation energy differences of branched versus linear systems as noted by the viscosity dependence in temperature. Here, however, we are now referring to differences in viscosity at a *fixed temperature* due to architecture. Indeed it is found that for low density (branched) polyethylene of comparable molecular weight and distribution as linear polyethylene, the zero shear (Newtonian) viscosity will be lower for the branched system. This is caused by the lower degree of molecular overlap by the branched species with neighboring molecules. In a more fundamental light this can be viewed in terms of *hydrodynamic volume* or *radius of gyration* both parameters of which are lower for a branched molecule than for its linear counterpart of the *same* molecular weight (see Figure 24). Some additional information of this general discussion above is provided by specifically controlling architecture and determining the resulting viscosity. Figure 25 shows two sets of actual data obtained on linear, trichain, and tetrachain block copolymers of equal molecular weight. As expected, the linear system (which would entangle most easily with its neighbors) displays the largest viscosity if all other factors are equal.

Molecular Shape

It might simply be stated that shape will clearly influence the fundamental parameter of radius of gyration which in turn will change the hydrodynamic volume and hence viscosity. However, to reinforce the importance of shape or conformation we can even see the effect of this variable in infinitely dilute systems where no entanglements are observed, i.e., we can demonstrate the slope dependence by just considering macromolecules isolated from one another but dispersed in a suitable solvent. Specifically, the technique of intrinsic viscosity is applicable here.⁸ It is known that the intrinsic viscosity (14) is given by

$$[\eta] = kM^a \quad (13)$$

where k and a are constant for a given polymer in a given solvent at a fixed temperature. The parameter M represents molecular weight (monodispersity assumed). The exponent " a " is particularly shape dependent and takes on values from 0.5 in a theta solvent to typical values of 0.7–0.9 for a random wormlike coil to that of 1.0 or greater for rodlike conformations. Indeed the biochemist often uses the intrinsic viscosity method to follow the helix coil conformational transition common to many biopolymers (see Figure 26). Specifically then, rodlike conformations raise the resistance to flow in contrast to that of a coiled molecule of the same molecular weight. This again is due to the large hydrodynamic volume or radius of gyration of the more extended conformations.

Before leaving conformational aspects, a special and interesting area of polymer rheology that is becoming more important is that regarding the flow of polymer liquid crystalline systems. While this area is one of considerable activity today and requires much further study, enough information often exists to demonstrate rather unique flow phenomenon. In brief, liquid crystalline systems tend to arise from rigid or stiff rodlike molecules although platelike systems may also form liquid crystalline textures. Basically, just as stacking plates in a cupboard, jiggling toothpicks in a flat dish or

⁸ It is assumed in the text that the basics of the intrinsic viscosity method are understood to the reader. Should this not be the case consult references (10, 14).

floating logs down a river, preferential alignment or packing takes place thereby leading to an *ordered system*. When this occurs for molecular systems that are still fluid, one obtains what is commonly called either liquid crystalline or mesophase systems. Such systems were first observed in low molecular weight systems in 1888 but have more recently been induced in certain rodlike polymeric systems (15). The result of this ordering can lead to a variety of ordered fluid states as sketched in Figure 27. For the polymers of interest to our discussion here, it is the nematic texture that typically results either by using an appropriate concentration in solution (lyotropic liquid crystal) or appropriate temperature of the bulk (thermotropic liquid crystal). Shear or external flows can also induce the liquid crystalline textures. The result is that when this texture is induced, the local ordering leads to an easy means of flow due to little or no entanglement. Thus, as expected, the viscosity will depend on the fluid structure. Indeed upon shearing these systems, the viscosity may appear to display analogous effects. For example, one general sketch is shown in Figure 28 which displays an interesting viscosity relationship that may arise in this system. Note that the caption helps provide part of the explanation of the sketch. In short, these unique ordered fluids only serve as a prime example of the relationship that a fluid's flow behavior has to its molecular structure. For additional details on this subject consult reference (15).

Elastic Effects in Polymer Melts

Suppose you were new to the polymer field and were asked to extrude a polymer melt in the shape of a rectangle (ribbonlike)—how would you construct the die orifice through which the polymer would be extruded? Indeed if you were unaware of the flow properties of polymer melts you might well construct a die orifice of the exact dimensions you hoped to achieve as shown in Figure 29. However, upon extruding a melt through this die you would likely find what is outlined by the two profiles in this same figure where the two profiles represent different extrusion rates (i.e. different $\dot{\gamma}$). It is noted that the higher extrusion rate gives a higher deviation from the desired profile. Why does this happen? The phenomenon is known as die swell or melt elasticity and its origin is again

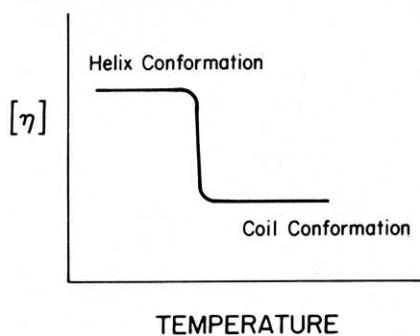


Figure 26. General behavior of the intrinsic viscosity $[\eta]$, versus temperature resulting in a helix-coil conformational transition.

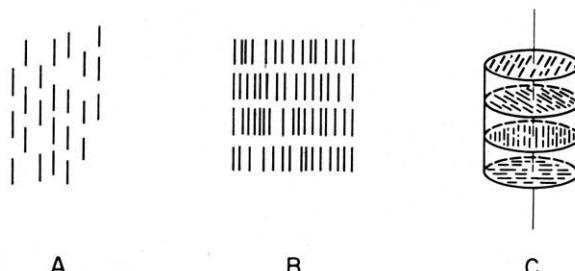


Figure 27. Three general types of liquid crystal fluid structures that may arise A, Nematic; B, Smectic; C, Chlorosteric.

directly coupled to the structure of the melt and such external variables as time, temperature, and pressure. Before commenting on the molecular nature of die swell, it should be stated that this behavior is common to polymer melts and even to solutions that have just been deformed. Some examples are processes such as spinning, film extrusion, pipe extrusion, and bottle blowing. Hence, die designers must recognize this behavior and consider it a part of the design criteria.

Just what causes the die swell behavior? It is coupled with the elastic nature of polymer melts and concentrated solutions. Viewing Figure 30 will help provide some molecular insight. Here we see coil-like molecules in a reservoir that are being extruded by passage through an orifice. While entanglements are not shown in the figure for simplicity, the reader can feel sure that they exist particularly if we are considering flexible chain polymers of sufficient M_w . One sees that each "rubber band" or "stretchable" molecule gets partially drawn out somewhat as it passes through the orifice, after which the retraction force strives to *reform the coil shape* again thereby promoting a lateral expansion to occur (swelling of the melt). For simplicity, it is a bit like stretching out a rubber band and upon removal of the load, it retracts and takes on its original dimensions. Figure 31 by Nielson (12), does indeed view the overall phenomenon as one of *memory* within the fluid as denoted by the recovery of the shape of the extruded element shown in black. A common but rather striking way to demonstrate this *elastic* effect of polymer fluids is to try the following. Place a high polymer solution in one beaker and water in another beaker of comparable size. Now stir both at same reasonable frequency ($\dot{\gamma}$). It is noted quickly that the meniscus of the water will appear as shown in Figure 32B while that of the polymer will be as shown in Figure 32A. Again the cause is that of chain elasticity and the rod climbing behavior is accounted for as follows. Picture Figure 33 depicts a top view of the experiment for the polymer solution. One sees the

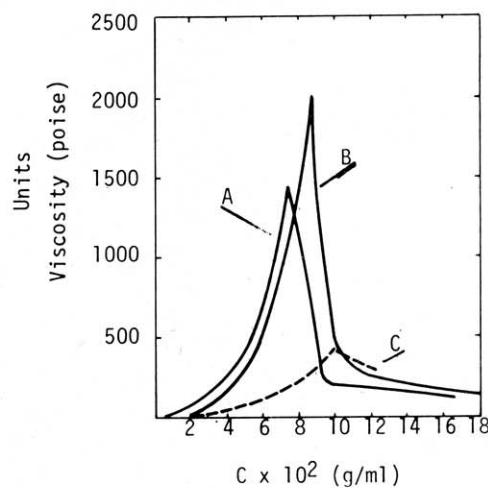


Figure 28. Viscosity at low shear stress ($\tau < 100$ dyne/cm 2) versus concentration for fractions of PBLG in *m*-cresol with molecular weights of A, 342,000 B, 270,000; C, and 220,000. Note that solution viscosity goes through a maximum with polymer concentration and that the maximum is also dependent upon molecular weight. (From (16)).

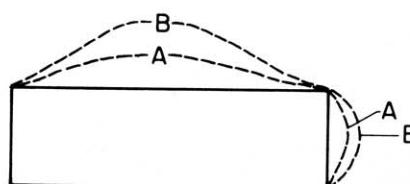


Figure 29. Schematic of the extrudate profiles (dotted lines) that might be obtained from extruding a polymer melt through a rectangular orifice (solid line). Line A represents a lower extrusion rate than for line B. Note—The profile lines are only shown for two sides of the orifice.

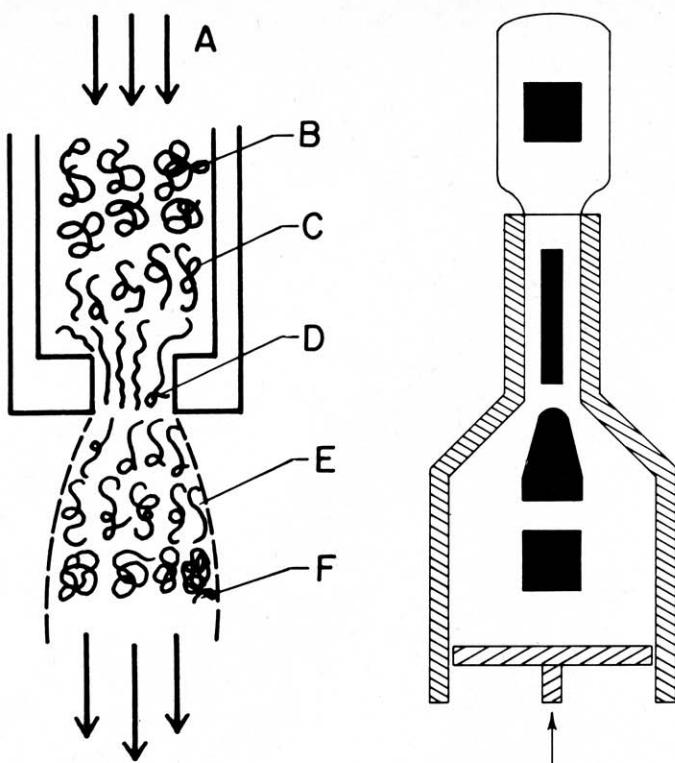


Figure 30. (left) Sketch depicting die swell behavior.

A The applied pressure to the reservoir of polymer melt.

B The unoriented polymer molecules.

C Polymer molecules begin to become somewhat oriented as they approach the die opening.

D Oriented polymer molecules passing through the die orifice.

E Entropic contracting elastic force causes the melt to result in a lateral swelling.

F Molecular orientation is nearly lost due to molecular relaxation. (Note that chain entanglements are not shown in this figure.)

Figure 31. (right) Schematic diagram of how the tensile (elongational) forces act on an element of polymer in the entrance region to a capillary and how the elasticity of the melt causes die swell when the forces are removed at the end of the capillary. (After Nielsen (7)).

streamlines of flow to be arcs which leads to a "pulling out" or partially stretching of polymer chain. This chain wishes to coil back up due to entropic driving forces and displays a retractive force with a component of that force given by the arrow in Figure 33. The result is a squeezing on the inner fluid of the vessel thereby promoting the inner fluid to "climb" the stirring rod. The reader may convince himself of this force component by wrapping a *stretched* rubber band around his finger. While watching his finger turn purple, as well as feeling the associated pain, the realization of the squeezing force will be readily recognized!

The above squeezing elastic force principle has been utilized in designing an elastic fluid pump by taking advantage of the elastic nature of the deformed melt (or solution). Figure 34 illustrates this principle. As the polymer is fed to the edge of this "pump," the trajectory of the polymer causes squeezing elastic forces which pump out the inner polymer melt from the hole in the center of the rotating disc. Such a pump would be useless for nonelastic fluids.

As might be expected, the magnitude of the elastic effects are coupled to both external variables (e.g., temperature and pressure) as well as to internal variables like molecular weight, chain flexibility, and molecular architecture. Based on your present molecular intuition developed to this point, it is not

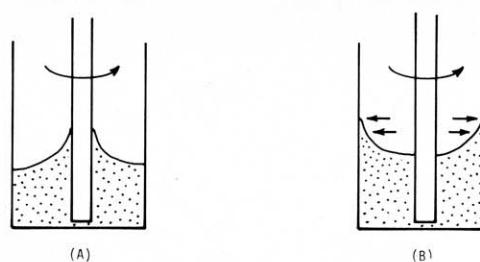


Figure 32. A, Sketch indicating the Weissenburg or rod climbing effect of a viscoelastic fluid caused by rotation of the rod in the fluid. B, Sketch showing how a Newtonian fluid "climbs" the outside of the stirring vessel due to centrifugal force.

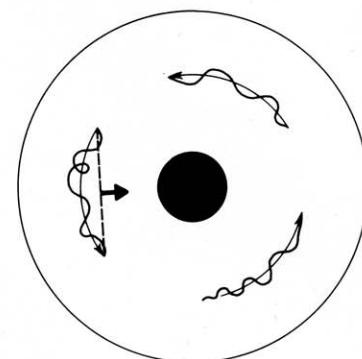


Figure 33. Schematic of the top view of the rod climbing experiment. The black dot is the stirring rod; the dotted line represents a force component resulting from the retraction forces of the chain (coiled lines).

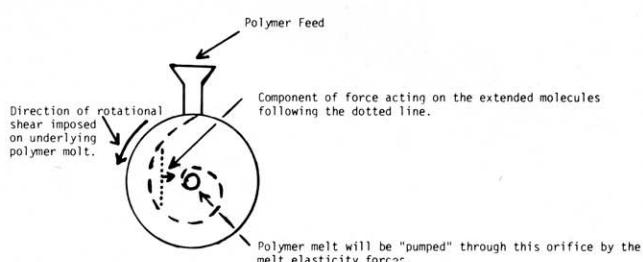


Figure 34. End view of viscoelastic or melt elastic pump (centripetal pump). The polymer is sheared by a rotating member as shown and the elastic forces cause the melt to be pumped through the center orifice.

surprising to find what is shown in Figure 35 where die swell (elastic recovery) is plotted along with viscosity against the variable of shear rate. Indeed, as the system becomes non-Newtonian, the die swell begins to increase since the system is now attempting to recover its structure that was disturbed by the higher values of $\dot{\gamma}$.

Final Remarks

In summary, then, we realize that polymer melts have both viscous (dissipative) and elastic (storage) characters. Both are dependent upon the system variables *as well as upon* external variables. Recognition of this viscoelastic nature of polymer systems must occur if proper utilization of these materials is to result. The author has attempted to put some molecular understanding to many of the characteristics observed for polymer melts and solutions. Much of this understanding is based on the simple earthworm like picture which is very often a useful and practical concept to apply. While not exhaustive by any means, this overview lecture will hopefully generate some appreciation of the complex flow behavior of viscous polymer fluids.

The interested reader wishing to pursue more detail re-

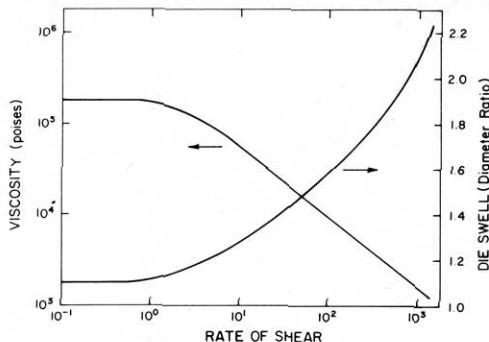


Figure 35. General behavior of die swell and viscosity as a function of the rate of shear in a capillary or similar duct. (From Nielsen (7)).

garding the subject of polymer rheology should consult the following references [1, 2, 7, 17-19] with particular emphasis on [1, 7, 17].

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