# The Viscosity Loss Trapezoid - Part 2: Determining General Features of VI Improver Molecular Weight Distribution Using Parameters of the VLT

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## ABSTRACT

Building on a previously presented concept of the Viscosity Loss Trapezoid (VLT), in this paper the author shows how the information contained in the VLT can produce a 'viscous' insight into the molecular weight distribution of an oil-soluble polymer such as a Viscosity Index Improver in formulated lubricants.

## BACKGROUND

In a much earlier paper published in 1964 (1), the author referred to experimental information generated by Mostafa (2) to explain differences in degradation response of two nearly identical average molecular weight ($MW_{avg}$) polyisobutylene (PIB) polymers in oil solution. Mostafa's work had shown that a critical $MW_{avg}$ existed above which his sonic device was much more efficient in degrading the polymer. In his paper (1), the author showed evidence that this effect would also apply to differences in molecular weight distribution depending on which side of the MW degradation threshold the bulk of the polymer existed. **Figure 1,** taken from that paper, was an idealized sketch indicating that

narrower molecular weight distributions would be more susceptible to degradation when above the degradation threshold of a given degradation-producing device and less susceptible when below the threshold than a broad molecular weight distribution of the same $MW_{avg}$. With the advent of very high shear rate viscometry over the last decade which permitted straightforward measurement of temporary viscosity loss (TVL), the opportunity came to extend the previous work.

Permanent and temporary viscosity loss levels of polymer-containing lubricants were one of the important concerns over 40+ years of their use in many applications -- engines, automatic transmissions, gear oils, power steering units, etc. (3). VI Improvers of different chemistries were known to have different flow properties. Different molecular weights of a given chemistry were known to give different levels of response to conditions producing permanent and temporary viscosity loss. One of the frequently stated needs was a means to characterize the rheological behavior, chemistry and molecular weight and distribution of a the VI Improvers in finished lubricants using simple laboratory techniques and equipment.

### Viscosity Loss Trapezoid

In the past few years, recognizing that new tools were available to complete older initiatives, the author has attempted to find a means of meeting the above needs. The effort has resulted in a concept called the Viscosity Loss Trapezoid (VLT) (4).



Figure 1 - Sketch of effect of difference in MW distribution for the same $MW_{avg}$ on shear stability. (Taken from (1).)
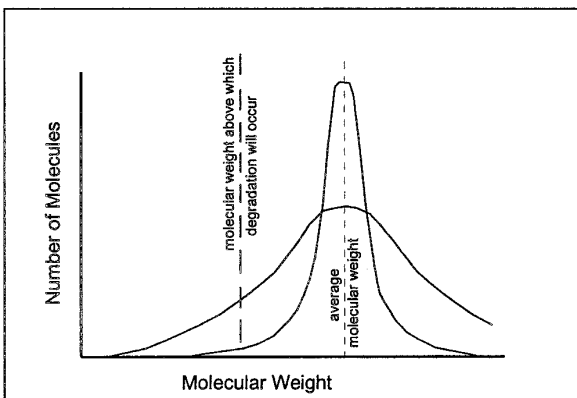
Applying this concept, four measures of the viscous characteristics of a lubricant are plotted as in **Figure 2** to define a geometrical figure -- a trapezoid. It is evident that this trapezoid reflects the viscous contribution and response of the given VI Improver in the blend being examined, from four viscous 'viewpoints'. Each of these 'viewpoints' reflect a different aspect of both the influence and the response of the polymer's molecular weight and molecular weight distribution to the four different conditions. It is apparent that, to the degree that these four viscous measures of the VI Improver's contributions are collectively unique, the trapezoid should be similarly unique. It is also evident that VI Improvers of the same chemical 'family' should show a 'family' resemblance in the shape of the resulting trapezoid.

The four viscous measures of the oil's response to stress used were:

   **State 1:** The viscosity of the fresh oil blend taken at an arbitrarily chosen moderately low shear rate (in this work, ~200 s$^{-1}$),

   **State 2:** The viscosity of the fresh oil taken at an arbitrarily chosen very high shear rate (in this work, ~$10^6$ s$^{-1}$)

   **State 3:** The low shear viscosity after the oil has gone through some repeatable, highly energetic form of mechanical polymer degradation (in this work the FISST, ASTM D 3945B), and

   **State 4:** The very high shear rate viscosity of the degraded oil.

These measures of viscosity also corresponded to both familiar and unfamiliar measures of viscosity loss. For example, the familiar 'temporary viscosity loss' (TVL) is given by the difference in viscosity between State 1 and State 2 while the familiar 'permanent viscosity loss' (PVL) caused by VI Improver degradation under extraordinary shearing forces, is given by the difference in viscosity between State 1 and State 3.

In the previous presentations and publications, the author also introduced three relatively unfamiliar measures of viscosity loss. One of these was termed 'high shear permanent viscosity loss' (HSPVL) and is given by the viscosity difference between State 2 and State 4. Another was termed 'degraded temporary viscosity loss' (DTVL) and is given by the viscosity difference between State 3 and State 4. Lastly, as a measure of the combination of PVL and TVL the author defined the 'overall
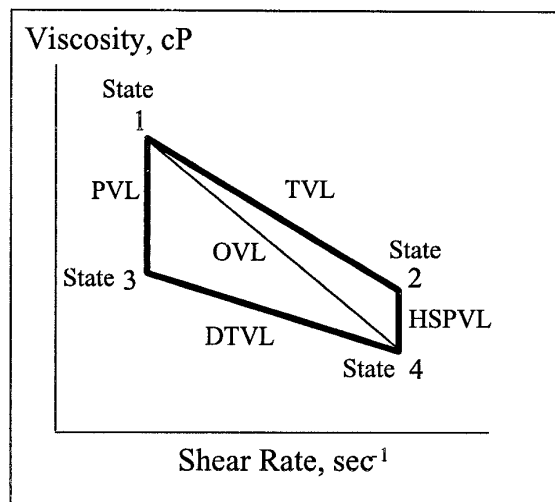


Figure 2 - Sample Viscosity Loss Trapezoid showing four viscosity values and five viscosity loss functions.

viscosity loss' (OVL) as the difference in viscosity between State 1 and State 4.

At first the Viscosity Loss Trapezoid approach was considered to be a simple tool by which to appraise the VI Improver type. However, as experience with the various trapezoidal forms was generated, the data suggested that the VLT might be extensible to gaining general information about the molecular weight and molecular weight distribution of the VI Improvers used in these lubricants.

This paper is a presentation of that concept as well as its underlying rationale and use of the VLT in obtaining insights into the molecular weight distributions of several VI Improvers in a common base oil.

## RATIONALE
### General

'VI Improver' is a term long used in lubricant circles to describe a polymeric material, soluble in, and often solvated by, an oil. It is added to a lubricant to improve its Viscosity Index (an empirical technique from the 1930's to compare the viscosity-temperature characteristics of lubricants).

Over the last 70+ years much information has been presented by many authors concerning both the theory and experimental results of polymer dynamics in solution (among others: **5-31**).

Polymer-in-oil solutions are a particularly interesting subset of the more general area of polymer solutions because

   1) such systems are widely encountered in lubrication

2) oil viscosity is high enough to have a considerably stronger influence on polymer solution flow dynamics than most simple, low molecular weight solvents.

## Shear Stress Effects on VI Improver Contribution to Viscosity

The strength of the VLT technique comes from the use of the viscometric measurements made of an oil when in each of the four previously mentioned 'States' or conditions. Three levels of shear stress produce these four conditions:

    a. relatively low,

    b. moderate to high, and

    c. extraordinarily high.

Used deductively, four aspects of one polymer-in-oil system or blend should be capable of giving insight into the important characteristics of the VI Improver producing such rheology including an interesting, if somewhat generalized, overview of its molecular weight distribution. This overview can be further amplified by obtaining the viscometric information at considerably different temperatures -- particularly when the VI Improver's solubility characteristics change with temperature.

## Relationship between Orientation and Degradation Phenomena

An important consideration in this rationale for application of the VLT to the estimation of initial and degraded MW distribution is the fact that the forces leading to orientation phenomena (the distortion of a VI Improver's polymer molecules in laminar flow producing States 2 and 4) must be less than the forces producing permanent degradation of the molecules (which results in the degraded viscosity values evident in States 3 and 4). In other words, it is a reasonable presumption supported by several investigations ((3), a published symposium

on the subject) that the forces required to orient a polymer molecule without degrading it are less than those forces degrading the polymer molecule. A corollary to this severity ranking of shearing effects is that there will be molecular weights within the molecular weight distribution of the VI Improver which are susceptible to orientation but not to degradation -- at least within the range of degradation energies familiar to automotive mechanisms such as the engine, automatic transmission, power-steering pump, and differential.

Orientation/degradation relationships may be made easier to understand by a visual construct of a 'viscous grip' possessed by the oil molecules surrounding and solvating the VI Improver macromolecules during flow (32,33)[1]. As the shear stress increases, the 'viscous grip' of the oil layers flowing at dissimilar velocities distend and stretch out the domain of the macromolecules -- first by orienting the macromolecule in the direction of flow[2] and then, at extraordinarily high shear stresses[3], snapping the polymer backbone (thus, degrading the polymer's viscous contribution) whenever the level of shear stress and the related 'viscous grip' can be raised sufficiently high. For linear polymers, of the VI Improver type, the backbone is considered the normal focus of bond breakage (3) whatever the source of mechanical energy.

It is common experience for those involved in the development and application of VI Improvers that different mechanical devices differ considerably in their VI Improver degradation effect (3). For this reason, different MW VI Improvers are made for different mechanisms. For example, polymer degradation in automotive engines is considerably less than that in hypoid gears. Similarly, differences in orientation and degradation susceptibility would be expected for different polymer chemistries, molecular weights, MW distributions, spatial configurations, concentrations, and solubilities in the oil (3, and in particular, 38).

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[1] It should be considered by those more technically proficient in flow dynamics involving polymer solutions that this conceptualization of a 'viscous grip' is more than simple momentum transfer between contiguous molecules of oil and polymer links since the motion of the polymer chain in flow is necessarily also influenced transversely across the flow lamilae occupied by the polymer coil by more distant inter- and intraactive polymer-oil /$polymer_1$-$polymer_{1,2,..x}$ effects. To the author's knowledge, this relationship has not been directly addressed in the literature to date.

[2] Actually believed (34,35) to be "ellipsoids ... rotated under high shear with a variable angular velocity which is related to the relative position of the ellipsoid's major axis in the flowing solvent. The degree of orientation at a given shear is also dependent on the polymer's molecular weight and configuration (in the solvated state). "(36).

[3] These levels of shear stresses would require shear rates most probably beyond the Reynold's number for laminar flow even for polymer-modified flow (37).

Another reasonable assumption -- and one helpful for the sake of simplifying subsequent interpretations -- is that orientation and shear degradation responses of each VI Improver be considered to have a certain threshold MW weight above which they become evident **(1,2,39,40)**. Both responses are dependent on four factors:

1. molecular weight,
2. molecular weight distribution,
3. molecular configuration, and
4. the proportion of molecules in the oil susceptible to either or both orientation and degradation.

**Figure 3** shows three conceptualizations of different molecular weight distributions for three soluble polymers in a base oil whose MW distribution is also shown. On the basis of the foregoing
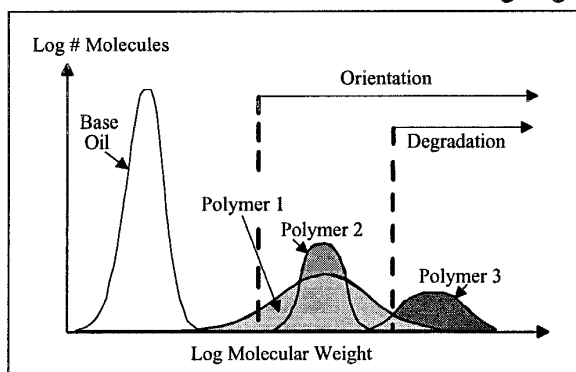


Figure 3 - Sketch of MW distributions of three illustrative forms of polymers in a base oil

assumption regarding the corresponding effects of orientation and degradation and their respective thresholds, it would be expected that these three polymer systems would show the following responses:

Polymer 1: The oil solution of this polymer would show considerable TVL and *some* PVL.

Polymer 2: The oil solution of this polymer would show considerable TVL but *no* PVL.

Polymer 3: The oil solution of this polymer would show considerable TVL *and* PVL.

The critical point is: since this appraisal of shear susceptibility can be made on the basis of the MW distributions shown, then it might also be expected that the converse information would be applicable -- *that sufficient information on the shear susceptibility of a VI Improver would give a reasonable, although somewhat relative and limited, interpretation of the MW distribution responsible for such response to the dual shearing forces.*

## Effect of Degradation on the Molecular Weight of Linear Polymers

A further aspect of shear degradation influencing the interpretation of the Viscosity Loss Trapezoid data is the manner in which a linear polymer molecule is torn apart by extreme shearing forces. It is reasonable that the probability of the location of breakage of the polymer 'backbone' is at the center of the coil where tension caused by oppositively moving sections of the polymer coil reaches a maximum. Thus, any linear polymer coil degraded by shearing forces is more likely to be broken into relatively equal segments of about half the molecular weight of the initial polymer molecule. Another important but easily overlooked relationship: all studies of polymer-in-oil degradation known to the author have shown that the degradation of a polymer always produces remnants having less viscous influence than the original polymer. That is, degradation always produces a loss in viscosity.

Applying this information, the MW distributions shown in **Figure 3** would be expected to become like those in **Figure 4** after shear degradation. Polymer 1 shows some loss of its highest
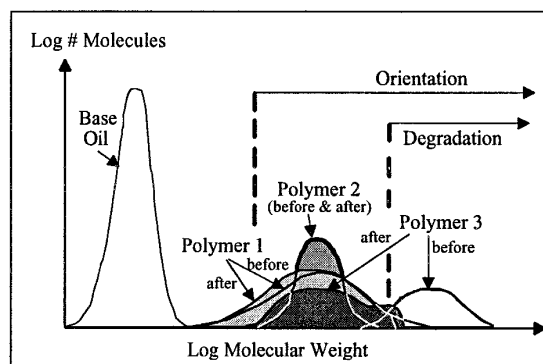


Figure 4 - Sketch of degradation effects on MW distributions of the three polymers shown in **Figure 3**.

molecular weight components and a related increase in lower molecular weight components. In contrast Polymer 2 does not change since none of its distribution is over the threshold of those molecular weights above which degradation occurs. Finally, Polymer 3 undergoes a massive change in molecular weight distribution as a consequence of most of its initial distribution being above the degradation threshold. The DTVL and HSPVL of the Viscosity Loss Trapezoid will reflect these changes and their relationship with the TVL and PVL. Such information is the basis of the concept of applying the VLT to gaining information about the MW distribution of VI Improvers.

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It should be understood that these three examples of both initial and final molecular weight distributions are only three of many possible forms of molecular weight distribution. Moreover, not all VI Improvers are linear polymers -- some are highly branched, some are considered 'fibril bundles' (miscellular-type associations of lower molecular weight polymers whose association is temperature dependent), still others are mixtures of two polymers with similar or dissimilar mixed MW distributions. Then, too, there are highly homogeneous synthetic base oils composed of much smaller but highly uniform size polymeric molecules from which modern lubricants are formulated in part or in whole.

## Orientation Tendency

From the point of view of the polymer molecule particularly but any molecule in general, orientation tendencies are determined by the aspect ratio of the molecule which, in turn, is affected by the molecule's degree of deformability in flow. Deformability, in turn, is affected by the stiffness of the polymer backbone relative to its length and the degree to which the polymer molecule may unfold into the oil matrix (i.e. the solubility of the polymer). In short, the degree of orientation is determined by the degree of departure from a spherical domain or aspect during exposure to the forces causing flow.

From the point of view of the oil matrix within which the polymer molecule finds itself embedded, the viscosity or 'viscous grip' of this matrix on the polymer molecule may be said to be the underlying cause of all polymer response since, as previously noted, it is through this matrix that both the proximate and somewhat more distant forces of shear are brought to bear upon the polymer molecule. Thus, higher viscosities will always be expected to bring about more distortion/orientation of the polymer molecule unless for any reason the polymer molecule contracts and, thus, limits its exposure to the oil matrix.

The degree to which such molecular orientation will reduce the viscosity at higher shear forces is dependent on 1) what viscous contribution the molecule has at lower shearing stresses, 2) how much of this individual contribution is subject to shearing forces, and 3) any effect of concentration on polymer-polymer interactive response to the shearing force. Thus, even smaller polymer molecules may collectively demonstrate meaningful orientation phenomena if their shape, stiffness, and number are appropriate. This latter relationship between numbers of molecules and their collective degree of susceptibility to orientation is important to the appraisal of orientation response in, for example, synthetic fluids.

## Axioms of the Viscosity Loss Trapezoid

Within the present range of knowledge of polymer-in-oil dynamics, there are many possible trapezoids that can be formed. There are also a number that are not rational and these can be defined by considering that there are certain 'axioms of the VLT'. From **Figure 2**, the most evident constraints to possible forms of the Viscosity Loss Trapezoid are:

1. The viscosity value of State 2 must be equal to or less than State 1.
2. The viscosity value of State 4 must be equal to or less than either States 1, 2, or 3.
3. The value of HSPVL must be equal to or less than PVL.
4. The value of DTVL must be equal to or less than TVL.

All of these relationships are, of course, limited by the precision and geometry of the viscometers used.

## EXPERIMENTAL INFORMATION
### Base Oil and Blends

Several commercial VI Improvers of different chemistries were obtained and blended into a common 150 Neutral base oil at a level sufficient to obtain a kinematic viscosity of approximately 16 cSt at 100°C -- a value reflecting the high SAE 40 classification range for engine oils. Blend information is given in **Table 1.** No dispersant-inhibitor packages were used in order to simplify the comparisons.

### Viscometric Equipment Used

**Low shear rate** data was obtained using a rotational viscometer especially developed (41) for good temperature control over a broad temperature range. This avoided the use of the usual large liquid bath with its considerable thermal inertia.. Using this instrument, temperature changes of 50°C could be effected in ten minutes or less. Equally important, the calibration values determined at anyone

| TABLE 1 - Component and Blend Information | | | |
|---|---|---|---|
| Base Oil and VI Improvers | Characteristics | Percent Added to Base Oil | Kin.Vis. 100°C, cSt |
| Base oil | 150 N | neat | 5.16 |
| Polymer O | Olefin Co-polymer | 1.85* | 16.29 |
| Polymer A1 | Polymethacrylate ($MW_{'high'}$) | 10.7 | 16.28 |
| Polymer A2 | Polymethacrylate ($MW_{'mod'}$) | 11.5 | 16.04 |
| Polymer A3 | Polymethacrylate ($MW_{'low'}$) | 12.0 | 15.83 |
| Polymer S1 | Styrene-Isoprene (linear) | 14.5 | 16.01 |
| Polymer S2 | Styrene-Isoprene ('Star') | 12.9 | 15.82 |
| * Provided as a solid | | | |

temperature was valid for all temperatures. Rotational viscometry at low shear rates was chosen in preference to the more common and more precise kinematic (capillary) viscometry. There were two reasons for this choice:

1. Since kinematic viscosity is a function of both viscosity and density, it was preferable to avoid density effects among oils by measuring the viscosity value directly.
2. Rather than have the broad shear rate range across the capillary imposed by both low and high shear rate capillary viscometry, it was considered very important to VLT interpretation to work with only one shear rate across the shearing gap.

Of the various levels of lower shear rate available with the instrument, a shear rate of 200 $sec^{-1}$ was arbitrarily selected for all of the VLT work to date. Other choices of relatively low values of shear rate would be expected to be equally informative.

**Very high shear rate** data was obtained at $10^6 sec^{-1}$ using the rotational TBS Viscometer at both 150° and 100°C. While 150°C is a common temperature of operation for this instrument, operating at 100°C required a special high-torque synchronous motor because of viscosities greater than 12 cP. This higher torque motor available for the instrument increases the torque capacity by about an order of magnitude.

While calibration of the viscometer followed ASTM D 4683 procedures, a simpler technique was used at 100°C by applying the procedures already developed for this absolute instrument (42).

At high shear rates, particularly with oils having shear stress dependent orientation effects, being able to apply a known, constant, and singular shear rate across the gap is an important element of VLT analyses. This is even more the case when attempting to operate at different temperatures. The absolute nature of the TBS viscometer has been shown to permit establishing an accurate shear rate at any temperature while the instrument is operating (42).

**Shear degradation** of the polymer-containing oils was obtained using ASTM Method D 3945B-86 (43). Repeatability is shown in **Figure 5** from data gathered over several months of effort and is somewhat better than found in the method.
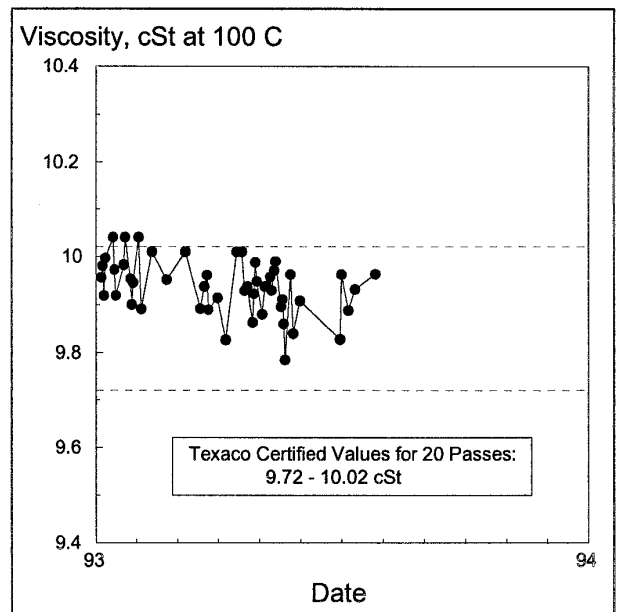


Figure 5 - Repeatability of FISST over several months

In the present work, as in the past studies by the author, 20 cycles through the FISST were applied to obtain the level of degraded oil for VLT analysis.

In generating degradation data for use in the VLT method, any source or device may be used as long as the data are reasonably consistent from test to test. Engine or automatic transmission tests are perhaps more acceptable than bench tests (if consistent) since the shear degradation occurring in such devices would give ultimate value in applying the VLT. However, as mentioned earlier in this paper, each mechanical device will give its own view of the VI Improver's influence and the final molecular weight distribution will be conditioned by the shear degradation level of the device.

## RESULTS OF VISCOMETRIC STUDIES

The base oil and each of the blends were analyzed viscometrically at both high and low shear rates. Results are shown in **Table 2**. From these data the various values of viscosity loss were determined and given in **Table 3** while their percent viscosity loss values are shown in **Table 4** for a more direct comparison.

**Table 4** clearly shows how much variation there is in the various viscosity loss parameters among the various VI Improvers studied. This table also shows clearly how these parameters varied from 100° to 150°C.

## VISCOSITY LOSS TRAPEZOIDS

From the data of **Table 2**, the associated Viscosity Loss Trapezoids can be formed. In the following portion of the paper, each of these VLTs is presented and then interpreted in another graphical construct as to the significance of the VLT data in suggesting the molecular weight distribution of the VI Improver being studied.

In the plots of the VLTs, the x-axis (abscissa) is logarithmic merely to convey the range of

**TABLE 2 - Viscometric Information at Low and High Shear Rates and 100° and 150°C**

| Blends | KV | Low Shear Rate, 200 sec$^{-1}$ | | | | Very High Shear Rate, 10$^6$sec$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 100°C | 100°C, cP | | 150°C, cP | | 100°C, cP | | 150°C, cP | |
| | cSt | fresh | FISST | fresh | FISST | fresh | FISST | fresh | FISST |
| 150 Neutral Base oil | 5.16 | 4.28 | 4.28 | 1.82 | 1.86 | 4.26 | 4.26 | 1.91 | 1.91 |
| Polymer O | 16.29 | 13.37 | 11.31 | 5.27 | 4.49 | 8.76 | 8.74 | 3.94 | 3.89 |
| Polymer A1 | 16.28 | 13.40 | 9.21 | 5.95 | 4.02 | 8.00 | 7.49 | 3.60 | 3.26 |
| Polymer A2 | 16.04 | 13.26 | 10.64 | 5.83 | 4.59 | 8.54 | 8.08 | 4.06 | 3.80 |
| Polymer A3 | 15.83 | 13.10 | 11.51 | 5.76 | 5.04 | 9.68 | 9.30 | 4.31 | 4.13 |
| Polymer S1 | 16.01 | 13.16 | 9.35 | 5.30 | 3.81 | 8.24 | 7.42 | 3.77 | 3.32 |
| Polymer S2 | 15.82 | 12.88 | 11.98 | 5.24 | 4.86 | 7.43 | 7.40 | 3.54 | 3.45 |

**TABLE 3 - Viscometric Information on the Various Loss Parameters at 100° and 150°C**

| Blends | 100°C, cP | | | | 150°C, cP | | | |
|---|---|---|---|---|---|---|---|---|
| | PVL | TVL | HSPVL | DTVL | PVL | TVL | HSPVL | DTVL |
| 150 Neutral Base Oil | 0.00 | 0.02 | 0.00 | 0.02 | -0.04 | -0.09 | 0.00 | -0.05 |
| Polymer O | 2.06 | 4.61 | 0.02 | 2.57 | 0.78 | 1.33 | 0.05 | 0.60 |
| Polymer A1 | 4.19 | 5.40 | 0.51 | 1.72 | 1.93 | 2.35 | 0.34 | 0.76 |
| Polymer A2 | 2.62 | 4.72 | 0.46 | 2.56 | 1.24 | 1.77 | 0.26 | 0.79 |
| Polymer A3 | 1.59 | 3.42 | 0.38 | 2.21 | 0.72 | 1.45 | 0.18 | 0.91 |
| Polymer S1 | 3.81 | 4.92 | 0.82 | 1.93 | 1.49 | 1.53 | 0.45 | 0.49 |
| Polymer S2 | 0.90 | 5.45 | 0.03 | 4.58 | 0.38 | 1.70 | 0.09 | 1.41 |

| TABLE 4 - Viscometric Information on the Various Loss Parameters at 100° and 150°C in Percent | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Blends | 100°C, cP | | | | 150°C, cP | | | |
| | %PVL | %TVL | %HSPVL | %DTVL | %PVL | %TVL | %HSPVL | %DTVL |
| Polymer O | 15.4 | 34.5 | 0.2 | 19.2 | 14.8 | 25.2 | 0.9 | 11.4 |
| Polymer A1 | 31.3 | 40.3 | 3.8 | 12.8 | 32.4 | 39.5 | 5.7 | 12.8 |
| Polymer A2 | 19.8 | 35.6 | 3.5 | 19.3 | 21.3 | 30.4 | 4.5 | 13.6 |
| Polymer A3 | 12.1 | 26.1 | 2.9 | 16.9 | 12.5 | 25.2 | 3.1 | 15.8 |
| Polymer S1 | 29.0 | 37.4 | 6.2 | 14.7 | 28.1 | 28.9 | 8.5 | 9.2 |
| Polymer S2 | 7.0 | 42.3 | 0.2 | 35.6 | 7.3 | 32.4 | 1.7 | 26.9 |

shear rate covered by the data even though only two very widely spaced shear rate values are used. The straight line connecting the viscosity values over this shear rate range is a construct to assist in appreciating the shear rate range between the two values plotted but is not meant to be an indication of the mid-range values of non-Newtonian viscosity over this entire range of shear rates which actually is an 'S' or ogee curve.

In the plots of suggested molecular weight distribution corresponding to the VLTs, both axes are shown as logarithmic in order to present reasonable comparison of the molecular weight range and the number of molecules of each component. These plots have no actual data presented but are wholly a construct suggested by the information provided by the VLTs.

**Base Oil VLT**

**VLT results on the 150 N base oil** is helpful in understanding the degree of precision of the technique when using modern rotational viscometry and also shows the basic behavior of a blend having no orientable or degradable components. **Figures 6a** and **6b** at 100° and 150°C, respectively, show essentially horizontal straight lines -- a collapsed trapezoid -- since there is, and should be, no component of the oil which can be oriented or degraded. Further, the data show that the base oil is Newtonian over this shear rate range and that the values at high and low shear rates agree within, at most, 0.1 cP from low shear rate to high shear rate. It is of interest to keep this simple behavior of the 150 N base oil in mind when studying the VLTs of the VI Improved blends.
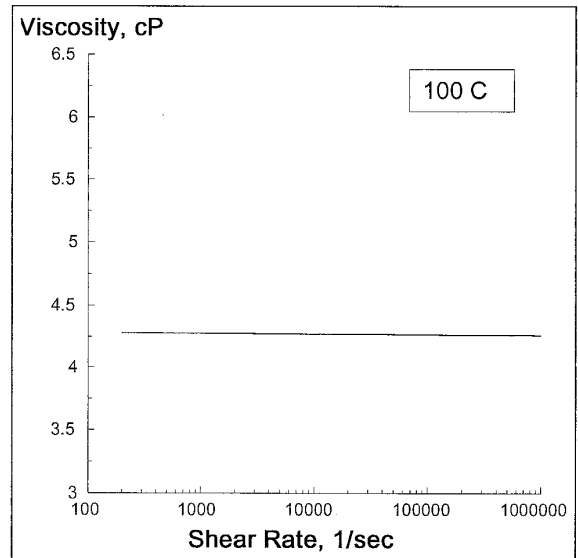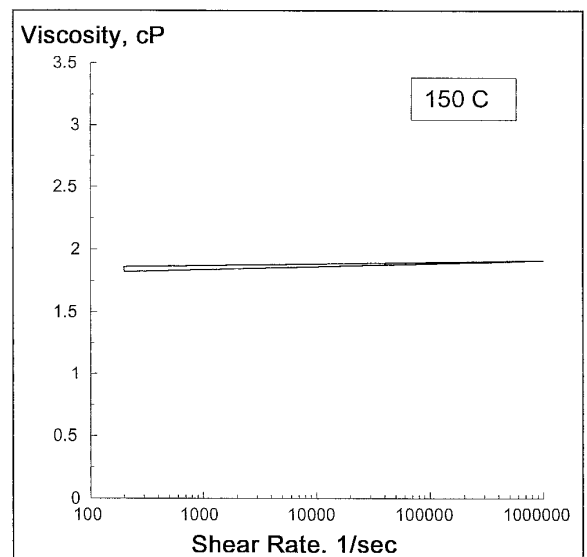


Figure 6a - VLT of base oil at 100°C



Figure 6b - VLT of base oil at 150°C

## Consideration of the VLT of the Base Oil

In **Figure 7** the interpretation of the two base stock VLTs of **Figures 6a** and **b** is given. It reflects the evidence that there is no orientable or degradable elements within this oil. Thus, the MW distribution shows only the low molecular weight distribution of the base oil.
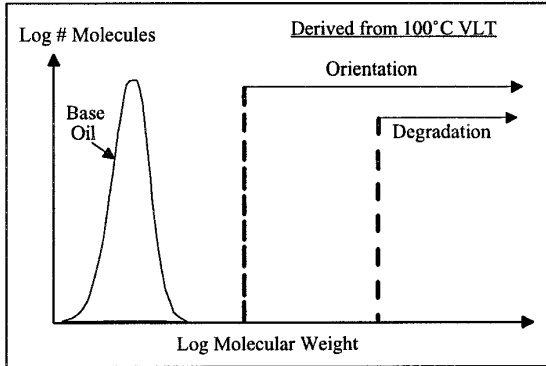


Figure 7 - Sketch of likely MW distribution of the base oil used in blending.

## Olefin Copolymer VLTs

**The olefin copolymer VLT** is shown in **Figure 8a** at 100°C and in **Figure 8b** at 150°C. It is evident from these figures that, while the blend shows considerable TVL and PVL at both temperatures, interestingly and significantly, the HSPVL is essentially nil at either. This is also shown in **Table 4**. Such behavior in HSPVL can be simply indicative that the orientation susceptibility is unaffected at high shear rates by any PVL. It would be
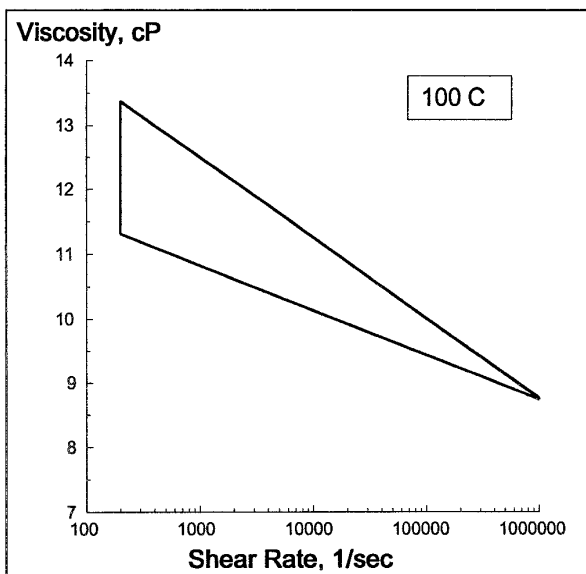


Figure 8a - VLT of olefin copolymer at 100°C
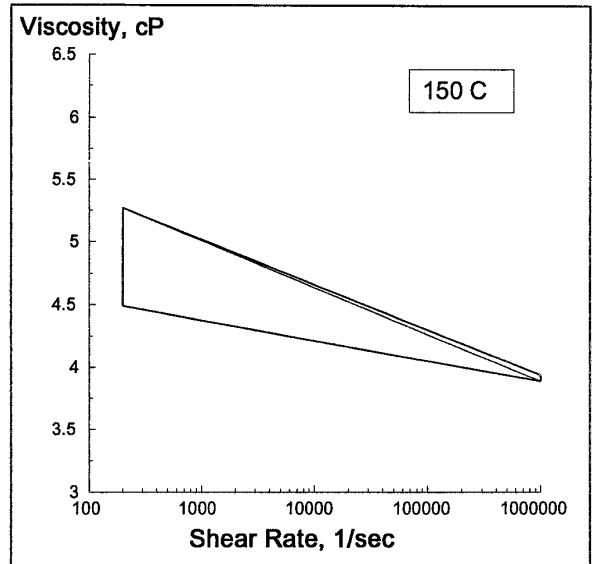


Figure 8b - VLT of olefin copolymer at 150°C

difficult to defend such a point of view since loss of the viscosity contribution of those orientable and degradable macromolecules would certainly affect the value of both parameters. Rather, further thought suggests that PVL with polymers of certain $MW_{avg}$ and MW distribution may generate half-MW shards which contribute more viscosity in the degraded state than in the oriented state -- although the overall viscosity contribution of the degraded polymer at high shear stress is never greater than the undegraded polymer. Such considerations will be given more attention in another paper on the relationship of the four parameters of the VLT.

**Figure 9** shows the corresponding molecular weight distribution reflecting the information in the VLTs at 100° and 150°C. Orientable/degradable and orientable/non-degradable macromolecules give
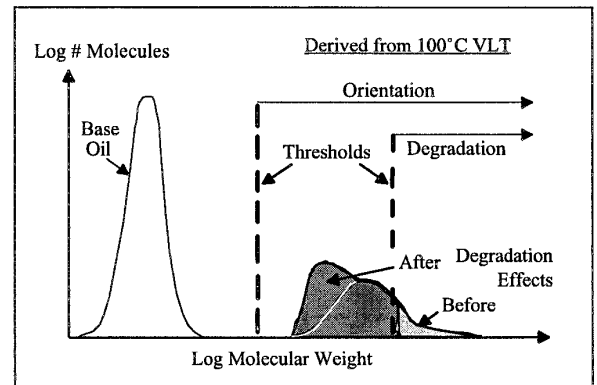


Figure 9 - Sketch of likely MW distribution of Polymer O in a base oil before and after degradation.

the TVLs shown in **Figures 8a** and **b**. When the orientable/degradable portion of the MW distribution suffer degradation, the higher MW forward edge of the original distribution curve is shown to move back near the degradation threshold as the degradation-prone molecules lose MW as shown by the PVL value in **Figures 8a** and **b** and in **Tables 3** and **4**. In the process they are viewed as being cleaved into MW fragments half the mass of the parent macromolecules. In this state, their MW is still in the orientation region where they add their lessened viscous influence to those macromolecules originally at this molecular weight. This process is shown in **Figure 9** by the darkened area representing the new MW distribution. This new distribution reflects the lessened orientation susceptibility and viscous contribution.

      **Orientation loss level** is an interesting view of the behavior of the VI Improver before and after degradation. **Tables 2,3** and **4** show that there has been a considerable change in the orientation loss of viscosity with degradation for the olefin copolymer. It is of interest and relevance to use the relationship

**% Orientation Loss = %(1-[TVL-DTVL]/TVL)**

to calculate such change in orientation effects. It is found that the process of degrading the VI Improver in the blend results in a DTVL having about 56% of the TVL at 100°C and 45% at 150°C (where the viscous grip is weaker in producing both TVL and DTVL). This can be viewed as a loss of 44% in orientation susceptibility at 100°C and 55% at 150°C by those larger macromolecules affected by degradation. The decrease in %TVL values in **Table 4** also show that the viscous grip of the oil weakens with increasing temperature.

### Polymethacrylate VLTs

      The next set of **Figures 10a** through **15** show the VLTs and associated MW distributions of a series of three members of a 'family' of polymethacrylate-based VI Improvers having relatively different molecular weights as previously noted in **Table 1**. Again, the VLTs were obtained at both 100° and 150°C to enhance the information generated by the VLT technique.

      **Plots of higher MW polymethacrylate VI Improver, Polymer A1**, are shown in **Figures 10a** and **10b** for the VLTs and in **Figure 11** for the conjectured molecular weight distribution.
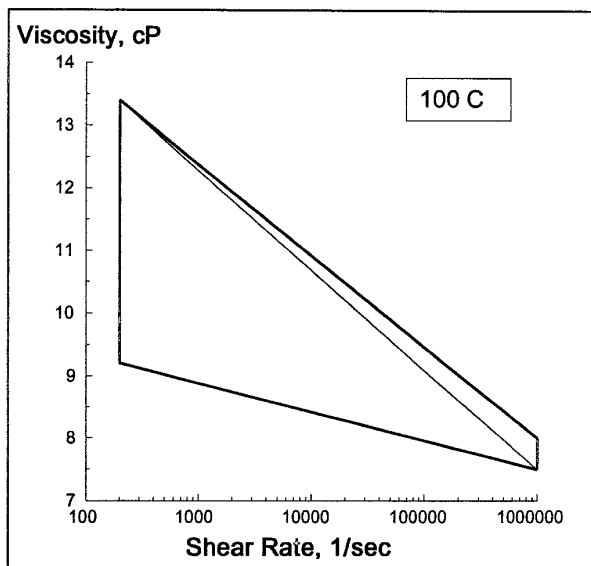


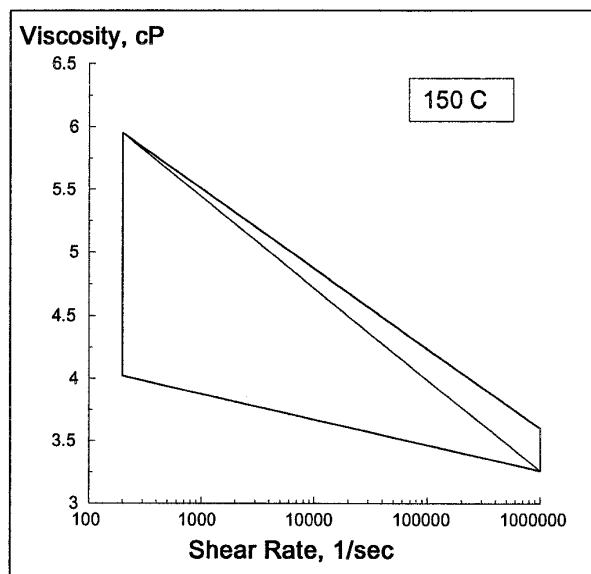Figure 10a - VLT of high MW polymethacrylate at 100°C.



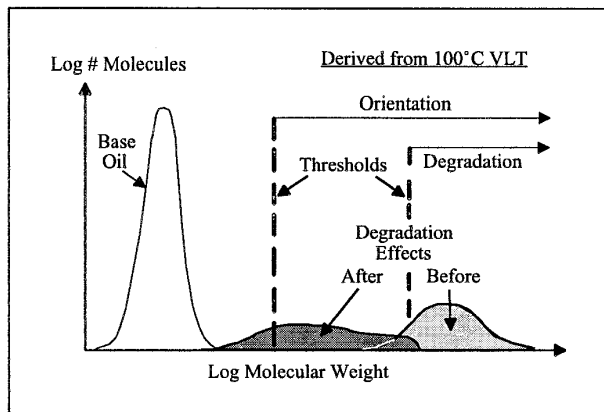Figure 10b - VLT of high MW polymethacrylate at 150°C



Figure 11 - Sketch of likely MW distribution of Polymer A1 in a base oil before and after degradation.

This VI Improver contributes considerable viscosity to the base oil at relatively low concentrations and seems to be fairly vulnerable to both forms of shearing forces -- orientation and degradation. Both the PVL and the TVL are markedly higher than the respective values for the other two polymethacrylate VI Improvers -- a consequence easily associated with the expected behavior of a higher MW polymer.

In contrast to Polymer O, it will be noted in **Table 4** that the %TVL (which is a measure of distention of the polymer coil) remains essentially constant -- 40.3% vs. 39.5% from 100° to 150°C. Polymethacrylates have long been known **(36)** to find mineral oils a fair, but not excellent, solvent at low temperatures. Since viscous grip is expected to diminish with the greater mobility and intermolecular distances of the oil molecules at higher temperatures, the fact that the %TVL of Polymer A1 remains nearly constant suggests that its polymethacrylate coils have retained this level of orientation by becoming more extended -- balancing the effects of the reduced viscous grip of the oil.

The values of TVL and DTVL in **Table 3** again can be used to show that Polymer A1 experienced a marked loss of 78% of its orientation susceptibility at 100°C and the same amount at 150°C.

The above information leads to the MW distribution plot shown in **Figure 11**. The initial MW distribution is shown as mostly in the orientation/degradation range with a fairly broad distribution which would be highly efficient in viscosity contribution. This corresponds to fair degree of TVL. After degradation, much of the TVL is lost as shown by the DTVL and the viscosity contribution shows marked PVL as well. The MW distribution curve is drawn somewhat flat to represent the probability that some of the highest MW macromolecules might produce half-MW shards that are still vulnerable to further degradation before the shards drop below the degradation threshold.

**Plots of the intermediate MW polymethacrylate VI Improver, Polymer A2**, are shown in **Figures 12a** and **12b** for the VLTs and in **Figure 13** for the MW distribution. In comparison to the size of the higher molecular weight polymethacrylate trapezoids shown in **Figures 10a** and **b**, the VLTs of the intermediate MW polymethacrylate polymer are smaller in area as would be expected with less TVL and PVL.
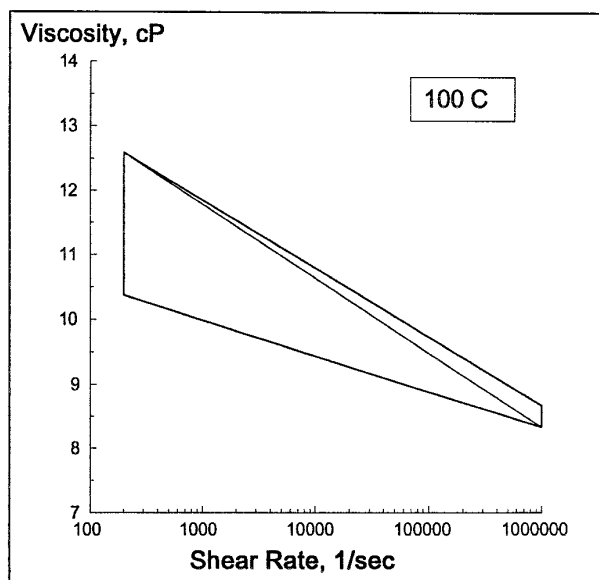


Figure 12a - VLT of moderate MW polymethacrylate at 100°C.
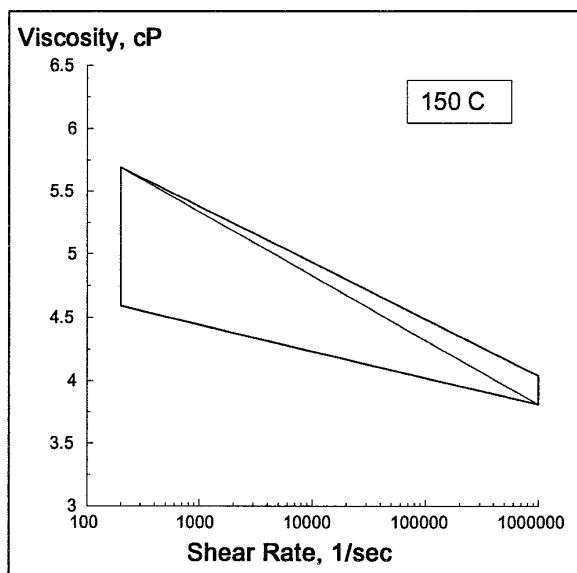


Figure 12b - VLT of moderate MW polymethacrylate at 150°C
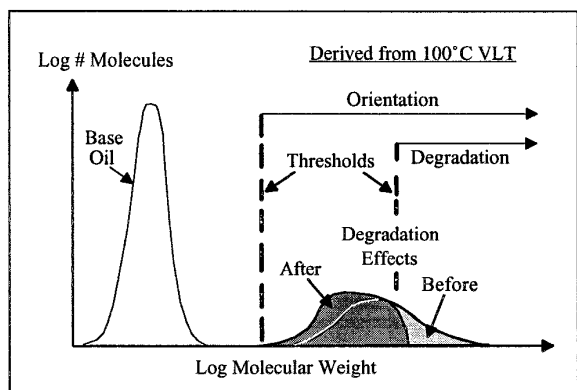


Figure 13- Sketch of likely MW distributions of Polymer A2 in a base oil before and after degradation.

In general, less trapezoid area is associated with greater resistance to PVL and a more horizontal configuration of the trapezoid is necessarily associated with fewer macromolecules subject to orientation whether this be by concentration or lower MW effects; the minimal trapezoid is, of course, the horizontal, straight line associated with simple oils as has been shown in **Figures 6a** and **6b**.

From **Table 4**, Polymer A2, in comparison to Polymer A1, shows both a reduction in the value of %TVL -- in agreement with its lower MW -- and a somewhat lower %TVL with increasing temperature -- 35.6% at 100°C and 30.4% at 150°C. It would appear that this member of the polymethacrylate VI Improver family is somewhat more soluble in mineral oil.

The values shown by the TVL and DTVL in **Table 3** indicate that with Polymer A2 the loss in orientation susceptibility is 48% at 100°C and 53% at 150°C -- suggesting a considerable reduction in the number of degradable macromolecules even though the total number of macromolecules present would be expected to increase because of the lower $MW_{avg}$ of this VI Improver and, thus, the need to add more macromolecules to the base oil in order to produce the same low shear rate blend viscosity.

Accordingly, the MW distribution shown in **Figure 13** is suggested by the VLT data. Less of the initial MW distribution is vulnerable to degradation since less of it extends over that threshold. However, sufficient amount of the highest MW components of Polymer A2 are sheared essentially in half and the viscosity contribution of the half-MW shards added to the original lower MW components of the VI Improver. It will be noted that the %DTVL in **Table 4** is actually greater than that of Polymer A1, showing that there are proportionately more of Polymer A2 initial macromolecules left in the orientation range after degradation than for Polymer A1. This suggests the tighter configuration of the MW distribution shown after degradation for Polymer A2.

**Plots of the lower MW polymethacrylate VI Improver, Polymer A3**, are shown in **Figures 14a** and **14b** for the VLTs and in **Figure 15** for the MW distribution. The reduction in degradation susceptibility is very evident.
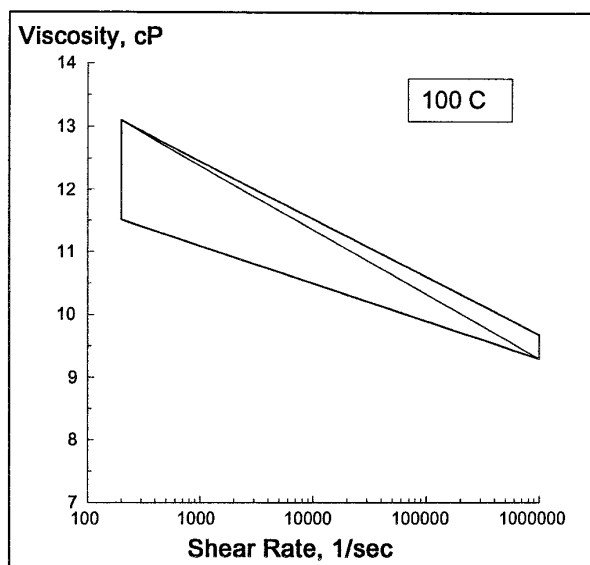


Figure 14a - VLT of low MW polymethacrylate at 100°C.
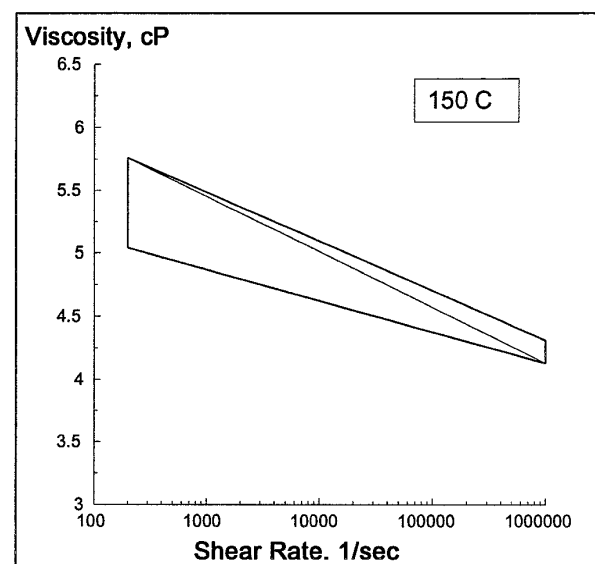


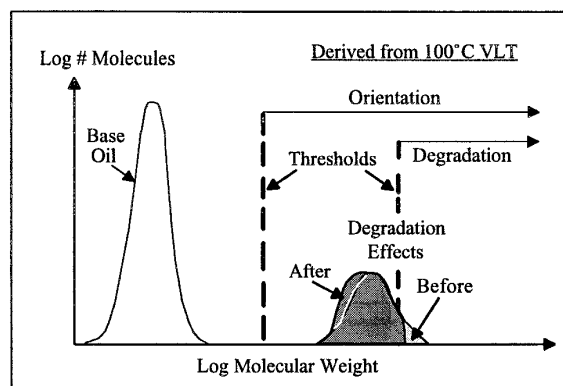Figure 14b - VLT of low MW polymethacrylate at 150°C



Figure 15 - Sketch of likely MW distributions of Polymer A3 in a base oil before and after degradation.

Similarly, it is evident that both the area and horizontal configuration of the VLTs for Polymer A3 are reduced in comparison to the VLTs of Polymers A1 and A2 shown in **Figures 10a** and **b** and **12a** and **b**.

Values of TVL and DTVL in **Table 3** show that 35% of the orientation susceptibility is lost at 100°C and 37% at 150°C, confirming the trend to lower loss of orientable polymer coils as the lower MW reduces the number of these coils in the degradation region. Again, the values of %TVL remain essentially constant with increasing temperature.

At this point in the development of the VLT-related MW distributions, it comes as no surprise to find Polymer A3 depicted as in **Figure 15**. A relatively small number of the macromolecules are shown extending into the degradation zone to reflect the relative minor PVL. Similarly, there is some but comparatively little loss of orientation response which leads to the depiction of an initial MW distribution mostly resident in the orientation zone which is buttressed after degradation at the lower MW edge by the relatively few half-MW shards.

**Styrene Isoprene VI Improvers**

The styrene isoprene VI Improvers in this study are said by the manufacturer to exist in two forms -- Polymer S1 is said to have a linear configuration while Polymer S2 is said to have a so-called 'star-shaped' configurations -- a central core with a number of long radial 'arms'.

<u>Plots of the Linear Styrene Isoprene, Polymer S1</u>, are given in **Figures 16a** and **16b** for the VLTs and **Figure 17** for the MW distribution. At 100°C the configuration appears somewhat similar to the higher MW polymethacrylate, Polymer A1.

Analyzing the %TVL values of **Table 4**, it is evident that these values fall off with increasing temperature -- from 37.4% to 28.9% with increase of temperature from 100° to 150°C. Apparently, this VI Improver finds the oil a good solvent at 100°C.

Determination of the orientation loss values for Polymer S1 from the TVL and DTVL data of **Table 3** shows a 61% orientation loss at 100°C and a 68% loss at 150°C -- less severe but in the same general range of severity as Polymer A1

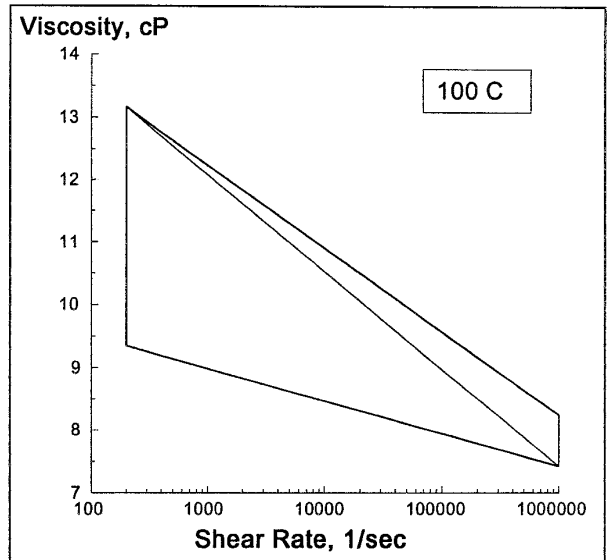Not surprisingly, the form of the MW distribution for Polymer S1 shown in **Figure 17** is



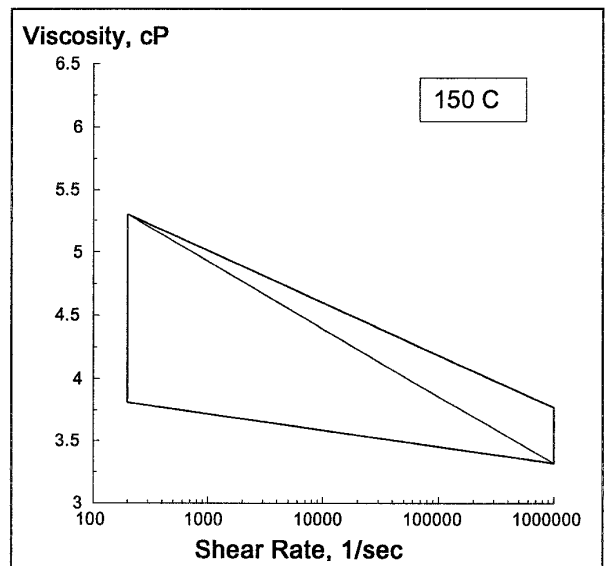Figure 16a - VLT of linear styrene-isoprene VI Improver



Figure 16b - VLT of linear styrene-isoprene VI Improver at 150°C
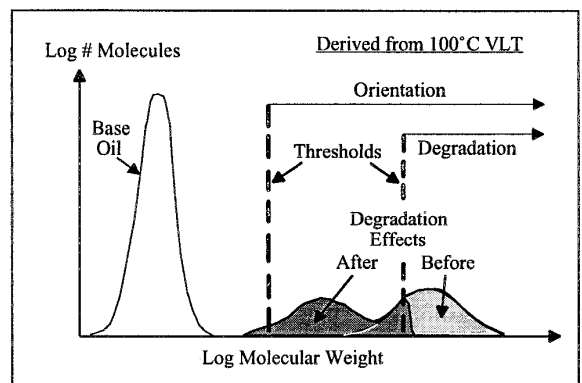


Figure 17 - Sketch of likely distributions of Polymer S1 in a base oil before and after degradation.

similar to that of Polymer A1 with the exception that there is more definition to the degraded MW distribution to reflect the higher level of orientation response at 100°C where the viscous grip for both polymers is presumed to operate more equivalently.

**Plots of the Styrene-isoprene 'star' VI Improver, Polymer S2**, are shown in **Figures 18a** and **18b** for the VLTs and in **Figure 19** for the MW distribution.

It would be expected that results from this different branched polymer configuration would be somewhat unusual compared with the linear polymers comprising the bulk of the study and, in fact, they are.

The VLTs differ significantly from the other VI Improvers studied as shown by the relatively highly sloped, narrow, configurations. While %PVL is very low at both temperatures, %TVL is essentially as high or higher than any of the other VI Improvers, depending on the temperature of study. From comments made earlier regarding the other VI Improvers, %TVL changes in a manner with increasing temperature indicating that Polymer S2 -- as Polymer S1 -- finds the oil a good solvent.

Orientation loss data obtained from the TVL and DTVL values of **Table 3** show that this polymer is considerably different with orientation losses of only 16% at 100°C and essentially the same amount, 17%, at 150°C. Further, while it is evident from the VLTs that PVL is much lower than the linear VI Improvers, conversely, TVL is the highest of the VI Improvers studied particularly after degradation. Evidently, degradation affects very few of the orientation-prone macromolecules comprising the 'star' VI Improver. Thus, it is evident that the 'star' configuration shows high susceptibility to orientation but low susceptibility to degradation.

From the foregoing information, the depiction of the suggested MW distribution before and after degradation seems straightforward. **Figure 19** indicates that almost all of Polymer S2 lies below the degradation threshold for this molecular configuration and that the MW distribution range is fairly narrow, at least in comparison to Polymer S1 which was quite degradation susceptible.
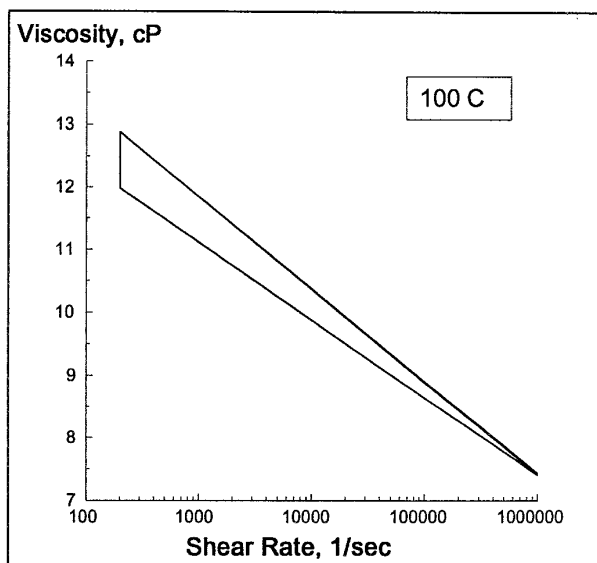


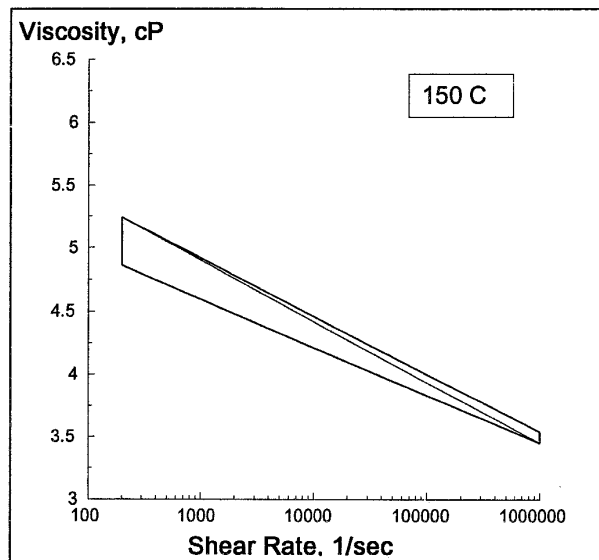**Figure 18a** - VLT of 'star' styrene-isoprene VI Improver at 100°C



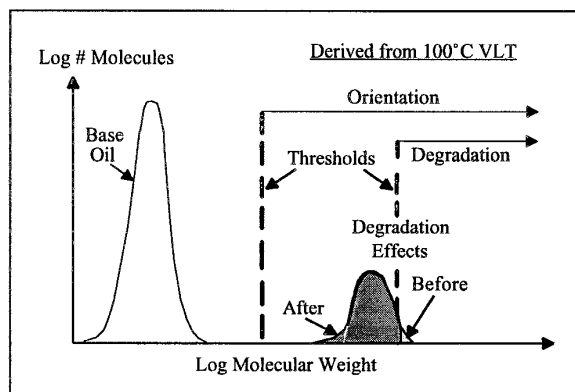**Figure 18b** - VLT of 'star' styrene-isoprene VI Improver at 150°C



**Figure 19** - Sketch of likely MW distributions of Polymer S2 in a base oil before and after degradation.

## DISCUSSION

As mentioned earlier in this paper, the four measures of the responses of the VI Improvers to low, very high, and extremely high shear stress can be used to identify the VI Improver. However, it was the primary purpose of this paper to show how such viscometric measures can be used to produce understanding of the polymer VI Improver components contributing to the blend viscosity.

Earlier in this paper (**Rationale** section), **Figures 2** and **3** were 'interpreted' as though they were actual MW distributions to predict what viscosity loss characteristics would result from the molecular weight changes shown. It was suggested that the relationship between MW and viscosity losses should be reciprocal. That is, if the change in molecular weight distribution can indicate the expected degree of change in the viscosity loss parameters, then the viscosity loss parameters values should be capable of roughly anticipating the MW distribution before and after polymer degradation. While the degree of understanding in using the VLT to gain insight into the MW distribution is just being suggested, it may provide a new view of the MW distribution from a vantage-point more pertinent to lubrication. Certainly, other methods such as light-scattering and exclusion chromatography have little direct understanding to offer regarding the configuration of the polymer coil in oil solution and its response to orientation and degradation.

There remains a considerable area of relationships among the four parameters to consider and relate. Perhaps this paper will encourage that process.

## SUMMARY

The author has suggested and applied a technique for using the the Viscosity Loss Trapezoid as a means of gaining insight concerning the MW distribution of VI Improvers in oil solution. The technique generates an apparent MW distribution before and after mechanical degradation of the VI Improver by determining the low and high shear behavior of the polymer-in-oil solution before and after mechanical degradation.

From this early beginning, the next step is to learn more about the MW distributions present by information from gel permeation chromatography. This would have the dual benefit of refining the interpretation of the VLT values and confirming its application.

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