

Viscosity and Molecular Weight Distribution of Ultrahigh Molecular Weight Polyethylene Using a High Temperature Low Shear Rate Rotational Viscometer*

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Synopsis

To obtain accurate measurements of the limiting viscosity number (LVN) or the intrinsic viscosity $[\eta]$ of solutions of ultrahigh molecular weight polyethylene (UHMWPE), a low shear floating-rotor viscometer of the Zimm-Crothers type was constructed to measure viscosities at elevated temperatures (135°C) and near zero shear rate. The zero shear rate measurements for UHMWPE whole polymer and UHMWPE fractionated by hydrodynamic crystallization were compared with viscosity measurements at moderate and high shear rates (up to 2000 s^{-1}) carried out in a capillary viscometer. The limiting viscosity number of UHMWPE decreases, as expected, with shear rate. The higher shear rate data could not be extrapolated to yield the correct zero-shear rate viscosities. Fractionation of UHMWPE gave 10 fractions ranging in LVN from 9 to 50 dL/g. A tentative integral molecular weight distribution for the whole polymer was calculated on the basis of the Mark-Houwink equation, but because it had been previously established only for lower molecular weight polyethylenes, it may not be accurate. A correlation was found between the LVNs for the fractions in the two types of viscometers.

INTRODUCTION

The successful use of ultrahigh molecular weight polyethylene (UHMWPE) in a wide variety of applications is due to its unique combination of desirable properties, attributable to a large extent to its very high molecular weight. Some of these desirable properties are its high abrasion and impact resistance, its low coefficient of friction, and its good chemical and stress crack resistance.

For example, it has found successful use for gears and slides in the textile, materials handling, mining, and paper industries where good mechanical durability and low friction are required. It is also the material of choice for orthopedic joint replacement such as hips, knees, ankles, and shoulders. With respect to the latter use, it is now recognized that UHMWPE is not completely inert, but is capable of undergoing both morphological and chemical change¹⁻¹³ as exemplified by alterations in crystallinity and molecular weight. These changes can take place prior to implantation when the material is

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radiation sterilized, as well as after implantation when the material is exposed to body fluids and high stresses over a prolonged period of time.

To elucidate the role of the various factors that contribute to the wear properties of UHMWPE, such as crack resistance, for example, studies have been carried out to examine the effect of radiation,¹⁻⁷ oxidative degradation,⁷ and other chemical changes² on molecular weight and crystallinity. The molecular weight studies usually consisted of extracting a sample with decalin or xylene^{8,9} to separate out the lower molecular weight components and estimating molecular weights from viscosity measurements using the Mark-Houwink relation previously established for lower molecular weight fractions.

The role of molecular weight was also examined in a determination of the level of molecular damage that can be tolerated before failure occurred. Fanconi,¹¹ using an infrared technique, monitored polyethylene chain scission following application of stress to molded samples of UHMWPE.

These and other published data strongly suggest that the molecular weight of UHMWPE plays a critical role in determining its long-term performance. However, the technique for measuring such high molecular weights reliably are subject to problems that still need to be overcome. The classical techniques of molecular weight measurement such as light scattering or osmometry, as well size exclusion chromatography (see below), are either too difficult for routine work or cannot be used with polyethylenes greater than about one million.

One of the most common methods of estimating molecular weight is by measurement of the limiting viscosity number (LVN), or intrinsic viscosity $[\eta]$, which may, for most linear polymers below 1 million, be empirically related to molecular weight by the Mark-Houwink relation. For lower molecular weight polymers, the use of a capillary viscometer with shear rates of the order of a few thousand reciprocal seconds is satisfactory because the viscosity is independent of shear rate. This relationship is far from the case with the ultrahigh molecular weight polymers. The non-Newtonian behavior of these polymers is well recognized in the literature as a problem that must be addressed if accurate measurements of the limiting viscosity number are to be made. As the shear rate increases, the shape and orientation of the molecule changes sufficiently so that the shear stress is no longer proportional to the shear rate.

Because capillary viscometers are not usually designed to provide a constant or very low shear rate, viscosity data for shear rate-sensitive materials must be obtained in a viscometer where the effect of shear rate is minimal or nonexistent. The Zimm-Crothers floating-rotor low shear viscometer¹⁴ although used mostly for biological molecules such as DNA, has also found application for high molecular weight synthetic polymers.^{15,16} In this viscometer, at the low shear rates of a few reciprocal seconds, the viscosity is independent of shear rate, so that the measured viscosity is essentially the zero-shear rate viscosity. Another important advantage is that the degradation due to shear, which can reduce the viscosity substantially, is very unlikely at these low shear rates. This degradation sometimes occurs in a capillary viscometer, during the course of a measurement, and is observed as a decrease in flow time as the sample is recycled through the viscometer.

It was therefore the objective of this research to construct and validate a high temperature low shear rate viscometer and to measure the viscosities of some of the UHMWPEs currently available.

Since most laboratories do not have access to a low shear rate viscometer, it was also considered useful to relate the zero shear rate viscosities to those obtained in a capillary viscometer. This has been done for a set of fractions derived from a whole polymer sample of UHMWPE for which a tentative molecular weight distribution is provided as well.

EXPERIMENTAL

Fractionation

Fractions of UHMWPE were prepared using a hydrodynamically induced crystallization procedure similar to the one reported by Pennings.¹⁷ A 0.1% solution of UHMWPE (Hercules Type 1900, Lot 99716), in decalin (99% Aldrich Chemical Co.,)¹⁸ sparged with nitrogen and containing 0.1% Santonox R, was cooled from 135° to 105°C with slow stirring over a 4-h period. When 105°C was reached, rapid stirring was begun and the surface of the solution was blanketed with a stream of preheated nitrogen. On cooling to 99°C, a precipitate formed on the stirrer. The bath was maintained at this temperature until no additional precipitate could be seen accumulating. The stirrer and precipitate were then removed and replaced with another preheated stirrer, and cooling was resumed. Fractions was collected at about every 2°C until the last fraction was removed at 78°C. Although no additional polymer gathered on the stirrer at this temperature, the solution was cloudy and yielded a "residue" fraction on filtration. The 10 fractions and the "residue" were dried to constant weight at 60°C in a vacuum oven.

Solution Preparation

One of the most difficult problems encountered in characterizing UHMWPE is sample preparation. During preliminary viscosity measurements, it was found that one of the principal causes of poor reproducibility was incomplete dissolution of the polymer. These materials are slow to dissolve because of their partial crystallinity and high molecular weight. They are also extremely sensitive to mechanical forces; a large viscosity decrease occurs if just a small amount of degradation takes place. At first, tetralin was used as a solvent for viscosity measurements, but it was not possible to achieve satisfactory reproducibility. This was very likely due to the tendency of tetralin to form peroxides which contribute to the degradation of the polymer. Consequently, measurements were made in decalin despite possible complications with its isomerism. The decalin had been purified by passing it through a silica gel column and sparged overnight with nitrogen following addition of antioxidant.

The following procedure was finally adopted which, except for the one case discussed below, appeared to redissolve the whole polymer and the fractions completely. Because the fractions were slow to dissolve, they were cut into pieces one millimeter or less on a side to increase the solution rate. A closed

bottle containing weighed solution and solvent, saturated with nitrogen, was heated to 180°C for 1 h with continuous gentle shaking to prevent agglomeration. After making certain that there were no observable undissolved particles or gel, the solution was filtered at about 180°C through a 5 μ Millipore "Mitex" filter, made of poly(tetrafluoroethylene).

The High Temperature, Low Shear Rate Viscometer

The essential features of the modified Zimm-Crothers viscometer are shown in Figure 1. Solvent or solution is placed between an inner glass cylinder, the rotor, and a fixed outer glass cylinder, the stator. The rotor, floating freely in the liquid, is centered within the stator by surface forces and is subjected to a constant torque. There are no mechanical devices attached to the rotor, which is supported by buoyancy. Unlike the Couette viscometer, all the energy loss occurs in the liquid, so that, the speed of the rotor is inversely proportional to the viscosity of the liquid. As a result, measurements may be made at low viscosities with good precision.

The drive system for the rotor is similar to one described elsewhere,¹⁵ operating on the principle of an electromagnetic induction motor. A resistive-capacitance circuit splits the current into two legs, each of which energizes the two opposing solenoids of the four solenoids which surround the viscometer. As a result, adjacent solenoids are 90° out of phase with each other. Torque on the rotor, produced by eddy currents induced in an aluminum cylinder sitting at the bottom of the rotor, is held steady by an adjustable constant current supply. The constant current supply is based on a Kepco bipolar operational amplifier capable of supplying 1.5 A at 74 V. The circuit used is the one described by the manufacturer of the unit for operation at constant current. The reference for the amplifier is a precision 60-Hz oscillator stabilized for both frequency and amplitude to better than 0.1%. As a result,

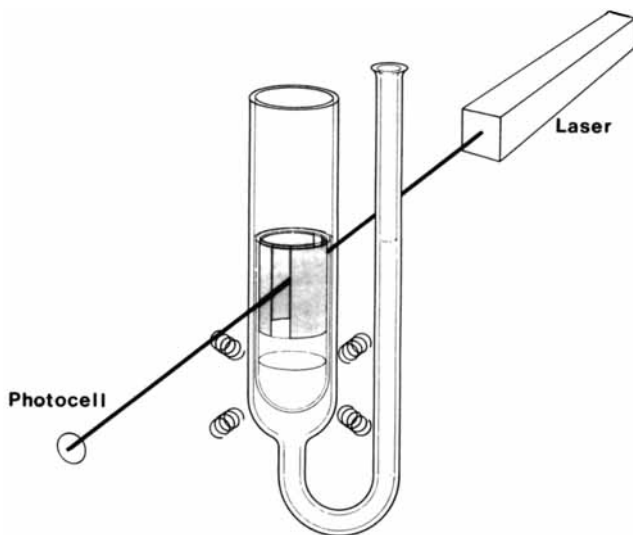


Fig. 1. Basic features of the high temperature low shear rate viscometer.

the root-mean-square value of the current for the entire circuit is stabilized to better than 0.1%.

To minimize the tendency to wobble at low velocities, the rotor and stator are fabricated from uniform bore glass tubing, about 30 mm in diameter, such that a 1-mm gap is left between them for the liquid. The top edge of the glass rotor is ground flat and free of nicks, and the bottom is rounded as symmetrically as possible.

The aluminum cylinder, which must also be symmetrical to reduce wobble, is machined carefully to fit the glass rotor at 135°C. The total weight of the rotor is adjusted by drilling the proper size hole through the center of this cylinder. Because the rotor is suspended by buoyancy, the size of this hole depends on the density of the solvent. The height of the insert should be such as to be within the confines of the magnetic field of the solenoids. To avoid shattering the glass, the glass rotor and aluminum are heated separately in a 150°C oven and then assembled hot and put into the stator in the bath. This procedure is necessary because of the difference in the rate of expansion of glass and aluminum.

The entire apparatus is clamped rigidly to a frame immersed in the high temperature oil bath. This rigid mounting was necessary to achieve good reproducibility. The bath was fitted with a cover so that measurements could be made under a blanket of argon. Solvent readings are reproducible to about 1% from day to day, even though the bath is cooled overnight and reheated on the morning of a run. The rotation time, or period, is determined by directing a laser beam through the rotor which has been coated with a wide band of chromium, except for two vertical clear windows a few millimeters wide and 180° apart. During rotation, the beam passes through these windows and impinges on the photocell, which, in conjunction with a Schmidt trigger assembly, starts and stops a counter-timer to measure the period of the rotor.

Sample is introduced into the side arm of the stator by means of a funnel. For polyolefins, the funnel must be heated to prevent cooling of the hot solution and precipitation of the polymer. The height of the rotor is then adjusted after it has been floated by adding or withdrawing liquid with a heated syringe. The centering effect is achieved by the surface tension of the meniscus. As pointed out by Zimm and Crothers,¹⁴ the shape of the meniscus is crucial for this centering; surface forces act to center the inner rotor if the liquid surface rises up from its rim to the stator. The optimum height of the rotor is determined by the height at which the magnetic coupling is a maximum; that is, where the period is shortest for a given current. At this height, the rotor speed is changing very slowly with height, so that a small error in height will lead to minimal error in the period.

Measurement Procedure (Low Shear Rate Viscometer)

Although the data for only one value of the torque, or the current, were finally used, the period was determined for a range of current values from 30 to 150 mA at 10 mA intervals. The periods were first determined for the solvent, then for the solution. The relative viscosity is the ratio of the period for the solution to that of the solvent at a given torque or current setting. The limiting viscosity number then is calculated in the customary way by plotting

the viscosity number $(\eta_w - 1)/c$ as a function of concentration and extrapolating to zero concentration. The measurements were restricted to very dilute solutions to make certain the data were in the linear concentration region.

The shear rate may be calculated from the equations given by Zimm and Crothers¹⁴

$$\dot{\gamma} = \frac{\pi R_1 + R_2}{P R_2 - R_1} \cdot \frac{8R_1^2 R_2^2}{(R_1 + R_2)(R_2 - R_1)} \cdot \ln R_2/R_1 \quad (1)$$

where R_2 , is the outer radius of the rotor, R_1 the inner radius of the stator, $\dot{\gamma}$ is the shear rate, and P the period. In our case, R_2 was 1.5 cm and R_1 was 1.4 cm so that

$$\dot{\gamma} = 90.94/P$$

The torque, T , established in the rotor is proportional to the product of the intensity of the inducing magnetic field and the current induced in the rotor. But the latter also depends on the magnetic field, which in turn depends on the current, i , supplied to the coil. Hence,

$$T = k_1 i^2 \quad (2)$$

But for a Newtonian fluid, the torque acting under constant rotor speed, ω is

$$T = k_2 \eta \omega, \text{ or } T = k_2 \eta / P \quad (3)$$

where η is the viscosity, P is the period of rotation, and k_1 and k_2 are proportionality constants. Hence

$$\eta = k_1/k_2 i^2 P \quad (4)$$

Assessing the Low Shear Rate Viscometer

To determine whether the instrument was behaving satisfactorily, viscosities were measured at 25 and 35°C of some narrow molecular weight distribution polystyrenes, including two Standard Reference Materials, SRM 705 and SRM 1479.¹⁹ The molecular weights ranged from 180,000 to 13×10^6 . The values of the limiting viscosity number are given in Table I. Excellent agreement is found for SRM 705 between our value and the certificate value. For SRM 1479, for which no viscosity is certified, the molecular weight derived from the "blob" model²⁰ using our low shear viscosity result and the weight-average molecular weight determined by light scattering are the same, namely 1.05×10^6 . The data for SRM 1479 are shown in Figure 2. Good agreement is also apparent by this method for sample F1300 (Toyo Soda), another narrow molecular weight polystyrene, with a molecular weight of 13.4×10^6 as measured by light scattering.

Equation (4) states that for the solvent, or for any Newtonian fluid, the viscosity, which is independent of shear rate, is proportional to Pi^2 . Because precession or any other form of unstable rotation is observable by a reduction

TABLE I
Limiting Viscosity Numbers Measured in the Low Shear Rate Viscometer

Sample	Solvent	Temp (°C)	[η](dL/g)		$M \times 10^{-6}$	
			Low shear viscometer	Certified value	Blob model	Measured
SRM 705	Cyclohexane	35	0.356	0.354		0.18
SRM 1479	Toluene	25	2.42		1.05	1.05
F1300 ^a	Toluene	25	18.5		13.3	13.4

^aSample of Toyo Soda Co.

in the speed of rotation,²¹ or an apparent increase in viscosity, the value of Π^2 was measured as a function of shear rate to determine the extent of any possible instability. As shown in Figure 3, Π^2 was constant above a shear rate of 3 s^{-1} , but at lower shear rates, such as at 1 s^{-1} , some upturn of the order of 0.5–0.8% was noticed, indicating a small amount of wobble. At shear rates greater than 7 or 8 s^{-1} , where the periods are 10 s or less, the possibility of turbulent flow exists. Hence, shear rates in this viscometer were confined to these limits. Specifically, because no evidence of upturn in the Π^2 vs. shear rate plots above 110 mA was found, our viscosity calculations were made with the data taken at 110 mA, or at a shear rate for the solvent of 3 s^{-1} . We note from Figure 3 that the viscosity is invariant not only for the solvent but also for UHMWPE in this range of low shear rates.

Zimm²² showed experimentally that if the product of the relaxation time, τ and shear rate, $\dot{\gamma}$ is less than 0.2, no variation of viscosity with shear rate

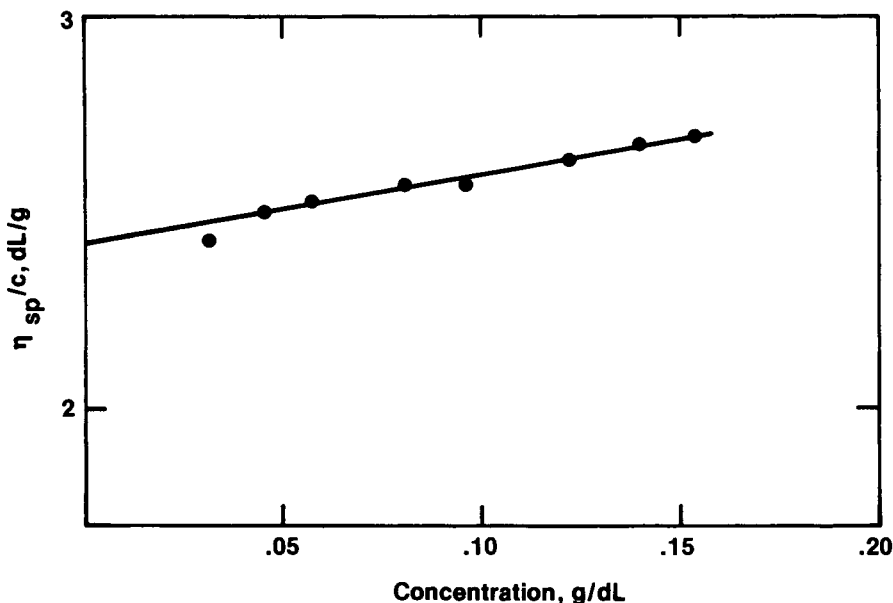


Fig. 2. Concentration dependence of viscosity of SRM 1479 (polystyrene, $M = 1.05 \times 10^6$) in toluene at 25°C measured in the low shear rate viscometer.

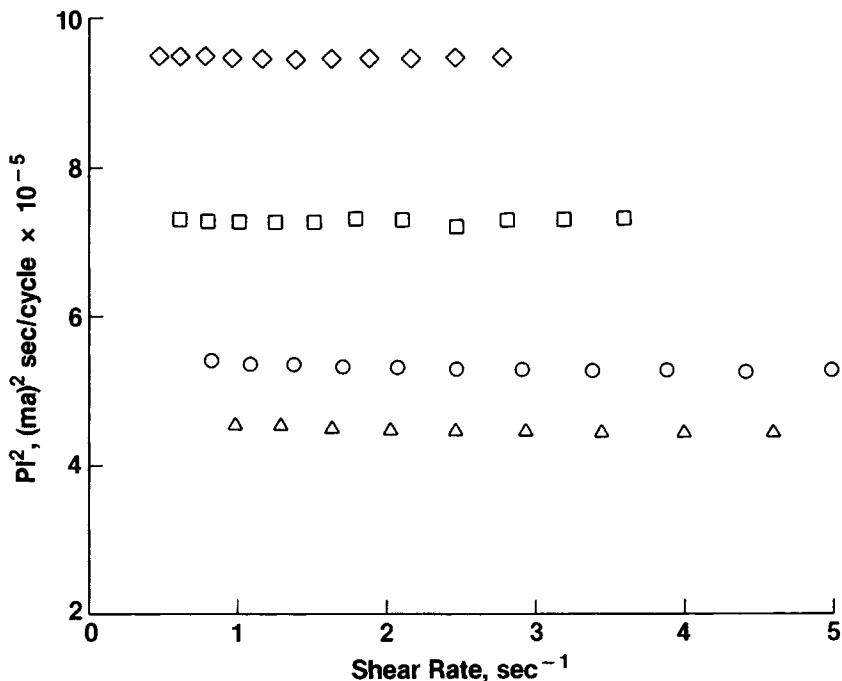


Fig. 3. Dependence of PI^2 on shear rate (triangles), of UHMWPE 99716 at 0.00989% (circles), 0.02951% (squares), and at 0.04612% (diamonds).

occurs. The relaxation time, τ is equal to

$$\alpha M [\eta] \eta_0 / RT \quad (5)$$

where M is the molecular weight of the polymer, $[\eta]$ is its limiting viscosity number, η_0 is the solvent viscosity, and α is a constant that depends on the nature of the molecule. For linear flexible molecules, α is about 40 $[\eta]$ in deciliters per gram. For our highest molecular weight sample of UHMWPE, assuming a molecular weight as high as 1×10^7 , we find a value of $\dot{\gamma}\tau$ less than 0.015, well within the region of constant viscosity.

RESULTS AND DISCUSSION

Viscosity of UHMWPE

Figure 4 shows the plots of viscosity number as a function of concentration measured in the low shear viscometer for three different samples of UHMWPE in decalin at 135°C. Concentrations were limited to very dilute values in order to stay within the linear concentration range. For sample 99974 which had the highest limiting viscosity number of 39.5 dL/g, the highest concentration was about 0.022% or 0.22 mg/mL, whereas for sample 99176, the highest concentration was almost 0.05%.

To establish the effect of shear rate on viscosity, measurements were made not only in the low shear viscometer, but also in a multibulb capillary

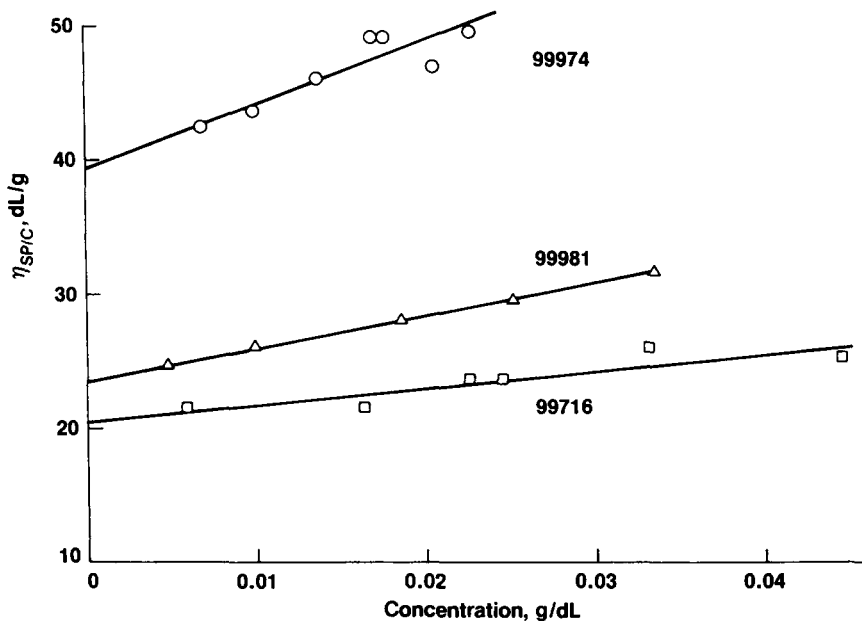


Fig. 4. Concentration dependence of viscosity for 3 different samples of UHMWPE: 99716 (squares), 99981 (triangles), and 99974 (circles) in the low shear rate viscometer in decalin at 135°C.

viscometer, in which the shear rates ranged from about 50 s^{-1} to about 150 s^{-1} and in a single bulb capillary viscometer, in which the shear rate is of the order of 2000 s^{-1} .

The single bulb viscometer was the ordinary Cannon-Ubbelohde type commonly used for quality control work. These data are shown in Figure 5. The values of the viscosity number, extrapolated to zero concentration, which were obtained in the multibulb viscometer are listed in Table II and are compared with the values obtained in the low shear viscometer. The data obtained with the routine capillary viscometer are also shown. It is apparent that extrapolation of data at the high shear rates of a capillary viscometer can lead to serious errors, and to obtain the correct values of intrinsic viscosity, measurements should be made at very low shear rates. This strong dependence on shear rate also explains in part why it is so difficult to obtain good inter-laboratory agreement. Not only does the shear rate vary as the inverse cube of the radius of the capillary, but it is also a function of the flow rate, which varies with the particular sample being measured.

Another source of error is due to the usual practice of measuring the flow times in capillary viscometers at only the single concentration in decalin of 0.05%.²³ It is at times erroneously assumed not only that this datum may be extrapolated to zero concentration using the same viscosity-concentration relationships found for lower molecular weight polymers, but also that such an extrapolation will yield a zero-shear rate-limiting viscosity number. However, for molecular weights of the order of 1×10^6 to 1×10^7 , which we believe is the range of molecular weights for UHMWPE, and limiting viscosity numbers of about 40 dL/g, a concentration as high as 0.05% is already in the

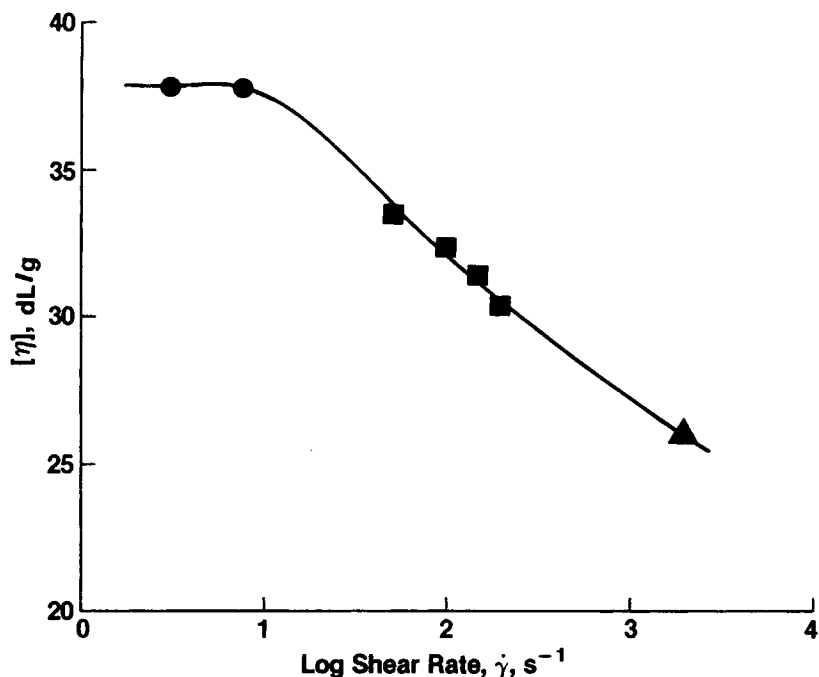


Fig. 5. Extrapolated viscosity number to zero concentration in decalin at 135°C as a function of shear rate in different viscometers: Low shear rate viscometer (circles), multibulb capillary viscometer (squares), routine capillary viscometer (triangle).

“semidilute” range.²⁴ The viscosity number is no longer expected to be linear with concentration and consequently, the viscosity-concentration relationships found for lower molecular weight polyethylenes cannot be expected to hold. Figure 6 shows our results for two different samples of UHMWPE, one at the higher end of the molecular weight range, the other at the lower. The straight line indicates the result obtained on extrapolation, making the just mentioned assumptions, and may be compared with the values obtained on extrapolation of the complete curve to zero concentration. Although the error is not too large for the lower molecular weight sample, it is quite serious for the higher one, and is in addition to error due to shear rate.

TABLE II
Viscosity Numbers of UHMWPE Samples Extrapolated to Zero Concentration
Decalin 135°C dL/g

Viscometer type:	→	Low shear	Multibulb	Conventional
Shear rate:	→	3 s ⁻¹	Ubbelohde	Ubbelohde
Sample	Max. conc.	Extrapolated viscosity numbers		
99716	0.05%	20.5	18.9	14.6
99881	0.03	23.5		17.8
99974	0.02	39.5	34.0	26.0

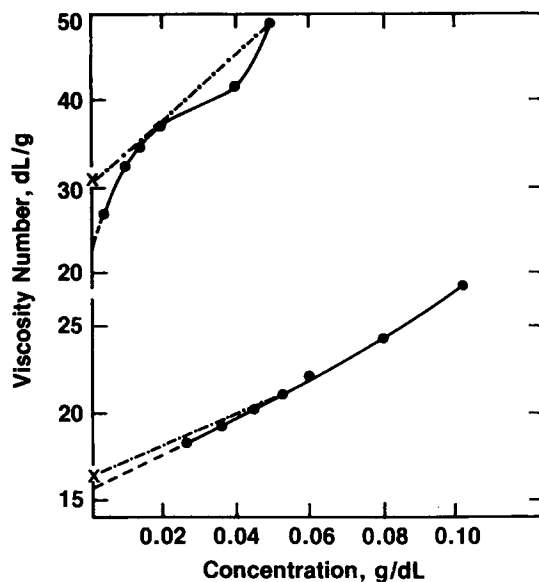


Fig. 6. Concentration dependence of the viscosity number for two samples of UHMWPE observed in a Ubbelohde viscometer in decalin at 135°C: dash-dot line, straight line extrapolation from 0.05% concentration; dash line, extrapolation from low concentration data.

The Molecular Weight Distribution of UHMWPE

Although limiting viscosity number may be related to molecular weight, it is not an absolute measure of this quantity. This relationship, expressed in the form of the Mark-Houwink equation, is extremely useful for molecular weights up to about 1 million. The Mark-Houwink parameters for polyethylene available in the literature was obtained for molecular weights below this value. Both experiment and theory demonstrate that these parameters do not apply necessarily to polymers in the ultrahigh molecular weight range.²⁰

Since usually the most convenient method for determining molecular weight and molecular weight distribution is by size exclusion chromatography (SEC), a sample of the whole polymer, 99716, and one of the lower molecular weight fractions, Fraction 8 (Table III), with an LVN of 14.0 dL/g were examined by this technique in 1,2,4-trichlorobenzene at 145°C. The columns were of the mixed bed polystyrene gel type, sold to be used for molecular weights of several million. Although separation was obtained for molecular weights up to only about 1 million, a large portion of both samples containing the higher molecular weight species remained unfractionated. Hence, no useful conclusions concerning molecular weight distribution could be derived from the data. Degradation of the sample in the columns may also be a source of error²⁵ in the case of these very high molecular weight polymers.

Since the molecular weight distribution of UHMWPE could not be determined by SEC, it was necessary to use the fractionation and viscosity data for this purpose. Molecular weights were calculated using the presently available Mark-Houwink constants, which, as indicated above, are likely to be in some error at the higher molecular weights. Once the correct Mark-Houwink

TABLE III
 Fractionation of UHMWPE 99716

Fraction number	Precipitation temperature (°C)	Weight fraction w_i	Viscometer			
			Low shear rate		Capillary	
			$[\eta]$ (dL/g)	$M \times 10^{-6a}$	η_{sp}/c (at $c = 0$) (dL/g)	$M \times 10^{-6a}$
1	99	0.0418	≈ 54	11.4	34.5	6.0
2	97	0.0420	35	6.1	26	4.0
3	95.5	0.0452	31.5	5.3	23.8	3.5
4	94.5	0.0297	27.2	4.3	20.5	2.9
5	91.5	0.0649	24.8	3.8	19.9	2.7
6	90	0.0727	23.3	3.4	17.8	2.3
7	88	0.0505	19.2	2.6	16.2	2.0
8	81	0.1088	14.0	1.7	11.5	1.3
9	79	0.1688	9.9	1.0	8.78	0.85
10	78	0.2602	9.2	0.91	8.6	0.83
Residue		0.1175	8.1	0.76	7.0	0.61

^aBased on $[\eta] = 6.2 \times 10^{-4} M^{0.70}$ (Chiang).

relation is determined, this tentative distribution may be modified. Nevertheless, some worthwhile generalizations can be made at the present time.

The Shulz technique²⁶ was used to calculate the integral distribution, in which no *a priori* assumptions are made regarding the analytical form of the distribution. The cumulative weight fraction, $C(M_i)$ for the i th fraction is computed by adding one-half of its weight fraction w_i to the weight fraction of all previous fractions.

$$C(M_i) = \frac{1}{2}w_i + \sum_{j=1}^{i-1} w_j \quad (6)$$

The cumulative distribution, $C(M_i)$ vs. molecular weight was then obtained from the limiting viscosity numbers, $[\eta]$ at zero shear rate, and Chiang's²⁷ Mark-Houwink relation for polyethylene in decalin at 135°C:

$$[\eta] = 6.2 \times 10^{-4} M^{0.70} \quad (7)$$

where $[\eta]$ is in dL/g.

Table III summarizes the results of the fractionation along with the LVN and estimated molecular weight for each fraction based on the low shear viscosity measurements. We estimate the precision to be $\pm 5\%$. However in the case of fraction 1, the highest molecular weight fraction, the reproducibility was poor, probably because of incomplete solubility, so that only an estimate can be made for LVN.

The first point on the integral distribution curve (Fig. 7) is the "residue" fraction which has an average molecular weight of about 800,000. This indicates the likely absence of a very large quantity of very low molecular weight material below about 500,000. A rapid rise takes place in the curve immediately thereafter showing 60% of the total polymer having an average

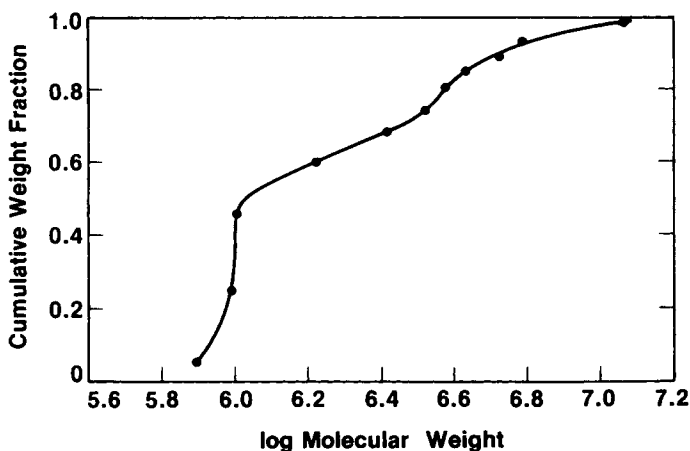


Fig. 7. Integral molecular weight distribution of UHMWPE 99716.

molecular weight of about 2×10^6 or less. Of this, more than 25% precipitated in the last stirrer fraction, with an average molecular weight of 1×10^6 . However, the precipitation temperature difference between this and the previous fraction is only 1 degree. It is quite unlikely that a recrystallization of these fractions would yield finer cuts because of the difficulty of maintaining sufficiently precise temperature control with this fractionation technique. An extraction procedure as described by Pennings,¹⁷ would probably be more fruitful.

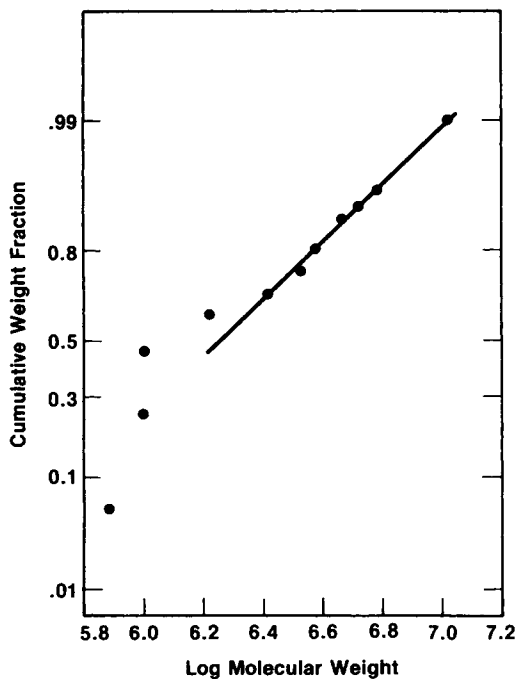


Fig. 8. Integral molecular weight distribution of UHMWPE 99716, probability plot.

The absence of a large amount of material with a molecular weight below 500,000 in the original, unprocessed polymer is especially noteworthy when compared to the reported molecular weight of UHMWPE in an acetabular prosthesis prior to and following long-term implantation. Crugnola et al.,⁸ employing an extraction procedure, found material ranging from 9000 to 810,000. Similar results were reported by Gibbons et al.⁹ and Eyerer and Ke.¹³ Thus, assuming a similarity in molecular weight distribution among various samples of UHMWPE, it would appear that significant alteration in the molecular weight distribution of the original starting material is occurring following manufacturing, implantation, xylene extraction, or all three.

The molecular weight distributions of many linear polyethylenes, as synthesized, have been shown to be log-normal. On examination of the probability plot for this fractionation, shown in Figure 8, one may conclude that this type of distribution occurs for the higher molecular weights, but not for the lower ones. It is quite possible that the bulge in the lower part of the curve is due to some degradation or is the result of blending of two or more "as-synthesized" polymers to give a product of the desired commercial specifications.

Relationship Between Capillary Viscosity and Low Shear Rate Viscosity

As reported above, LVN is more sensitive to the high, but not precisely predictable, shear rates found in a capillary viscometer, in contrast to the shear rate-independent values found in the low shear rate viscometer used in this work. Since the latter is not a commercially available instrument, it was of interest to determine whether a consistent and reproducible relationship exists between the values found in the two instruments. If so, zero shear rate viscosities could be estimated from capillary viscosity measurements, perhaps with the help of a standard UHMWPE polymer. For this purpose, separate portions of the filtrate were measured both in the low shear viscometer and in a #75 Cannon-Ubbelohde viscometer in decalin at 135°C. In Figure 9, the viscosity numbers for each solution of each fraction are plotted, the low shear rate viscometer data are ordinate, the capillary viscometer data as abscissa. As expected, the deviation from the 45 line increases with viscosity, and therefore molecular weight. The low shear rate viscosity number is as much as 33% greater than the value observed in the capillary viscometer. The LVNs for these fractions, derived from the viscosity numbers on this curve, are shown as circles, and fall on the same curve. The LVNs for whole polymers, of which one (indicated by a filled triangle) is the source of these fractions, are plotted similarly. Two of these points, however, are off the curve, indicating this relationship may be dependent on molecular weight distribution.

It is possible, however, that for a given manufacturing process, in which the distributions are similar, a unique relationship could be established, so that under certain circumstances a zero shear rate viscosity could be estimated from capillary viscosity.

CONCLUSION

The accurate measurement of the viscosity of UHMWPE requires measurement at a shear rate no greater than about 50 s^{-1} and preferably closer to 10

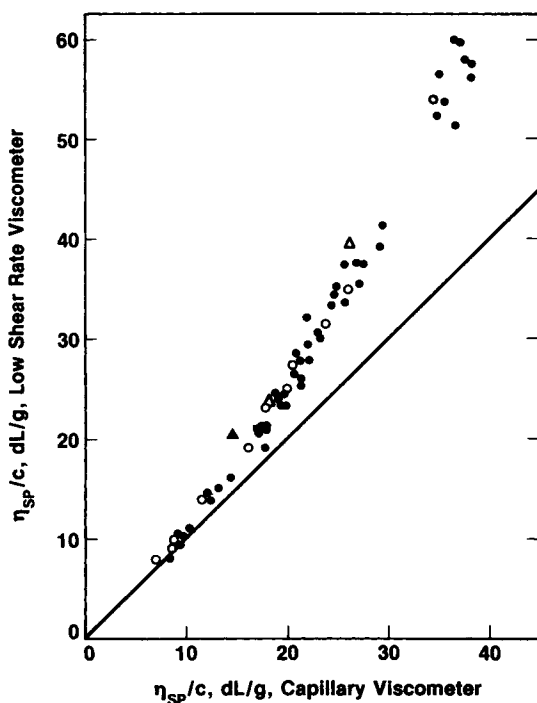


Fig. 9. Viscosity numbers obtained in the low shear viscometer plotted against those observed (without shear rate correction) in the Ubbelohde viscometer. Filled circles are values for the fractions; open circles are the extrapolated values of these viscosity numbers to zero concentration. The triangles are the extrapolated values for the 3 whole polymers; the filled triangle is for the whole polymer which was the source of these fractions.

s^{-1} . This measurement should be carried out at very low concentrations (0.05%) so that the viscosity number-concentration curve is linear. The freely floating low-shear viscometer described in this paper may be used for this measurement at elevated temperatures. We find that the use of this viscometer is quite simple, and the measurement may be made rapidly.

Fractionation of a sample of UHMWPE indicates that more than half of the material has a molecular weight less than 2×10^6 , with little material of molecular weight below about 500,000. A probability plot of integral molecular weight distribution supports the suggestion that UHMWPE may be a blend of two polymers.

Finally, a relationship was shown to exist between zero shear rate viscosity and capillary viscosity thus permitting the possible prediction, based on capillary viscosity, of zero shear rate viscosity.

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