

Use of a Sequential Extraction Technique to Determine the MWD of Bulk UHMWPE

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Synopsis

The molecular weight distribution (MWD) of bulk ultrahigh molecular weight polyethylene (UHMWPE) was determined by an increasing temperature sequential extraction technique. Using decahydronaphthalene (decalin) as the solvent, 5 g samples of UHMWPE were fractionated stepwise from room temperature to 190°C in 10°C increments. Results via high temperature capillary viscometry show that intrinsic viscosity ($[\eta]$) ranges from 12.0 to 37.0 dL/g or that the viscosity average molecular weight (\bar{M}_v) ranges from approximately 1.6 to 7.4×10^6 . When the integral distribution is plotted against \bar{M}_v on logarithmic probability graph paper, a straight line (i.e., a Wesslau distribution) results. Although the present methodology is tedious, many previous problems which have led to degradation are overcome by this technique.

INTRODUCTION

Much attention has been directed to studies of the molecular weight distributions of high polymers. Two different types of techniques have been used—those which provide direct access to the molecular weight distribution using the whole polymer and those involving a fractionation procedure followed by a molecular weight determination of the fractions. Of the two the indirect methods are the ones most widely used. Several investigators have reviewed either the experimental or theoretical aspects of fractionation,¹⁻⁵ while others have reviewed the many methods of determining polymer molecular weights.⁶⁻¹¹

The commercial importance of polyethylene has prompted numerous molecular weight distribution studies. Methods for the molecular weight determination of polyethylene include viscometry, osmometry, gel permeation chromatography (GPC), light scattering, ebulliometry, cryoscopy, and ultracentrifugation. Tung,¹¹ Trementozzi and Newman,¹² and Raff and Allison¹³ have reviewed much of the early work applied to polyethylene. The molecular weight ranges reported in the literature are for viscometry (\bar{M}_v) 653– 6.7×10^6 ,^{14,15} for osmometry (\bar{M}_n) 1750– 4.3×10^5 ,^{16,17} for GPC (\bar{M}_w) 8100– 8.9×10^5 ,^{18,19} and (\bar{M}_n) 6400– 4.7×10^5 ,^{19,20} for light scattering (\bar{M}_w) 1.9×10^4 – 6.1×10^6 ,^{21,22} for ebulliometry (\bar{M}_n) 900– 3.4×10^4 ,^{15,23} for cryoscopy (\bar{M}_n) 1.0×10^4 – 8.0×10^4 ,^{24,25} and for ultracentrifugation (\bar{M}_w) 3600– 3.4×10^6 .^{26,27}

The primary methods used to fractionate polyethylene are fractional precipitation, equilibrium centrifugation, fractional crystallization, gel permeation, and fractional solution either by column elution or by temperature dissolution. Although the majority of this literature is directed towards the evaluation of low molecular weight polyethylene ($\bar{M}_w < 10^6$), several workers have reported \bar{M}_w values for polyethylene fractions $> 10^6$.^{14,22,27-32} Only

Trementozzi,²² Karasev et al.,²⁹ and Strazielle and Benoit³¹ have reported more than 10% of the polymer having an $\bar{M}_w > 10^6$, however.

In recent years ultrahigh molecular weight polyethylene (UHMWPE) has been increasingly used ($\bar{M}_w = 2 \times 10^6 - 6 \times 10^6$). Due to its superior resistance to wear and abrasion, low coefficient of friction, high impact strength, and high resistance to chemicals, UHMWPE has found use in such areas as ore chutes, bowling alley lanes, electroplating drums, snow skis, and implantable prosthetic devices. To date the properties of these end products have been based on the molecular weight distribution of the powder precursors. To improve the future design of such products, the present objective is to develop the procedures necessary to determine the total molecular weight distribution of bulk UHMWPE. The fractionation is accomplished using an increasing temperature sequential extraction technique.

EXPERIMENTAL

Ultrahigh molecular weight polyethylene (IMPAX 5M + UHMW-NAT, Impact Plastics, Inc.) was obtained in block form after being processed from either 1900 UHMW (Hercules, Inc.) or Hostalen GUR UHMW powders (American Hoechst, Inc.). The solvent used in this experiment was decahydronaphthalene (decalin, Fisher Scientific). 2,6-di-*tert*-butyl-4-methylphenol (BHT, Aldrich Chemical Co.) was used as the antioxidant, and Seaford dry nitrogen gas provided the inert atmosphere.

The apparatus designed for the determination of the molecular weight distribution (MWD) of UHMWPE is comprised of two parts (Fig. 1): a distillation chamber (1) and a sample fractionation chamber (2). Chamber (1)

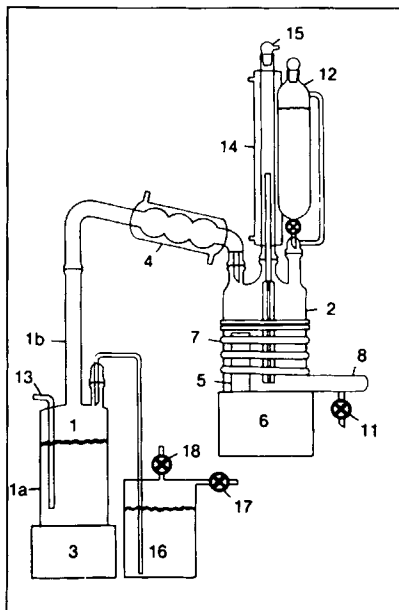


Fig. 1. Schematic diagram of the increasing temperature sequential extraction apparatus.

consists of a boiler (1a) heated by a hotplate (3) and a refluxing column (1b). Decalin is distilled from this chamber by way of condenser (4) (tap water cooled) into the sample chamber (2). The samples are placed in nickel-chromium wire gauze baskets (5). Chamber (2) is heated to within 10°C of the desired temperature by hotplate (6) with the remainder of the heat supplied by heat tape (7) which is controlled to within $\pm 0.2^\circ\text{C}$. Sample aliquots are removed via the stopcock (11). A 3% antioxidant solution of decalin is stored in an addition funnel (12), while an addition chamber (16) under nitrogen pressure via valve (17) provides fresh solvent to chamber (1). The flow of solvent is controlled via the pressure relief valve (18).

Approximately 5 g of UHMWPE was machined into $15 \times 15 \times 2$ mm slabs and placed into the sample basket (5). After the system was purged with nitrogen, 100 mL of the antioxidant solution was added (12) into the sample chamber (2), and the volume was increased to 750 mL by distillation. Two days later an aliquot was taken. All except 50 mL of solution was removed from the sample chamber with each aliquot. This procedure was repeated in a minimum of 24 h increments until successive aliquots were clear of polymer (< 22 days each). The process was repeated in 10°C increments from room temperature to 190°C .

The molecular weights were determined using the first aliquot at each temperature, after equilibration in an oil bath at $135 \pm 0.01^\circ\text{C}$. As a first indication that the method was working, intrinsic viscosities were determined using either a Cannon #1, or an equivalent Ubbelohde capillary viscometer. At least six flow times were determined for each solution to the nearest 0.01 s using two gates which had been fabricated from fiber optics. The total quantity of UHMWPE as well as the concentration of each fraction was determined by measuring the total volume of each aliquot and then drying down the aliquot to constant weight, first using a rotary flash evaporator and then using a vacuum oven. Using the relative viscosity η_{rel} and the concentration c (g/dL), the intrinsic viscosity $[\eta]$ was calculated using the single-point intrinsic viscosity eq. (1) which has been applied to polyethylene.^{14, 33-36}

$$\eta_{\text{rel}} = 1 + c[\eta] \exp^{0.320[\eta]c} \quad (1)$$

From these single point viscosity measurements, molecular weights could be approximated from³⁷

$$\log(\bar{M}_v) = 4.7479 + 1.3527 \log[\eta] \quad (2)$$

RESULTS

Table I summarizes the fractionation data for one UHMWPE sequential extraction experiment. For the 10 fractions obtained, the $[\eta]$'s range from a low of 12.0 dL/g ($\bar{M}_v = 1.6 \times 10^6$) to a high of 37.0 dL/g ($\bar{M}_v = 7.4 \times 10^6$). Volatile and residual fractions amounted to only 0.002 of the sample. A mass balance showed that less than 0.001 was unaccounted for throughout the 6-month long test procedure. When the fractionation data was assumed to represent monodisperse fractions, computations indicated that $\bar{M}_n = 2.3 \times 10^6$, $\bar{M}_w = 2.6 \times 10^6$, and polydispersity, $D = 1.14$. In Figure 2 the differen-

TABLE I
 Fractionation Data for One Bulk UHMWPE Material
 (Impax 5M + UHMW-NAT)

T ($^{\circ}\text{C}$)	c (g/dL)	$[\eta]$ (dL/g)	\bar{M}_v ($\times 10^{-6}$)	w	$w_i \cdot M_i$ ($\times 10^{-6}$)	w_i/M_i ($\times 10^6$)
80.0–90.0	0	0	0	0.00104 ^a		
90.0–100.0	0.0276	12.00	1.61	0.00150		
100.0–110.0	0.0653	14.75	2.13	0.2636	0.424	0.164
110.0–120.0	0.0308	17.40	2.67	0.3093	0.659	0.145
120.0–130.0	0.0186	21.80	3.62	0.1838	0.491	0.0688
130.0–140.0	0.00872	24.45	4.22	0.1075	0.389	0.0297
140.0–150.0	0.00824	25.75	4.53	0.0546	0.230	0.0129
150.0–160.0	0.00224	29.15	5.36	0.0303	0.137	0.00669
160.0–170.0	0.00949	29.15	5.36	0.0202	0.108	0.00377
170.0–180.0	0.00239	32.15	6.12	0.0160	0.0979	0.00261
180.0–190.0	0.00299	34.70	6.78	0.00720	0.0488	0.00106
	0.00185	36.95	7.39	0.00369	0.0273	0.000499
				0.000937 ^b		
				$\Sigma = 0.9996$	$\Sigma = 2.612$	$\Sigma = 0.4350$
				$\Sigma = 0.9962^c$		

^aVolatile fraction.

^bResidual fraction.

^cSum of weight fractions (w_i): $\bar{M}_n = (\Sigma w_i)/(\Sigma w_i/M_i) = 2.29 \times 10^6$, $\bar{M}_w = (\Sigma w_i \cdot M_i)/(\Sigma w_i) = 2.62 \times 10^6$. Polydispersity (D) = $\bar{M}_w/\bar{M}_n = 1.14$.

tial (w) and integral (W) intrinsic viscosity distributions show that the median $[\eta]$ equals 16.0 dL/g ($\bar{M}_v = 2.4 \times 10^6$) and that 5% of the molecules have an $[\eta]$ greater than 28.0 dL/g ($\bar{M}_v = 5.0 \times 10^6$). When W is plotted against the $\log \bar{M}_v$, a Wesslau distribution³⁸ was obtained (Fig. 3). Such a distribution seemingly confirmed the low polydispersity.²⁸ However, the simplification of the expression which partitions the various molecular species¹⁶ and the need for greater shear correction factors with increasing chain length

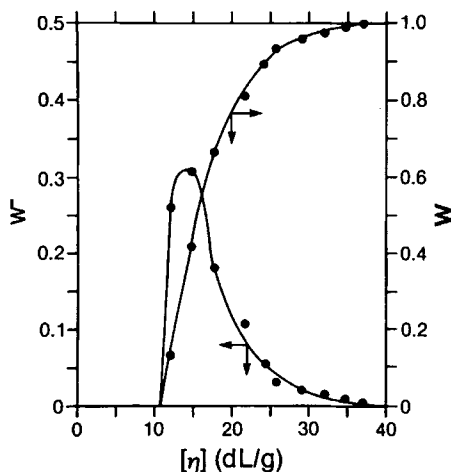


Fig. 2. Differential and integral intrinsic viscosity distribution of a bulk sample of UHMWPE (IMPAX 5M + UHMW-NAT).

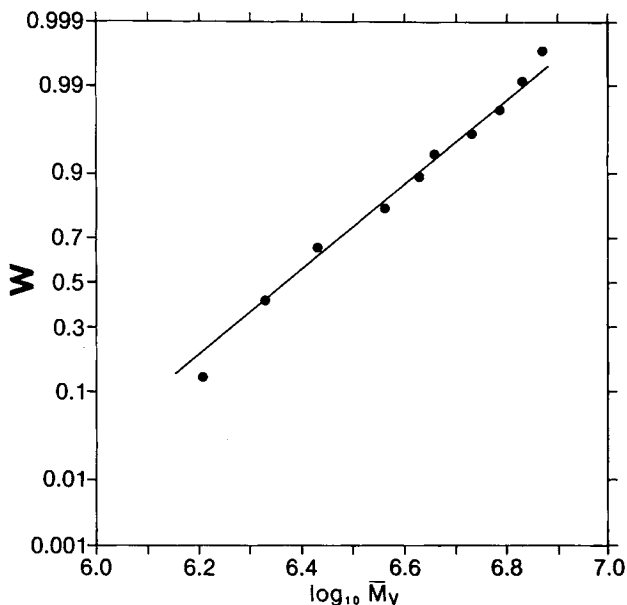


Fig. 3. Fit of the MWD of a bulk sample of UHMWPE (IMPAX 5M + UHMW-NAT) to a log normal line.

suggest that further work by an absolute method, e.g., light scattering, might increase D somewhat.

DISCUSSION

The present methodology of fractional solution by sequential temperature extraction,^{15,28,39-41} overcomes many of the previous problems which have been associated with the fractionation of bulk UHMWPE specimens. In the past, insufficient solvent temperature has led to apparent gel fractions whereas high-frequency shaking or high-speed stirring has led to mechanical fracturing. Excessive temperature gradients have caused thermal-mechanical fracture, and chemical degradation has resulted from the absence of an inert atmosphere and an antioxidant. Oftentimes a study has reported reproducible but, nevertheless, erroneous measurements because of these experimental difficulties. Indeed, ultrahigh molecular weight polymers will undergo chain scission at a lower critical shear stress, will fracture more often than smaller molecules, and will rupture more frequently with increasing swelling pressure and solvation.⁴² Because these degradation phenomena tend to approach a critical chain length, erroneous results may even appear reproducible between different groups of investigators.

The present experiment represents the true distribution of a bulk UHMWPE product within the inherent limitations of capillary viscometry. No gel fraction was found, dry nitrogen and "BHT" were used to reduce chemical degradation, no stirring was involved, and both the solvent power and the swelling pressure were controlled by slow stepwise heating over a period of several months. Evidence which substantiates that degradation did not occur was the monotonous increase in $[\eta]$ and the observation of a log normal

MWD. The reproducibility of the results (in all, three successful experiments were run), and the excellent mass balance lend further credibility to these results.

Molecular weight distribution information such as this should provide further insight into the structure-property relationships of various bulk UHMWPE's.

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