The Mark–Houwink–Sakurada Equation for the Viscosity of Linear Polyethylene

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In this review, the parameters K and α found in the literature for the Mark–Houwink–Sakurada equation relating viscosity to molecular weight have been critically evaluated for linear polyethylene, and values have been recommended for six commonly used solvents. These are decalin, 1,2,4-tricholorobenzene, 1-chloronaphthalene, tetralin, *o*-dichlorobenzene, and *p*-xylene. In addition, the literature values of K for several different theta solvents are presented.

Key words: biphenyl; 1-chloronaphthalene; decalin; deconal; *o*-dichlorobenzene; dodecanol; Mark–Houwink–Sakurada; polyethylene; size exclusion chromatography; molecular weight; octanol; tetralin; 1,2,4-trichlorobenzene; 3,5,5-trimethyl hexyl acetate; viscosity; *p*-xylene.

1. Introduction

Many of the unique and advantageous properties of high polymers are critically dependent on molecular weight, so that its proper measurement is essential for control and specification. Because synthetic polymers consist of a mixture of molecules with a range of molecular weights, a molecular weight measurement yields an average value, the type of average being dependent on the technique employed. For example, osmotic pressure measurements yield the number average molecular weight

$$M_n = \sum n_i M_i / \sum n_i, \tag{1}$$

where n_i is the number of molecules of species i of molecular weight M_i. On the other hand, light scattering, another absolute technique, measures the weight average molecular weight M_w

$$M_w = \sum w_i M_i / \sum w_i, \tag{2}$$

where w_i is the weight fraction of molecules of molecular weight M_i. In Fig. 1, a typical differential molecular weight distribution curve for a polymer is shown, with the different averages indicated.

Osmotic pressure and light scattering are the principal techniques employed for the determination of absolute molecular weights, i.e., from fundamental physical measurements rather than by calibration with polymers of known molecular weight. A less complicated and widely used indirect method is the measurement of the limiting viscosity number (LVN) known also as the intrinsic viscosity $[\eta]$. This yields a viscosity average molecular weight, which is usually close in value to the weight average molecular weight.

To obtain the molecular weight from the limiting viscosity number, an empirical relationship between the two is employed. This relationship, which is specific for polymer, solvent, and temperature, is known as the Mark–Houwink–Sakurada equation, or more commonly, the Mark–Houwink equation,

$$\mathrm{LVN} = [\eta] = KM^a, \tag{3a}$$

or

$$\log \mathrm{LVN} = \log [\eta] = \log K + a \log M, \tag{3b}$$

where K and a are empirically determined constants. These Mark–Houwink constants are evaluated by measuring the viscosities and molecular weights of a series of polymers over a wide range of molecular weights and fitting the best straight line to Eq. (3b). The molecular weights are determined, preferably, by an absolute method such as light scattering or osmotic pressure.

The only apparatus needed to measure LVN is a commercially available capillary viscometer, a constant temperature bath, and a timer. The flow times t for several dilute solutions of different polymer concentration, as well as that of the solvent, are measured and the viscosity number, or the

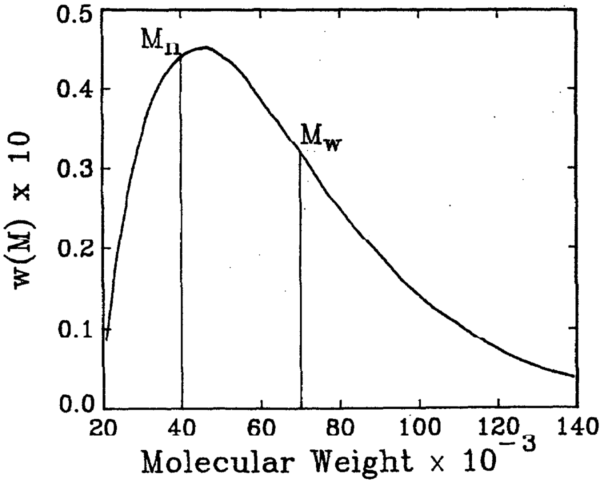

FIG. 1. Typical differential molecular weight distribution of a synthetic polymer. Molecular weight in g/mol.

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specific viscosity divided by the concentration, may be obtained from the relationship

$$\eta_{sp}/c = (t - t_0)/t_0 c, \tag{4}$$

where c is the concentration and t and t_0 are the flow times for the solution and the solvent, respectively, both corrected for kinetic energy effects. Ordinarily the limiting viscosity number is obtained by a linear extrapolation of the viscosity number to zero concentration. A more precise way of obtaining LVN from flow times is discussed elsewhere.[1]

Once LVN has been measured, the molecular weight may then be calculated using tabulated values of K and a. It is the purpose of this report to make a critical evaluation of the Mark–Houwink constants reported for linear polyethylene in the literature.

When molecular weights are derived via the Mark–Houwink relation and viscosity measurements, the "viscosity average" molecular weight is obtained,

$$M_v = \left[\sum w_i M_i^a\right]^{1/a}. \tag{5}$$

It is apparent that M_v is not a fixed quantity but will depend on a, a measure of the interaction of the polymer and the solvent.

The polymer samples used in determining the Mark–Houwink relation should be as narrow in distribution as possible because the width of the distribution will influence the values of K and a. Bohdanecký and Kovář[2] have shown that f the fractions are broad the constants will differ depending on whether the number average or the weight average molecular weights of the fractions were used in the calculation. They have shown that for some common distributions, when the fractions are broad and a is small, the log viscosity-log molecular weight plot will be lower than that derived from narrow fractions if weight average molecular weights are used, and higher if number average molecular weights are used. If M_w/M_n, a measure of polydispersity, is less than 1.5, the values of a and K are reliable to 10%–15%, the error being smaller if weight rather than number average molecular weights is used.

The most likely cause for error in the determination of the constants is uncertainty in the value of the molecular weight of the fractions. The expected limit of systematic error in a careful determination of molecular weight by light scattering for polyethylenes in the molecular weight range of 10 000–500 000 was about 11%,[3] due principally to uncertainty in an essential optical constant. It was somewhat poorer for polymers above 1 000 000. In the case of osmotic pressure measurements, the expected limit of systematic error was of the order of 4%. In most osmotic pressure measurements, the total error is usually higher, and may be as high as 10%. The precision in viscosity measurements was of the order of 1% or 2%.

The values of K and a are statistically correlated so that the effects of their uncertainties on the value of the molecular weight for a given LVN are not independent. For example,[4] in the case of polyethylene in 1-chloronaphthalene, for which $a = 0.684$ and $K = 5.55 \times 10^{-4}$ dL/g, the standard error in the former was 0.010 and in the latter 0.64×10^{-4} dL/g. The resulting standard error for various values of M was shown to be

M	Standard error
10 000	370
100 000	2 030
1 000 000	43 000

Since viscosity is a function of molecular size and not strictly molecular weight, the constants K and a apply only to a given polymer at a specified temperature and solvent and should be limited to the molecular weight range for which they were determined. In addition, the polymer must be linear, unbranched, and not crosslinked. It must be emphasized that the Mark–Houwink relation has received common acceptance only because of its simplicity and convenience. More complex relationships exist,[5] which may be reduced to Eq. (3) for limited molecular weight ranges, but which are more cumbersome for everyday use.

The Mark–Houwink parameters have been found useful as well in the analysis of size exclusion chromatography (SEC) data. The calibration of SEC columns should, ideally, be carried out with fractions of known molecular weight of the polymer type being investigated. Since such fractions are generally not available, a "universal calibration"[6] technique is employed. Available fractions of known molecular weight of some other polymer, such as the narrow distribution anionic polystyrenes, may be used for calibration. This requires that the Mark–Houwink parameters be known for both polymers in the solvent used for analysis. For those systems where the universal calibration method is applicable, reasonable estimates of the molecular weight and molecular weight distribution are obtained. Hence the Mark–Houwink relation serves not only for the determination of molecular weight by viscosity but also by size exclusion chromatography.

2. Criteria for Evaluation of Data

The classical techniques for characterizing high polymers such as, for example, the measurement of LVN, osmotic pressure, or light scattering, are now textbook methods with the result that experimental details are generally omitted in literature reports. Yet some of these methods are subject to large errors which can lead to incorrect Mark–Houwink constants. For example, the temperature should be controlled carefully in viscosity measurements, and should not vary more than ± 0.03 °C. The concentration of polymer should be known accurately, requiring care in making up solutions and in the prevention of evaporation and degradation. This is particularly true for polymers such as polyethylene which are soluble only at elevated temperatures. Osmotic pressure measurements require the proper choice and conditioning of membranes suitable for the polymer-solvent system studied. In light scattering, the elimination of dust is crucial, requiring special cleaning methods which very often depend on the particular polymer system under investigation. Since all of these molecular weight methods require extrapolation to zero concentration, the method of extrapolation as well as certain other aspects of data treatment are of concern in the evaluation and analysis of data.

The frequent omission of experimental details can sometimes make critical evaluation difficult. However, there are certain criteria which were considered especially important in evaluating the reliability of a set of data. These were

(1) the narrowness of the fractions;

(2) their range of molecular weights;

(3) whether absolute measurements were used to determine molecular weight.

As previously shown, the viscosity will depend not only on the molecular weight, but also the molecular weight distribution, requiring that narrow fractions be employed in establishing the constants. In addition, the fractions should cover as wide a molecular weight range as possible because there is no reason to expect that the empirically derived values of K and a, determined over a narrow molecular weight range, will hold outside that range. Finally, whenever possible, those values of K and a were considered most reliable for which absolute rather than indirect measurements of the molecular weight were used in the determination. At times the molecular weights of the fractions used to establish the constants found in the literature were derived by indirect methods such as size exclusion chromatography, which depends on calibration with polymers of previously determined molecular weight, or by viscosity measurements in another solvent, for which the Mark–Houwink relationship had been previously established in the literature. Since all determinations of K and a are traceable to absolute measurements, every other type of indirect molecular weight determination will include additional errors due to conversion and calibration.

In this report, the values of the Mark–Houwink constants for polyethylene in just about every solvent reported in the literature have been included. Each paper has been examined critically in Sec. 3, and the constants derived from data which appear to be the most reliable are given, with some discussion of the reasons for the choice. It is not possible to set error limits on these constants for the reasons given above.

Table 1 provides a listing of K and a for these solvents. The values of K for theta solvents are given in Table 2. Recommended values of K and a are shown in Table 3. It is to be noted that the values of K, and the limiting viscosity numbers calculated from them, are in units of mL/g. Units of dL/g are frequently used as well. To convert a limiting viscosity number, given in units of mL/g to dL/g, the former is divided by 100.

TABLE 1. Values of Mark–Houwink constants for linear polyethylene

Solvent	Temp. °C	K mL/g$\times 10^3$	a	MW range	Sample type	MW method	Ref.
Decalin	135	46	0.73	30 000–640 000	F	LS	7
	135	62	0.70	20 000–1.05×10^6	F	LS	8
	135	67.7	0.67	30 000–1.0×10^6	WP	LS	9
	135	53	0.725	4 000–500 000	F	C	10
1,2,4-Trichlorobenzene	135	52.6	0.70	4 000–676 000	F	LS/MO/VPO	11
	130	39.2	0.725	8 800–630 000	F	LS/MO	4
	130	51	0.706	7 600–600 000	F	SEC	12
	130	49.5	0.715	20 000–180 000	WP	SEC	13
	130	43.4	0.724	37 000–81 000	WP	SEC	14
	140	32.3	0.735	1 000–1×10^6	F	LS	15
	135	52.3	0.70	7 600–425 000	F	VISC	16
	135	95.4	0.64	50 000–222 000	F	LS	17
	140	39.5	0.726	5 000–700 000	F	VISC	18
1-Chloronaphthalene	129	27.1	0.71	50 000–1×10^6	F	LS	19
	125	43	0.67	50 000–1×10^6	WP	LS	20
	130	55.5	0.684	8 800–630 000	F	LS/MO	4
Tetralin	130	51	0.725	3 800–96 000	F	MO	21
	120	32.6	0.77	3 000–500 000	F,WP	VISC	22
	130	43.5	0.76	22 000–263 000	F	MO	23
o-Dichlorobenzene	138	50.6	0.7	20 000–188 000	F	LS	24
	135	209.2	0.735	100 000–400 000	F,WP	VISC	25
p-xylene	105	17.6	0.83	11 000–180 000	F	MO	26
	105	16.5	0.83	140 000–500 000	F	LS	27

Symbols:
F—fractions.
WP—whole polymers.
LS—light scattering.
C—conversion of viscosity data in one solvent to viscosity in another.
MO—membrane osmometry.
VPO—vapor pressure osmometry.
SEC—size exclusion chromatography.
VISC—molecular weights determined from Mark–Houwink relation in a different solvent, usually decalin.

TABLE 2. Values of K for theta solvents for polyethylene

Solvent	Temp °C	K (mL/g)	MW range	MW method	Ref.
3,5,5-Trimethyl Hexyl Acetate	126	346	12 400–583 000	LS/MO	29
Biphenyl	127.5	323	20 000–300 000	LS/VISC	30
	128	380	17 500–583 000	LS/MO	29
	127.5	330	51 000–442 000	VISC	31
Dodecanol	137.3	307	20 000–1.05×10^6	LS/VISC	30
	138	316	8 000–32 000	LS/VISC	30
	144.5	328	8 700–583 000	LS/MO	29
Diphenyl methane	142.2	315	20 000–1.05×10^6	LS/VISC	30
	142.2	322	21 000–136 000	VISC	31
Decanol	153.3	302	20 000–1.05×10^6	LS/VISC	30
Diphenyl ether	161.4	295	20 000–1.05×10^6	LS/VISC	30
	163.9	309	14 300–204 000	VISC	31
Octanol	180.1	286	20 000–1.05×10^6	LS/VISC	30

TABLE 3. Recommended values of Mark–Houwink constants for linear polyethylene

Solvent	Temp. °C	K (mL/g)	a	MW method	Ref.
Decalin	135	62×10^{-3}	0.70	LS	8
1,2,4-Trichloro-benzene	135	52.6	0.70	LS/MO/VPO	11
	130	39.2	0.725	LS/MO	4
1-Chloro-naphthalene	130	55.5	0.684	LS/MO	4
Tetralin	130	51	0.725	MO	20
o-Dichloro-benzene	138	50.6	0.7	LS	23
p-xylene	105	17.6	0.83	MO	25

3. The Mark–Houwink Constants in Various Solvents

3.1. Decalin

Only two sets of data are available in which absolute measurements were made on fractions in decalin (decahydronaphthalene), one by Henry,[7] the other by Chiang.[8] The works discussed in the other references in Table 1 involve either whole polymers or the indirect determination of molecular weight in which the results in one solvent were converted into another, as described above. Since Henry's data appear to be more scattered than Chiang's, we prefer Chiang's results which give

$$[\eta]=62\times10^{-3}M^{0.70}\ \text{mL/g at }135^\circ \qquad (6)$$

in the range of 20 000–1 000 000 molecular weight. In Fig. 2, the data of Francis *et al.*[9] for unfractionated polyethylene are also plotted, showing the expected difference between fractionated and unfractionated samples.

3.2. 1,2,4-Trichlorobenzene

As shown in Table 1, nine separate determinations of K and a have been found in the literature for 1,2,4-trichlorobenzene with four based on the determination of absolute molecular weight of fractions. These are by Peyrouset *et al.*,[11] by Wagner and Hoeve,[4] by Wild *et al.*,[15] and by Williamson and Cervenka.[17] In all other cases, molecular weights were determined indirectly by viscosity measurements in some other solvent for which the Mark–Houwink constants were taken from the literature, or by SEC mea-

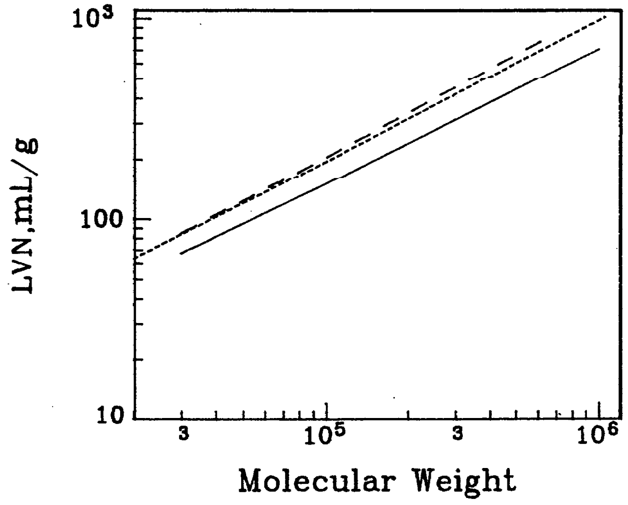

FIG. 2. Mark–Houwink relation for linear polyethylene in decalin. Solid line, Francis *et al.* (Ref. 9); dashed line, Henry (Ref. 7); dotted line, Chiang (Ref. 8). Molecular weights in g/mol.

surements which are subject to calibration errors. Again, these indirect methods are considered less desirable. A possible exception is found in the results of Barlow *et al.*,[18] who used an iterative procedure in conjunction with the published molecular weight distribution for the NBS Standard Reference Material 1475 to obtain the molecular weights of their fractions. Their results were very close to those of Wagner and Hoeve. The fractions used by Peyrouset *et al.* were obtained by preparative fractionation using size exclusion chromatography, and ranged in molecular weight from about 4000 to 680 000. For the very lowest molecular weight fractions molecular weights were not measured by the absolute methods used for the higher fractions but by vapor pressure osmometry, which is an indirect method. The fractions used by Wagner and Hoeve were obtained by column elution and ranged from about 9000 to 630 000. All the molecular weights were obtained by either light scattering or osmotic pressure. No data for individual fractions were given by Wild *et al.*, making it impossible to evaluate their results. Only four fractions were measured by Williamson and Cervenka—an insufficient number for establishing K and a reliably. Since it is difficult to choose between the first two results, and since, as shown in Fig. 3, the Mark–Houwink relations are so similar, both are listed and are equally recommended. From Ref. 11:

$$[\eta] = 52.6\times10^{-3}M^{0.70}\ \text{mL/g at } 135\,^\circ\text{C} \qquad (7)$$

in the range of 4000–680 000 molecular weight. From Ref. 4:

$$[\eta] = 39.2\times10^{-3}M^{0.725}\ \text{mL/g at } 139\,^\circ\text{C} \qquad (8)$$

in the range of 9000–630 000 molecular weight.

In Figure 4, these are plotted along with the other published values for fractions listed in Table 1. Most of the results are close to each other except for the data of Wild *et al.* and Whitehouse, as indicated in the figure.

In both figures, data are shown for NBS Standard Reference Materials 1482, 1483, and 1484, which are narrow fractions of linear polyethylene. The certified values of molecular weight and limiting viscosity number for these fractions are given in the Appendix.

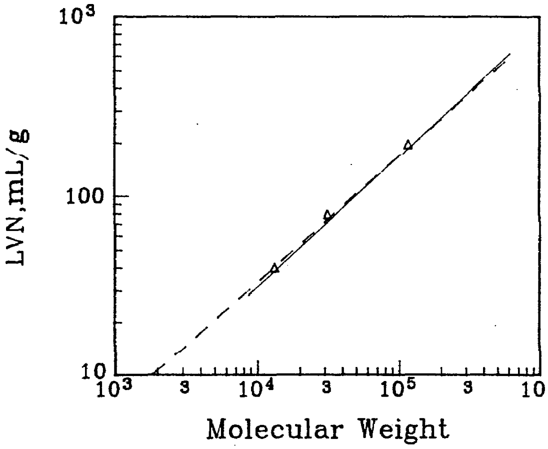

FIG. 3. Mark–Houwink relation for linear polyethylene in 1,3,4-trichlorobenzene. Solid line, Wagner and Hoeve (Ref. 4); dashed line, Peyrouset *et al.* (Ref. 11). Triangles represent certified values for SRM linear polyethylene fractions. Molecular weights in g/mol.

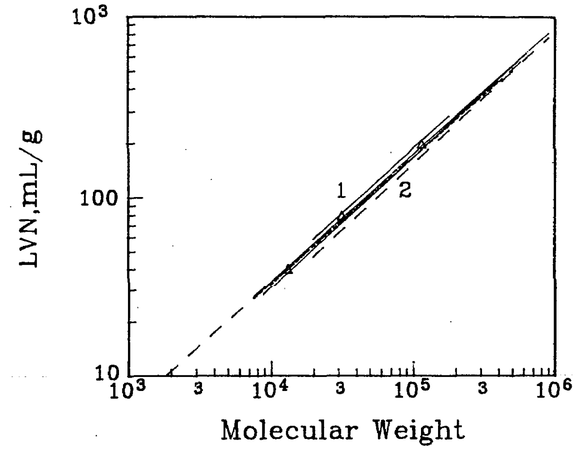

FIG. 4. Mark–Houwink relation for linear polyethylene in 1,2,4-trichlorobenzene. All the data in Table 1 are plotted. Line 1, Whitehouse (Ref. 13); line 2, Wild *et al.* (Ref. 15). Triangles are SRMs. Molecular weight in g/mol.

3.3. 1-Chloronaphthalene

As indicated in Table 1, only a few determinations have been made in 1-chloronapthalene, and only one since 1960. The older determinations were made either with poorly fractionated samples or with whole polymers. The more recent determination[4] was carried out with the same set of fractions used to obtain the Mark–Houwink constants in 1,2,4-trichlorobenzene and is the most reliable, giving

$$[\eta] = 55.5\times10^{-3}M^{0.684}\ \text{mL/g at } 130\,^\circ\text{C} \qquad (9)$$

in the range of 9000–630 000 molecular weight.

This is plotted, along with the other Mark–Houwink relations in Fig. 5. Since the samples used in obtaining these older relations were broader in molecular weight distribution, they lie below the line given by Eq. (9).

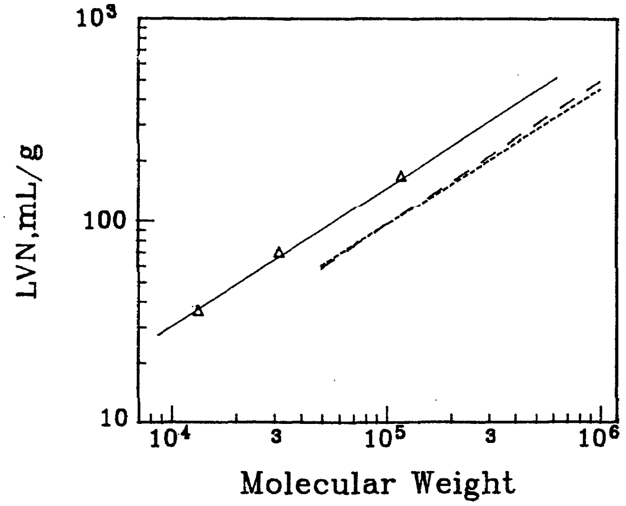

FIG. 5. Mark–Houwink relation for linear polyethylene in 1-chloronaphthalene. Solid line, Wagner and Hoeve (Ref. 4); dashed line, Kotera *et al.* (Ref. 19); dotted line, Atkins *et al.* (Ref. 20). Triangles are SRMs. Molecular weights in g/mol.

3.4. Tetralin

Although tetralin (tetrahydronaphthalene) had been generally used as a solvent for viscosity determinations when linear polyethylene was first available commercially, decalin is generally used for this purpose now. Tetralin has the disadvantage of forming hydroperoxides when in contact with air above 70 °C, resulting in the possibility of polymer degradation, particularly at the 130–135 °C temperature required for polyethylene viscosity measurements. Most of the data found in the literature for this solvent have some deficiencies and cannot be recommended as a reliable source of Mark–Houwink constants. For example, some authors did not indicate whether whole polymers or fractions were employed. When fractions were specified in some cases, viscosity and molecular weight values for the individual fractions were not given. The most reliable data appear to be those of Tung[21] (Fig. 6), who measured the number average molecular weight of his fractions by osmotic pressure, an absolute method, except for a few of the very low molecular weight fractions. For these, the molecular weight was measured by ebulliometry. In Fig. 6, a composite curve is also shown of several authors' data of varying quality, published by Wesslau.[22] The results of Kaufman and Walsh[23] are limited in molecular weight range. Therefore the recommended relation is Tung's

$$[\eta] = 51\times10^{-3} M^{0.725} \text{ mL/g at } 130\,^\circ\text{C} \qquad (10)$$

in the range of 3800 to 96 000 in number average molecular weight.

3.5. *o*-Dichlorobenzene

Of the two investigations of the Mark–Houwink relation for polyethylene in *o*-dichlorobenzene listed in Table 1, the more complete data are those found in the work of Dawkins and Maddock.[24] However, only five fractions of polyethylene were used. It is not clear whether the molecular weights of these fractions were obtained by viscosity measurements in decalin, requiring the use of a previously established Mark–Houwink relation, or whether they were determined by light scattering. The molecular weight range of the fractions is only from 20 000 to 188 000. Their values for the Mark–Houwink constants result in the equation

$$[\eta] = 50.6\times10^{-3} M^{0.7} \text{ mL/g at } 138\,^\circ\text{C}. \qquad (11)$$

Although not specifically stated in their paper, the single significant figure in the value of a may indicate considerable uncertainty.

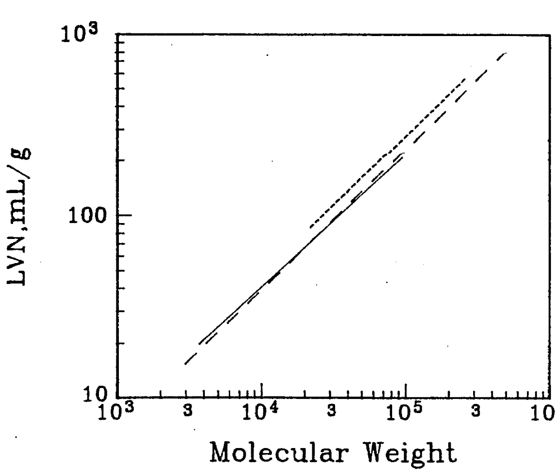

FIG. 6. Mark–Houwink relation for linear polyethylene in tetralin. Solid line, Wesslau (Ref. 22); dashed line, Kaufman and Walsh (Ref. 23); dotted line, Tung (Ref. 21). Molecular weights in g/mol.

3.6. Xylene

There are two sets of data for xylene as a solvent for viscosity determinations, one by Krigbaum and Trementozzi[26] and another by Trementozzi.[27] In the former, the number average molecular weights were obtained by osmotic pressure determinations for nine fractions ranging in molecular weight from 11 000 to 180 000, whereas in the latter set only four fractions were measured by light scattering to give M_n over a much narrower range of 140 000–180 000. The Krigbaum–Trementozzi result is therefore recommended,

$$[\eta] = 17.6\times10^{-3} M^{0.83} \text{ mL/g at } 105\,^\circ\text{C} \qquad (12)$$

for the range 11 000–180 000 in number average molecular weight.

3.7. Theta Solvents

Theta solvents are poor solvents and are not generally used for molecular weight determinations, but rather are used for estimating unperturbed dimensions.

One requisite of a θ solvent is that the exponent a in the Mark–Houwink relation be equal to 0.5, with the result that the variation in viscosity among different solvents is reflected only in the value of K. Theta condition viscosities have been measured in many solvents and it has been observed that K, and therefore the unperturbed dimensions of polyethylene, are remarkedly independent of the nature of the solvent when corrected for temperature.[28,29] In Table 2 are listed the values of K for various θ solvents and θ temperatures. Because of some temperature dependence, the K values at different temperatures will vary, but they are very similar nonetheless. The form of the Mark–Houwink equation for θ solvents is therefore

$$[\eta] = KM^{0.5}. \qquad (13)$$

Since the values of K reported by different workers for the same solvent are very close to each other, no attempt was made to choose among them. Almost all of the molecular weights were determined from the viscosity measurements in a good solvent, such as decalin, and the Mark–Houwink equation for that solvent. This is indicated by VISC in Table 2, whereas absolute determinations are designated by LS or MO for molecular weights determined by light scattering or membrane osmometry, respectively.

4. Acknowledgment

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Appendix 1. Molecular Weights and Limiting Viscosity Numbers of Linear Polyethylene Standard Reference Materials (SRMs)

		Limiting viscosity no. (mL/g)	
SRM	Molecular weight (weight average)	1,2,4-trichlorobenzene 130 °C	1-chloronaphthalene 130 °C
1482	13 600	40.2	36.4
1483	32 100	79.4	70.6
1484	119 600	197.9	169.4