The Mark–Houwink–Sakurada Relation for Poly(Methyl Methacrylate)

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In this third review of a series, the literature values for the viscosity-molecular weight relationship (Mark–Houwink–Sakurada) for poly(methyl methacrylate) have been critically evaluated. Although most of the studies have been concerned with conventionally produced poly(methyl methacrylate), some work has also been done with the isotactic polymer. The Mark–Houwink relations for the following solvents are discussed: benzene, toluene, acetone, chloroform, 2-butanone, and tetrahydrofuran, as well as for several other infrequently used solvents. The values of the coefficient K in the relation $[\eta] = KM^{0.5}$ for several theta solvents are also reported.

Key words: benzene; 2-butanone; chloroform; Mark–Houwink; methyl ethyl ketone; molecular weight; tetrahydrofuran; toluene; viscosity.

1. Introduction

This is the third in a series of reports critically evaluating the parameters K and a found in the literature for the Mark–Houwink (Mark–Houwink–Sakurada) expression:

LVN, or $[\eta] = KM^a$,

where LVN is the limiting viscosity number or the intrinsic viscosity $[\eta]$ (given here in units of mL/g), M is the molecular weight, and K and a are empirical constants. The first two reports[1,2] dealt with two widely used polymers, polyethylene, and polystyrene. The polymer considered here is poly(methyl methacrylate), (PMMA), which is also in widespread use. Unless otherwise mentioned, the data refer to conventionally produced PMMA which is generally considered to be a mixture of syndiotactic and isotactic forms of the polymer. As in the first two reports, most of the work to determine Mark–Houwink parameters was published during the period 1950–1970, and although absolute methods of measuring molecular weights were then available, the measurements were for the most part not made by absolute methods such as light scattering or osmotic pressure, but by indirect methods such as viscosity measurements and previously determined Mark–Houwink relations. As explained before,[1] this tends to increase the uncertainty of the final results. Error limits are not provided because the information in the literature is not sufficiently detailed.

2. The Mark–Houwink Constants for Poly(Methyl Methacrylate) in Various Solvents

2.1. Benzene

Determinations of the viscosity-molecular weight relations for poly(methyl methacrylate) in benzene have been published as far back as 1941.[3] However, after the publication in 1962 of the work of Fox *et al.*,[4,5] very little has appeared in the literature except for the paper of Moore and Fort[6] and that of Dobbin *et al.*[7] In the paper by Moore and Fort, the effect of temperature on the Mark–Houwink parameters was examined. Unfortunately most of the fractions were in the limited high-molecular weight range of from 300 000 to 400 000. This could result in a large error in estimating K and a values which are generally intended for use over a broad range of molecular weights. In the case of Dobbin *et al.* the parameters were derived from size exclusion chromatography on the unfractionated polymer. The latter authors believe that their method, although very useful, is not as reliable as the classical techniques employing fractions with molecular weights determined separately for each fraction. Their K and a values are inconsistent with those of other investigators.

In Table 1 the values of K and a published by several authors are listed together with the method of determining molecular weight and the molecular weight range. Fox *et al.* determined the number average molecular weights of a set of fractions ranging from 300 to 726 000 by ebulliometry and osmometry. The results were expressed in the form of two sets of parameters, one for molecular weights up to 44 000, the other from 44 000 to 726 000. As discussed previously[2] a is not usually constant over the entire molecular weight

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TABLE 1. Mark–Houwink constants—poly(methyl methacrylate) in benzene

Author	$T/°C$	$K/(10^{-3}$ mL/g)	a	No. of samples	M.W. range	M.W. method	Ref.
Baxendale *et al.*	25	7.45	0.76	10	60 000–100 000	membrane osmometry	8
Fox *et al.*							
($M_n > 44\,000$)	30	6.27	0.76	5	44 000–726 000	membrane osmometry	4
($M_n < 44\,000$)	30	104	0.5	10	300–44 000	membrane osmometry, ebulliometry	
Cohn-Ginsberg *et al.*							
($M_w > 35\,000$)	30	5.2	0.76	9	35 000–2.5×10^6	light scattering	5
($M_w < 35\,000$)	30	195	0.41	7	3 000–35 000	light scattering	
Schulz and Meyerhoff		5.5	0.76	10	25 000–7.5×10^6	sed/diffusion	9
Meyerhoff and Schulz		8.35	0.73	9	77 000–7.4×10^6	sed/diffusion	10
Eriksson	20	15.1	0.70	7	79 000–931 000	sed/diffusion	11
Moore and Fort	25 32 39 46 53 60	6.15 6.46 6.74 6.81 6.52 4.46	0.76 0.75 0.75 0.75 0.76 0.79	6	48 000–406 000[a]	membrane osmometry	6
Dobbin *et al.*		68.1	0.56	whole polymer	40 000–240 000	size exclusion chromatography	7

[a] Most of the fractions lie in the 300 000–400 000 range.

range and a value of 0.5 is expected in the low-molecular weight region.

The change in the value of a with molecular weight is attributable[12] to differences in the permeability of the polymer coil to the flow streamlines, resulting in free draining at low-molecular weight and partial draining at the higher ones. This change in a is continuous, but authors prefer to express the viscosity-molecular weight relationship in the simple Mark–Houwink form, especially since the molecular weight range covered by an investigator is usually sufficiently limited to provide a reasonably constant value of a. Theory suggests and experience generally confirms that the value of a is not less than 0.5, the value in theta solvents.

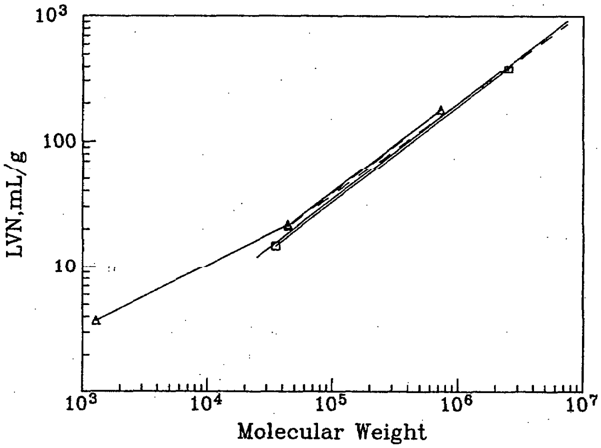

FIG. 1. Log limiting viscosity number vs long molecular weight of poly(methyl methacrylate) in benzene. Solid lines (squares), data of Cohn-Ginsberg *et al.* (Ref. 5). Solid lines (triangles), data of Fox *et al.* (Ref. 4). Dashed line, data of Meyerhoff and Schulz (Ref. 10). Solid line (no symbols) data of Schulz and Meyerhoff (Ref. 9).

In the paper by Cohn-Ginsberg *et al.*[5] in which the weight average rather than number average molecular weights were measured by light scattering on the same fractions used by Fox *et al.*, somewhat different values of K and a were obtained, reflecting a finite, although small, polydispersity of the fractions. However the value of 0.41 for a for molecular weights below 35 000 is likely to be in error. It is the belief of Fox *et al.* that although their results agree with much of the previous work in the literature, as shown in Fig. 1, their disagreement, where it occurred, was due to the very broad distributions of the fractions used by early investigators.[3,8] Most of the results shown in Fig. 1 may be well represented by the following relations provided by Fox and by Cohn-Ginsberg for poly(methyl methacrylate) prepared in the conventional way by free radical polymerization.

$$[\eta] = 6.27\times10^{-3}M_n^{0.76}\ \text{mL/g},\quad M > 44\,000\ (\text{at }30\,°\text{C}),$$

$$[\eta] = 104\times10^{-3}M_n^{0.5}\ \text{mL/g},\quad M < 44\,000,$$

when number average molecular weights are used, and

$$[\eta] = 5.2\times10^{-3}M_w^{0.76}\ \text{mL/g},\quad M > 35\,000,$$

when weight average molecular weights are used.

TABLE 2. Mark–Houwink constants—poly(methyl methacrylate) in toluene

Author	T/°C	$K(10^{-3}$ mL/g)	a	No. of samples	M.W. range	M.W. method	Ref.
Cohn-Ginsberg *et al.*	30	7.0	0.71	6	192 000–2.6×10^6	viscosity	5
Patrone and Bianchi ($M<70\,000$)	25	78	0.5	10	2 400–69 800	vapor pressure and membrane osmometry	15
Chinai *et al.*	25	7.1	0.73	7	410 000–3.2×10^6	light scattering	16
Moore and Fort	25	8.12	0.71	6	48 000–406 000[a]	membrane osmometry	6
	32	7.70	0.71				
	39	7.24	0.72				
	46	7.00	0.72				
	53	6.63	0.73				
	60	6.60	0.73				

[a] Most of the fractions lie in the 300 000–400 000 range.

Although several authors have found no differences in the Mark–Houwink relation for isotactic and conventionally produced PMMA, Krause and Cohn-Ginsberg[14] did find a difference in both acetone and benzene. However the difference in benzene is so small that the authors felt that a new Mark–Houwink equation was not necessary. As noted below, they do propose a new one for acetone.

2.2. Toluene

The four sets of data providing Mark–Houwink parameters for poly(methyl methacrylate) in toluene are shown in Table 2. In three of these, molecular weights were, for the most part, determined by absolute measurements and hence are preferred over the data of Cohn-Ginsberg *et al.*[5] who obtained their molecular weights from viscosity measurements in benzene. Patrone and Bianchi[15] carried out their measurements in the low-molecular weight region from 2400 to 70 000, and obtained a slope of 0.5, not an unexpected result for this range. The data of Moore and Fort[6] cover the molecular weight range from 48 000 to 406 000, with most of the points lying between 300 000 and 400 000. The data of Chinai *et al.*[16] range from 410 000 to 3.2×10^6. As shown in Fig. 2, the results of Patrone and Bianchi, and Chinai *et al.* can be considered to be very close to each other if it is assumed that the Chinai *et al.* relation may be extended down to a molecular weight of 70 000. The Cohn-Ginsberg data are in disagreement with both. The preferred, hitherto published, relations for poly(methyl methacrylate) in toluene at 25 °C are therefore:

$$[\eta]=78\times10^{-3}M^{0.5}\ \text{mL/g}\ (M<70\,000),$$

$$[\eta]=7.1\times10^{-3}M^{0.73}\ \text{mL/g}\ (M>70\,000).$$

However it is possible to combine the data from these two papers to obtain the single quadratic relation:

$$\log[\eta]=-0.272+0.0431\log M+0.0617(\log M)^2.$$

This relation provides a good fit of the data as shown in

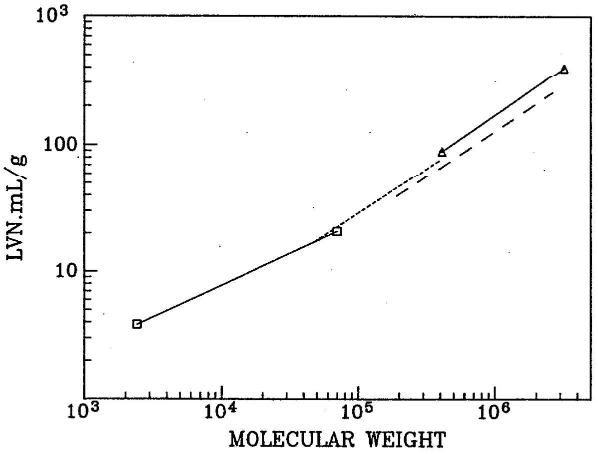

FIG. 2. Log limiting viscosity number vs log molecular weight of poly(methyl methacrylate) in toluene. Solid line (squares) data of Patrone and Bianchi (Ref. 14). Dotted line, data of Moore and Fort (Ref. 6). Solid line (triangles) data of Chinai *et al.* (Ref. 15). Dashed line, data of Cohn-Ginsberg *et al.* (Ref. 5).

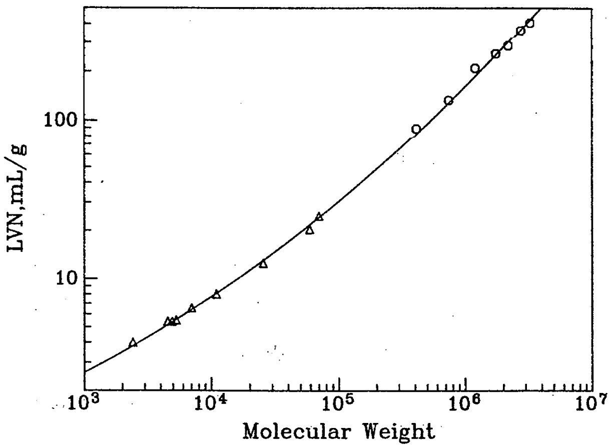

FIG. 3. Log limiting viscosity number vs log molecular weight of conventional poly(methyl methacrylate) in toluene. Data of Patrone and Bianchi (triangles) and of Chinai *et al.* (circles) fit to $\log[\eta]=-0.272+0.0431\log M+0.0617(\log M)^2$.

TABLE 3. Mark–Houwink constants—poly(methyl methacrylate) in acetone

Author	$T/^\circ C$	$K/(10^{-3}\ mL/g)$	a	No. of samples	M.W. range	M.W. method	Ref.
Bischoff and Desreux	25	7.5	0.70	9	80 000–1.4×10^6	light scattering	13
Schulz and Meyerhoff		5.5	0.73	10	25 000–7.4×10^6	sed/diffusion	9
Kapur	25	2.45	0.80	9	65 000–2×10^6	membrane osmometry	19
Cantow and Schulz		5.3	0.73	7	115 000–7.4×10^6	light scattering	18
Billmeyer and deThan	25	7.5	0.70	4 whole polymers	34 000–306 000	light scattering	20
				6 fractions	620 000–980 000		
Cohn-Ginsberg *et al.*	30	7.7	0.70	6	94 000–2.6×10^6	viscosity	5
Krause and Cohn-Ginsberg (isotatic PMMA)	30	23	0.63	7	54 000–1.13×10^6	light scattering	14
Moore and Fort	25	6.6	0.71	6	48 000–406 000^a	membrane osmometry	6
	32	6.5	0.71				
	39	6.4	0.72				
	46	6.2	0.72				
Dobbin *et al.*		5.02	0.618	whole polymer	40 000–240 000	size exclusion chromatography	7

^{a}Most fractions lie in the 300 000–400 000 range.

Fig. 3 and makes it possible to calculate molecular weight from viscosity over the molecular weight range of 3000 to 3×10^6.

McCrackin[17] has shown that it is possible to fit this and other data to Han's equation using an only two-parameter fit.

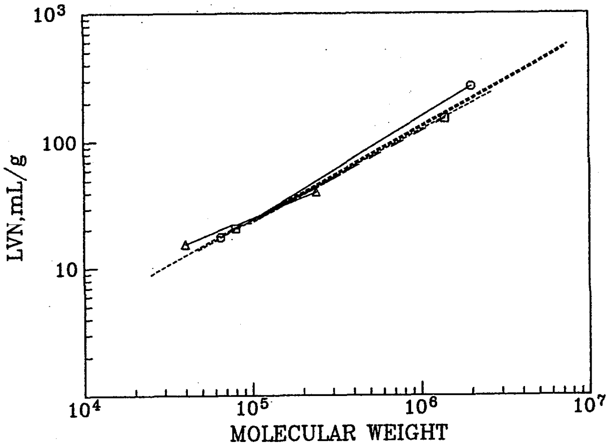

FIG. 4. Log limiting viscosity number vs log molecular weight of conventional poly(methyl methacrylate) in acetone. Dashed line (squares) data of Bischoff and Desreux (Ref. 12). Dotted lines, data of Cohn-Ginsberg *et al.* (Ref. 5), Schultz and Meyerhoff (Ref. 9), Cantow and Schulz (Ref. 16), and Moore and Fort (Ref. 6). Solid line (circles) data of Kapur (Ref. 17). Solid line (triangles) data of Dobbin *et al.* (Ref. 7).

2.3. Acetone

Most of the viscosity data for poly(methyl methacrylate) in acetone (Table 3) was acquired in the 1950s and the more reliable data, such as that of Bischoff and Desreux[13] and of Schulz and Meyerhoff[9] agree well with the later data of Cohn-Ginsberg *et al.*[5] It is possible that the somewhat higher value of a, 0.73, found by Schulz and Meyerhoff and by Cantow and Schulz,[18] rather than the 0.70 value found by

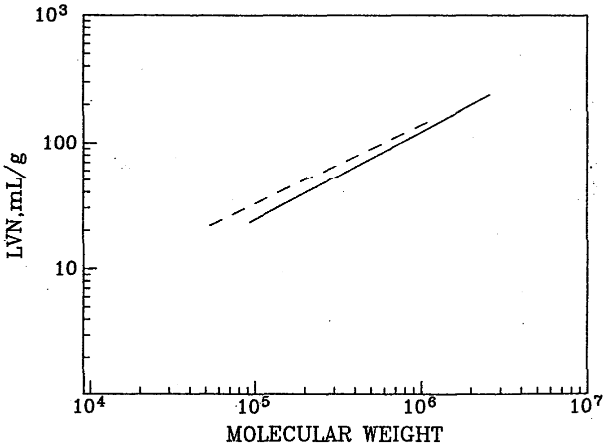

FIG. 5. Log limiting viscosity number vs log molecular weight of conventional and isotactic poly(methyl methacrylate) in acetone. Solid lines, data of Cohn-Ginsberg *et al.* (Ref. 5) for conventional poly (methyl methacrylate). Dashed line, data of Kraus and Cohn-Ginsberg (Ref. 13) for isotactic poly(methyl methacrylate).

TABLE 4. Mark–Houwink constants—poly(methyl methacrylate) in chloroform

Author	T/°C	K/(10^{-3} mL/g)	a	No. of samples	M.W. range	M.W. method	Ref.
Bischoff and Desreux	25	4.8	0.80	9	83 000–1.5×10^6	light scattering	13
Meyerhoff and Schulz		4.85	0.80	9	77 000–7×10^6	sed/diffusion	10
Cohn-Ginsberg *et al.*	30	4.3	0.80	8	130 000–2.6×10^6	viscosity	5
Schulz and Meyerhoff		5.5	0.79	9	25 000–7.5×10^6	sed/diffusion	9
Schulz *et al.*		5.5	0.79	9	145 000–7.6×10^6	light scattering sed/diffusion	21
Tsvetkov and Klenin		5.1	0.79	15	60 000–3.7×10^6	sed/diffusion	22
Chinai *et al.*	25	3.4	0.83	6	410 000–3.3×10^6	light scattering	16
Cantow and Schulz		6.0	0.79	9	25 000–7.8×10^6	light scattering	18
Dobbin *et al.*		11.7	0.755	whole polymer	40 000–240 000	size exclusion chromatography	7
Moore and Fort	25	5.81	0.79	6	48 000–406 000[a]	membrane osmometry	6
	32	5.24	0.80				
	39	5.02	0.80				
	46	4.89	0.80				
	53	3.90	0.82				

[a] Most of the fractions lie in the 300 000–400 000 range.

the other investigators is due to curvature in the 7 000 000 molecular weight region. From Fig. 4 it may be seen that most of the results may be represented by a single relation such as the one of Bischoff and Desreux:

$$[\eta]=7.5\times10^{-3}M^{0.70}\ \text{mL/g (at 25 °C)}.$$

Two sets of results differ markedly from the above. One, as in the case of benzene, is the K and a generated by Dobbin *et al.*[7] from size exclusion chromatography. As before, these are not expected to be as reliable as the classically derived parameters. Another exception is the a value of 0.80 of Kapur,[19] which is much greater than that obtained by other workers. Measurements of molecular weight greater than 500 000 by osmotic pressure are difficult and can be highly inaccurate, because of the inverse relation between osmotic pressure and molecular weight. This would contribute to a large uncertainty and may explain the large value of a reported. In Fig. 4 it is seen that the greatest difference between Kapur's Mark–Houwink relation and those of the other investigators occurs at the higher molecular weight where the error in osmotic pressure would be the greatest.

The data of Krause and Cohn-Ginsberg,[14] Fig. 5, illustrate the effect of isotacticity. In contrast to the case of benzene, where as indicated above, the effect is minimal, the K and a values for the isotactic poly(ethyl methacrylate) are quite different from those of the conventionally produced polymer. They found the Mark–Houwink equation for isotactic poly(methyl methacrylate) to be

$$[\eta]=23\times10^{-3}M^{0.63}\ \text{mL/g (at 30 °C)}.$$

2.4. Chloroform

There is very close agreement in the literature for the value of the Mark–Houwink parameters for poly(methyl methacrylate) in chloroform, with most investigators determining the molecular weights of fractions by absolute techniques. It is difficult to choose between the results of Bischoff and Desreux[13] and Meyerhoff and Schulz,[10] which are almost identical, as seen in Table 4. Both fall in the middle range of K and a values. The latter is recommended only because of the wider range of molecular weights employed.

$$[\eta]=4.85\times10^{-3}M^{0.80}\ \text{mL/g (at 25 °C)}.$$

The only set of data seriously disagreeing with the above relation is again due to Dobbin *et al.*[7] which was obtained using size exclusion chromatography.

2.5. 2-Butanone (Methyl Ethyl Ketone)

The viscosity data of Billmeyer and deThan for PMMA in butanone[20] covering a very wide range of molecular weights from 34 000 to 9.8×10^6, although obtained with four whole polymers and six fractions, agree very closely with the results obtained over a more limited range by Bischoff and Desreux.[13] As seen in Table 5, the results of the other investigators are also very similar. We therefore choose Bischoff and Desreux's parameters for the Mark–Houwink relation:

$$[\eta]=6.8\times10^{-3}M^{0.72}\ \text{mL/g (at 25 °C)}.$$

TABLE 5. Mark–Houwink constants—poly(methyl methacrylate) in butanone

Author	$T/°C$	$K/(10^{-3}$ mL/g)	a	No. of samples	M.W. range	M.W. method	Ref.
Cohn-Ginsberg *et al.*	30	6.83	0.72	3	$221\,000–1.7\times10^6$	viscosity	5
Chinai *et al.*	25	7.1	0.72	7	$410\,000–3.5\times10^6$	light scattering	16
Bischoff and Desreux	25	6.8	0.72	4	$760\,000–1.4\times10^6$	light scattering	13
Billmeyer and deThan	25	6.8	0.72	4 whole polymers	34 000–306 000	light scattering	20
				6 fractions	620 000–980 000	light scattering	

TABLE 6. Mark–Houwink constants for poly(methyl methacrylate) in THF

Author	$T/°C$	$K/(10^{-3}$ mL/g)	a	No. of samples	M.W. range	M.W. method	Ref.
Rudin and Hoegy (data of Grubisic *et al.*)	25	12.8	0.69	5	$170\,000–1.3\times10^6$	light scattering	23
Janca *et al.*	25	0.859	0.887	5	$27\,000–2.3\times10^6$	viscosity	25
Dobbin *et al.*		19.9	0.66	whole polymer	40 000–240 000	size exclusion chromatography	7
Provder *et al.*							
($M<31\,000$)	25	211	0.406			light scattering	27
($M>31\,000$)		10.4	0.697			membrane osmometry	

2.6. Tetrahydrofuran (THF)

There appears to be little agreement and poor documentation in the accounts describing the determination of the Mark–Houwink relation for poly(methyl methacrylate) in tetrahydrofuran (THF), as shown in Table 6. Dobbin *et al.*[7] obtained their values for K and a via size exclusion chromatography, which, as noted before, does not necessarily provide the most accurate value of K and a, and in addition, is limited in molecular weight range. Rudin and Hoegy[23] have calculated the Mark–Houwink parameters from the data obtained on five fractions by Grubisic *et al.*,[24] which is also limited to a molecular weight range of 170 000 to 300 000. The range of Janca *et al.*[25] data is greater, but the molecular weights were determined using a Mark–Houwink relation in benzene which was never published. Their a value is unusually high, 0.887, and is in contrast to the approximately 0.7 value of the other authors. Ouano[26] gives a value of 0.73 for a but the value of K is reported only in graphical form. The values given by Provder *et al.*[27] are the best available, his "true values" appear to be based on the directly measured molecular weights determined by osmotic pressure and light scattering. Unfortunately specific data and other details of the measurement are not provided. They found the Mark–Houwink exponent for molecular weights less than 31 000 to be 0.406 rather than 0.5, which as noted above, is in contradiction to both theory and most experimental results. For molecular weights greater than 31 000, the expression of Provder *et al.* is

$$[\eta] = 10.4\times10^{-3}M^{0.697}\ \text{mL/g}\ (M>31\,000)\ (\text{at } 25\ ^\circ\text{C}).$$

2.7. Other Solvents

Mark–Houwink parameters are also available for a variety of other solvents. These solvents are rarely employed for viscosity measurements however and usually only one literature reference per solvent could be found, so that a critical comparison could not be made. These are listed in Table 7.

TABLE 7. Mark–Houwink constants for poly(methyl methacrylate) in infrequently used solvents

Solvent Author	T/°C	$K/(10^{-3}$ mL/g)	a	No. of samples	M.W. range	M.W. method	Ref.
N-amyl methyl ketone							
Moore and Fort	25	50.6	0.51	6	48 000–406 000[a]	membrane osmometry	6
	32	41.1	0.53				
	39	35.0	0.55				
	46	24.3	0.57				
	53	7.12	0.69				
	60	10.4	0.65				
Ethylene dichloride							
Cohn-Ginsberg *et al.*	30	5.3	0.77	7	63 000–2.6×10^6	viscosity	5
Billmeyer and deThan	25	17	0.68				20
N,N-Dimethylformamide							
Kossler *et al.* (using Kambe's data)	10 (M_w)	29.4	0.594	8	83 000–1.1×10^6	light scattering, membrane osmometry	28, 29
	25 (M_w)	25	0.625				
	30 (M_w)	20.7	0.628				
	50 (M_w)	20.7	0.632				
	25 (M_n)	40.4	0.787	8			
Ethyl acetate							
Erikkson	20	21.1	0.64	8	79 000–931 000	sed/diffusion	11
Methyl isobutyrate							
Cohn-Ginsberg *et al.*	30	99	0.67	6	192 000–2.6×10^6	viscosity	5
Nitroethane							
Casassa and Stockmayer	25	5.70	0.74	2 fractions 6 whole polymers	100 000–537 000 21 000–1.7×10^6	light scattering	30
Tetrachloroethane							
Moore and Fort	25	12.8	0.73	6	48 000–406 000[a]	membrane osmometry	6
	32	12.6	0.73				
	39	12.5	0.73				
	46	12.4	0.73				
	53	12.2	0.73				
2,2,3,3, Tetrafluoropropane							
Hamori *et al.*							
conventional	25	7.2	0.79	7	77 000–915 000	viscosity	31
isotactic	25	7.05	0.78	11	280 000–995 000	viscosity	

[a] Most of the fractions lie in the 300 000–400 000 range.

2.8. Theta Solvents

As indicated previously,[2] theta solvents are rarely used for molecular weight determinations, except perhaps in the case of polystyrene in cyclohexane, but are useful for estimating unperturbed dimensions. This application has been of particular interest in the case of poly(methyl methacrylate) in further demonstrating the differences between atactic and isotactic configurations.[32]

For theta solvents the Mark–Houwink exponent a according to well established theory,[33] is 0.5, so that the equation takes the form:

$$[\eta] = KM^{0.5}.$$

Although the value of K is fairly constant for most polymers in theta solvents, some variation has been noted for PMMA not only with solvent but also with molecular weight for the same solvent. Some of this may be due to experimental error, but some may also be due to a variation of tacticity among fractions. In the compilation in Table 8 most molecular weights used to evaluate K were determined from viscosity measurements and the Mark–Houwink relations for one of the nontheta solvents listed above. However, light scattering and end group analyses were employed to determine molecular weight by Krause and Cohn-Ginsberg for their work with isotactic PMMA in acetonitrile.[32]

TABLE 8. Values of K in theta solvents for conventional poly(methyl methacrylate) unless otherwise specified

Solvent Author	T/°C	$K/(10^{-3}$ mL/g)	No. of samples	M.W. range	M.W. method	Ref.
Acetonitrile						
Fox (conventional PMMA)	45	42–57 (varies with M)	6	102 000–2.6×10^6	viscosity	34
Krause and Cohn-Ginsberg (isotactic PMMA)	27.6	75.5	5	28 000–187 000	light scattering, end group analysis, viscosity	32
Butyl Chloride						
Inagaki and Kawai	35.4	5.92	4	130 000–676 000	sed/diffusion	35
p-Cymeme						
Sakurada *et al.*						
conventional PMMA	159.7	57.5	4	66 000–1.7×10^6	viscosity	36
isotactic PMMA	152.1	56.6	4	66 000–1.3×10^6	viscosity	
3-Heptanone						
Sakurada *et al.*						
conventional PMMA	33.7	63.1	4	66 000–1.7×10^6	viscosity	36
isotactic PMMA	40.0	87.0	4	66 000–1.3×10^6	viscosity	
4-Heptanone						
Fox	31.5– 33.8 (varies with M)	43–67	6	8 000–1.7×10^6	viscosity	34
3-Octanone						
Fox	72	48–53	3	127 000–2.6×10^6	viscosity	34
n-Propanol						
Sakurada *et al.*						
conventional PMMA	84.4	68	4	66 000–1.7×10^6	viscosity	36
isotactic PMMA	75.9	76.1	4	66 000–1.3×10^6	viscosity	
Butanone/Isopropanol 1:1						
Chinai and Bondurant						
conventional PMMA	25	59.2	7	300 000–2.8×10^6	light scattering	37
Sakurada *et al.*						
isotactic PMMA	30.3	90	4	66 000–1.3×10^6	viscosity	36

TABLE 9. Recommended viscosity-molecular weight relations for poly(methyl methacrylate)

Solvent	T/°C	Equation
Benzene		
$M_n < 44\,000$	30	$[\eta] = 104\times10^{-3}\,M_n{}^{0.5}$
$M_n > 44\,000$	30	$[\eta] = 6.27\times10^{-3}\,M_n{}^{0.76}$
$M_w < 35\,000$	30	$[\eta] = 5.2\times10^{-3}\,M_w{}^{0.76}$
Toluene		
$M < 70\,000$	25	$[\eta] = 78\times10^{-3}\,M^{0.5}$
$M < 70\,000$	25	$[\eta] = 7.1\times10^{-3}\,M^{0.73}$
	25	$\log[\eta] = -0.272 + 0.0431 \log M + 0.0617(\log M)^2$
Acetone		
Conventional PMMA	25	$[\eta] = 7.5\times10^{-3}\,M^{0.70}$
Isotactic PMMA	30	$[\eta] = 23\times10^{-3}\,M^{0.63}$
Chloroform	25	$[\eta] = 4.8\times10^{-3}\,M^{0.80}$
2-Butanone (MEK)	25	$[\eta] = 6.8\times10^{-3}\,M^{0.72}$
Tetrahydrofuran (THF)		
$M > 31\,000$	25	$[\eta] = 10.4\times10^{-3}\,M^{0.697}$

2.9. Recommended Values of *K* and *a*

The recommended viscosity-molecular weight relations for conventional poly(methyl methacrylate), unless otherwise noted, are give in Table 9.

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