Viscometric Determination of the Molecular Weight of Polymers in the Low Molecular Weight Region

CONSTANTINOS TSITSILIANIS and GEORGE STAIKOS,
Department of Chemical Engineering, University of Patras, GR-26110 Patras, Greece

Synopsis

In order to overcome the difficulty of the determination of the molecular weight of a polymer in the low molecular weight region by viscometry using the Mark–Houwink–Sakurada (MHS) equation, we have proposed the Dondos–Benoit relationship $[\eta]^{-1} = -A_2 + AM^{-1/2}$, for a number of polymer–solvent systems, for which we give the numerical values of the parameters A_1 and A_2. Furthermore, we suggest a method for the determination of the above parameters using the MHS constants a and k.

INTRODUCTION

It is well known that viscometry, which is subjected to a very small experimental error and does not require a complex instrumentation, is the most popular method for the determination of the molecular weight of the polymers. The dependence of the intrinsic viscosity $[\eta]$ on the molecular weight M of a polymer is usually described by the empirical Mark–Houwink–Sakurada (MHS) relation

$$[\eta] = kM^a \tag{1}$$

where the parameters k and a depend on the nature of the polymer and on the polymer–solvent interactions.[1] The exponent a tends to the limit 0.8 or 0.77 according to recent calculations,[2] as the solvent quality gets better. Unfortunately, this equation is not valid in the region of the low molecular weights,[3,4] where the exponent a approaches the limit 0.5, the value which characterizes the behavior of a polymer in θ conditions, so that a rather complicated correction of the MHS equation is required for the determination of the molecular weight of a polymer in the low-molecular-weight region.[5]

Dondos and Benoit,[6] using the idea of segment density[7] for the interpretation of the viscosity data, have introduced the following semiempirical relation, particularly applicable in the low-molecular-weight region:

$$[\eta]^{-1} = -A_2 + A_1M^{-1/2} \tag{2}$$

where A_2 is a constant characteristic of the polymer–solvent pair and A_1 is a constant characteristic of the polymer. The parameter A_2 is a measure of the goodness of the solvent and is equal to zero at θ conditions. The parameter A_1

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has been correlated[5] with the unperturbed dimensions parameter K_θ and it is approximately equal to K_θ^{-1}.

In this paper we test the Dondos–Benoit (DB) eq. (2) for a large number of polymer–solvent systems. In the following we present a comparison between this equation and the MHS equation in the determination of the molecular weight of polymers in the low-molecular-weight region, and finally we propose an equation giving the A_2 parameter of the DB equation as a function of the MHS exponent a.

RESULTS AND DISCUSSION

In Figure 1 $[\eta]^{-1}$ is plotted as a function of $M^{-1/2}$ according to eq. (2) for the following four polymer–solvent systems: (a) polystyrene (PS)/tetrahydro-

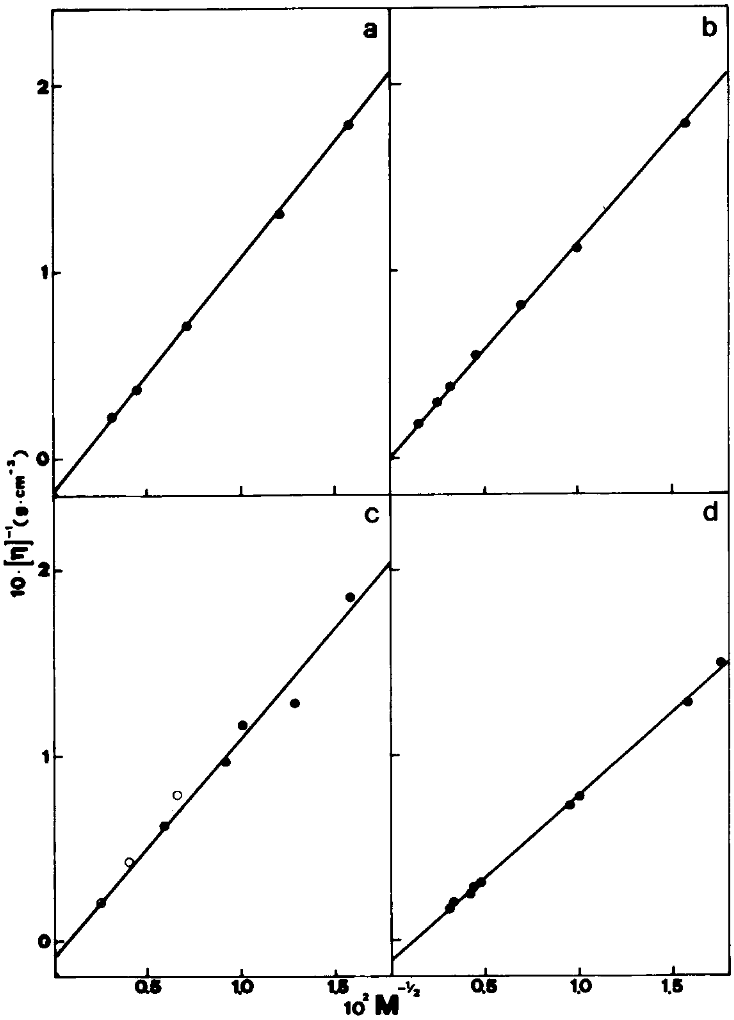

Fig. 1. Plots of $[\eta]^{-1}$ vs. $M^{-1/2}$ for the following polymer–solvent systems: (a) PS/tetrahydrofuran, at 25°C (our data); (b) PS/cyclohexane, at 34.5°C (data from Ref. 4); (c) PMMA/benzene, at 25°C [data from Ref. 15 (○) and this work (●)]; (d) PVAc/acetone at 60°C (data from Ref. 17).

TABLE I
The Dondos–Benoit Equation for Various Polymer–Solvent Systems

Polymer	Solvent	T (°C)	Dondos–Benoit equation, intrinsic viscosity $[\eta]$ (cm^3 g^{-1})	Mol wt range ($M \times 10^{-3}$)	MHS exponent a[a]	Ref.
PS	Tetrahydrofuran	25	$[\eta]^{-1} = -18 \times 10^{-3} + 12.3M^{-1/2}$	4–110	0.76	This work
PS	Cyclohexane	34.5	$[\eta]^{-1} = 11.3\,M^{-1/2}$	4–411	0.50	4
PS	Benzene	25	$[\eta]^{-1} = -16.3 \times 10^{-3} + 11.4M^{-1/2}$	4–160	0.75	4.10
PS	Chloroform	25	$[\eta]^{-1} = -12.2 \times 10^{-3} + 10.7M^{-1/2}$	3–105	0.75	7
PS	Toluene	25	$[\eta]^{-1} = -11.6 \times 10^{-3} + 11.1M^{-1/2}$	2–125	0.74	11,12,13
PS	Butanone	25	$[\eta]^{-1} = -6.9 \times 10^{-3} + 12.7M^{-1/2}$	3–125	0.60	13
PS	*Cis*-decalin	25	$[\eta]^{-1} = -10.1 \times 10^{-3} + 13.4M^{-1/2}$	4–120	0.57	14
PS	*Trans*-decalin	30	$[\eta]^{-1} = -1.8 \times 10^{-3} + 12.2M^{-1/2}$	35–379	0.54	9
PS	*Trans*-decalin	40	$[\eta]^{-1} = -4.1 \times 10^{-3} + 12.4M^{-1/2}$	35–379	0.57	9
PS	*Trans*-decalin	50	$[\eta]^{-1} = -5.6 \times 10^{-3} + 12.5M^{-1/2}$	35–379	0.595	9
PS	*Trans*-decalin	65	$[\eta]^{-1} = -6.8 \times 10^{-3} + 12.4M^{-1/2}$	35–379	0.615	9
PS	*Trans*-decalin	80	$[\eta]^{-1} = -7.5 \times 10^{-3} + 12.5M^{-1/2}$	35–379	0.63	9
PS	Dioxane	25	$[\eta]^{-1} = -10.4 \times 10^{-3} + 11.6M^{-1/2}$	10–210	0.66	This work
PMMA	Benzene	25	$[\eta]^{-1} = -4.7 \times 10^{-3} + 11.5M^{-1/2}$	4–150	0.76	15, this work
PMMA	Toluene	25	$[\eta]^{-1} = -2.5 \times 10^{-3} + 12.8M^{-1/2}$	2–70	0.72	8, 16
PVAc	Acetone	6	$[\eta]^{-1} = -11.2 \times 10^{-3} + 8.9M^{-1/2}$	3–110	0.72	17
PV_2P[b]	Ethanol	25	$[\eta]^{-1} = -13.4 \times 10^{-3} + 9.2M^{-1/2}$	7–200	0.74	This work
PtBS[c]	Tetrahydrofuran	30	$[\eta]^{-1} = -16.8 \times 10^{-3} + 15.2M^{-1/2}$	27–175	0.70	18

[a] Calculated from viscometric data in the medium and high mol wt region.

[b] Poly(vinyl-2-pyridine).

[c] Poly(*t*-butyl styrene).

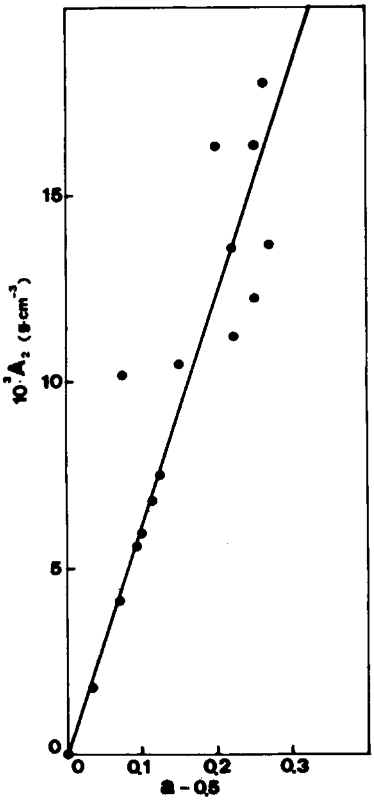

Fig. 2. Variation of the parameter A_2 of the DB equation as a function of the MHS exponent a.

furan at 25°C, (b) PS/cyclohexane at 34.5°C, (c) poly(methyl methacrylate) (PMMA)/benzene at 25°C and polyvinylacetate (PVAc)/acetone at 6°C. The molecular weight of the polymers was lower than 200,000. As we can see, there exists a good linearity, observed even for molecular weights down to 3000, and this permits us to use the eq. (2) for the determination of the molecular weight of a polymer in the above mentioned molecular weight region.

In Table I we give the DB equation for a great number of polymer–solvent systems. The viscosimetric results have been taken mainly from the literature, and some of them have been obtained by us. The numerical values of the constants A_1 and A_2 have been obtained by linear regression of the eq. (2).

We have to point out here that it is rather difficult to find in the literature viscometric data extending to the low molecular weight region for many polymers and so to calculate the constants of eq. (2). In order to overcome this difficulty, we tried to calculate the values of the constants A_2 and A_1, using the MHS constants encountered in abundance in the literature.[8]

In Figure 2 we present the relation between the constant A_2 of the DB equation and the exponent of the MHS equation for a number of polymer–solvent systems. This relation is described by the following equation:

$$A_2 = 65.2 \times 10^{-3}(a - 0.5) \qquad (3)$$

TABLE II
Comparison between M_{DB} and M_{MHS} for Some Polymer Samples

Sample	M_w	Solvent	$[\eta]$ ($cm^3\ g^{-1}$)	Ref.	M_{MHS}[a]	M_{DB}
PS	4000	Benzene	6.0	4	7900[b]	3900
PS	4800	Benzene	6.7	5	8200[b]	4700
PS	7700	Benzene	8.4	5	11,200[b]	7100
PS	20,400	Benzene	15.9	4	5800[b]	20,700
PS	2000	Toluene	4.7	11	5200[c]	2400
PS	20,400	Toluene	15.5	11	26,400[c]	21,300
PMMA	2600	Benzene	4.7	This work	7200[d]	2800
PV_2P	3450	Ethanol	7.0	This work	4800[e]	3500

[a] The Mark–Houwink–Sakurada molecular weight M_{MHS} has been calculated through the equations shown in footnotes b–e.

[b] $[\eta] = 7.8 \times 10^{-3} M^{0.75}$, Ref. 4.

[c] $[\eta] = 8.62 \times 10^{-3} M^{0.736}$, Ref. 11.

[d] $[\eta] = 5.5 \times 10^{-3} M^{0.76}$, Ref. 15.

[e] $[\eta] = 1.33 \times 10^{-2} M^{0.74}$, this work.

It is clear now that we can use the eq. (3) in order to calculate the value of A_2 for any system for which the exponent a is known.

We have already pointed out that the parameter A_1 is approximately equal to K_θ^{-1}. Therefore, A_1 could be calculated using the known K_θ value of a polymer[8] or through a K_θ calculated by the method of Munk and Gutierrez.[9] According to this method, knowing the MHS parameters k and a of a system, we can calculate the K_θ value of a polymer. We can conclude here that if we know the MHS parameters k and a, we can calculate the parameter A_2 of the DB equation, through eq. (3) and the parameter A_1 using the Munk and Gutierrez method, if we do not know the value of K_θ.

APPLICATIONS—CONCLUSIONS

In order to check the above formulation, we have calculated the molecular weight of some polymer samples using the viscometric equations of Table I. Table II shows the results of these calculations in comparison with those resulting from the MHS equation. As we can see in Table II, the molecular weights calculated by the DB equation, M_{DB}, are in excellent agreement with those determined by light scattering techniques, M_w. On the other hand, the MHS equation, as expected, does not give correct results in the low molecular weight region which is considered here.

In conclusion we point out that the Dondos–Benoit equation (2) could be used for the determination of the molecular weights of polymers by viscometry if we are in the low molecular weight region, i.e., $M < 100{,}000$.

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