Practical Evaluation of the [η]–M Relationship

D. W. VAN KREVELEN and P. J. HOFTYZER, *Algemene Kunstzijde Unie (AKU), Arnhem, The Netherlands*

Synopsis

The Mark-Houwink equation for the relationship between the intrinsic viscosity of a polymer solution and the molecular weight can be expressed in the more general form: $[\eta] = 32K_\theta(M/1000)^a$, where the constant K_θ has a theoretical meaning and the constant a is approximately equal to 0.7.

Introduction

The intrinsic viscosity $[\eta]$ of a polymer solution is defined as[1,2]

$$[\eta] = \lim_{\substack{c \to 0 \\ s \to 0}} (\eta - \eta_0)/\eta_0 c \qquad (1)$$

where η is the viscosity of the solution, η_0 is the viscosity of the solvent, c is concentration of polymer, and s is the shear rate.

The units used for the viscosities η and η_0 can be chosen arbitrarily, as they cancel in eq. (1). The dimension of a reciprocal concentration for $[\eta]$ is retained, however, with the above definition. Unfortunately, different concentration units are used by different authors, and in some papers the units are not even mentioned. In this paper, the concentration unit to be used will be grams per 100 cubic centimeters, as in the greater part of the literature.*

For a given combination of polymer and solvent, and at a given temperature, the intrinsic viscosity appears to be a unique function of the molecular weight M. This function is generally expressed in the form of a simple power function:

$$[\eta] = KM^a \qquad (2)$$

containing two empirical constants, K and a. This relationship is often called the Mark-Houwink equation.[3] In practice, the molecular weight M is always a distributed quantity. The constants K and a are therefore based on measurements of polymer fractions with a very narrow molecular weight distribution. If applied on an unfractionated polymer it gives the so-called viscosity-average molecular weight ($\bar{M}_v$).

* We believe, however, that a dimensionless concentration unit is to be preferred. A suitable dimensionless concentration unit would be the number of gram equivalents of monomer units present in the dissolved polymer, divided by the number of gram molecules of solvent.

Once this relationship has been determined for a given system, it provides the possibility of rapid routine determinations of the molecular weight of a given polymer, on the understanding that the molecular weight distribution remains the same. A large number of values of K and a for several systems can be found in the literature.

As for each combination of polymer and solvent different values for K and a have been found, these values should in some way be characteristic of the nature of the polymer and of the polymer–solvent interaction. Several attempts have been made to give the empirical $[\eta]$–M relationship a theoretical basis. Although these studies have led to a number of interesting conclusions, a complete theoretical interpretation of intrinsic viscosity data does not yet exist.

Another important point is the possibility of predicting the $[\eta]$–M relationship for an arbitrary combination of polymer and solvent. An ideal starting point for such a prediction would be a theoretical basis of the phenomena, as mentioned above. Failing such a basis, in this paper an attempt is made to derive a new empirical method for predicting the $[\eta]$–M relationship.

The Empirical Relationship $[\eta] = KM^a$

As has been stated before, up to now all attempts to provide a theoretical basis for eq. (2) have failed. On the contrary, in some cases where a theoretical approach has been rather successful, a plot of $[\eta]$ against M on a log-log scale showed a curved line.

This means that the correlation of experimental points by means of straight line on a log-log scale, and so also eq. (2), should be considered an approximation only.

This is in accordance with the large deviations in the values for constants K and a, shown by literature data. Even in measurements with the same combination of polymer and solvent, but performed by different investigators, different values for K and a have been found.

It appears that the literature values for K and a for a given system are not independent, but show a distinct regression. This is to be expected, if eq. (2) is an approximation of a curved line. If for the approximation a lower value of a is chosen, a higher value of K must be used for agreement with the experimental data.

An extreme example of this effect can be found in two literature values for the $[\eta]$–M relationship of polyvinylpyrrolidone in water. One article[4] mentions the values $K = 6.76 \times 10^{-4}$ and $a = 0.55$, whereas another article[5] gives $K = 4.1 \times 10^{-5}$ and $a = 0.85$. These two relationships coincide at $[\eta] = 0.116$ for $M = 1.15 \times 10^4$, that is, within the experimental region of M values mentioned in both articles.

For a large number of literature data, the following regression was found by us:

$$\log K = -1.42 - 3.00a \tag{3}$$

TABLE I
Values of a for Some Polymer–Solvent Systems

Polymer	a							
	Benzene	Toluene	Xylene	Cyclo-hexane	Tetralin	Decalin	Acetone	Methyl ethyl ketone
Polyethylene (low pressure)			0.83		0.76	0.72		
Polyethylene (high pressure)			0.63			0.74		
Polypropylene (atactic)	0.69	0.73	0.63	0.78		0.79		
Polypropylene (isotactic)					0.90	0.80		
Rubber	0.74	0.67		0.72				
Polybutadiene	0.77			0.74				
Polyisobutylene	0.60	0.63		0.71				
Polystyrene	0.74	0.71		0.50				0.61
Polymethoxystyrene		0.62						0.68
Polychlorostyrene		0.64						0.59
Poly(methyl methacrylate)		0.73					0.71	0.72
Poly(vinyl acetate)	0.64						0.71	0.71
Poly(vinyl methyl ether)	0.60							0.58

A number of natural polymers, e.g., carbohydrates and their derivatives, showed a different behavior. They were left out of considerations in the regression analysis leading to eq. (3).

Combination of eqs. (2) and (3) leads to

$$[\eta] = 0.032 \ (M/1000)^a \qquad (4)$$

Equation (4) provides a first approximation of the relationship between $[\eta]$ and M for an arbitrary combination of polymer and solvent in which only one empirical constant, a, is retained.

The value of a appears to be dependent on the nature of polymer and solvent, as can be seen in Table I. A separation of this effect into specific increments of polymer and solvent is not possible. Mean values for a for a number of polymers can be found in Table II.

TABLE II
Mean Values of a for Some Polymers

Polymer	a_{average}	Standard deviation
Polyolefins (total)	0.71	0.09
Polyethylene (low pressure)	0.74	0.05
Polyethylene (high pressure)	0.67	—
Polypropylene (atactic)	0.72	0.10
Polypropylene (isotactic)	0.78	0.13
Polybutene (isotactic)	0.74	—
Rubbers (total)	0.68	0.09
Polyisobutylene	0.65	0.06
Polystyrene compounds (total)	0.67	0.08
Polystyrene (atactic)	0.68	0.07
Polyacryl compounds (total)	0.67	0.11
Poly(methyl methacrylate)	0.72	0.08
Polyvinyl compounds (total)	0.66	0.10
Poly(vinyl acetate)	0.66	0.08
Poly(vinyl chloride) and poly(vinyl bromide)	0.72	0.16
Heterochain polymers (total)	0.71	0.10
Polyesters	0.74	0.09

The experimental values of $[\eta]$ as a function of M for the individual combinations of polymer and solvent show deviations from the values corresponding with eq. (4).

These deviations may be taken into account by introducing an empirical constant κ into eq. (4), which results in

$$[\eta] = 0.032\kappa(M/1000)^a \qquad (5)$$

Equation (5) again has two empirical constants, like eq. (2). The constant κ has the advantage over K, however, that it is almost independent of the value chosen for a, so that it is characteristic of the polymer–solvent system.

TABLE III
Values of κ for Some Polymer–Solvent Systems

Polymer	Benzene	Toluene	Xylene	Cyclo-hexane	Tetralin	Decalin	Acetone	Methyl ethyl ketone
Polyethylene (low pressure)			2.86		2.60	3.85		
Polyethylene (high pressure)			2.92			1.99		
Polypropylene (atactic)	1.11	1.02		1.26		1.05		
Polypropylene (isotactic)			2.34		0.76	1.52		
Rubber	0.96	1.58		1.64				
Polybutadiene	1.09			1.79				
Polyisobutylene	0.85	0.83		1.42				
Polystyrene (atactic)	0.53	0.70		0.81				0.79
Polystyrene (isotactic)	0.57	0.62						
Polymethylstyrene	0.68	0.53						
Polymethoxystyrene		0.63						0.48
Polychlorostyrene		0.54						0.81
Poly (methyl methacrylate)		0.57						0.52
Poly(vinyl acetate)	1.46						0.49	0.84
Poly(vinyl methyl ether)	2.29						0.77	2.38

TABLE IV
Mean Values of κ for Some Polymers

Polymer	κ	Standard deviation
Polyethylene	2.75	0.68
Polypropylene	1.19	0.43
Polybutene	0.81	—
Natural rubber and polybutadiene	1.51	0.48
Polyisobutylene and neoprene	0.88	0.39
Polystyrene and derivatives	0.67	0.19
Polyacrylates	0.49	0.20
Polyacrylonitrile	2.18	0.51
Poly(vinyl acetate)	0.98	0.33
Poly(vinyl butyrate) (and higher acids)	0.55	0.06
Poly(vinyl chloride) and poly(vinyl bromide)	0.94	0.40
Polyvinyl alcohol and poly(vinyl ethers)	2.14	—
Nylon	3.53	—
Polyesters	1.94	0.45
Polyurethane	1.58	0.09
Poly(ethylene oxide)	1.39	0.21

Values of κ for a number of systems are shown in Table III. Mean values of κ for a number of polymers, irrespective of the solvent effect, can be found in Table IV.

Theoretical Basis of Intrinsic Viscosity Relationships

In the literature a number of theoretical studies about the relationship between $[\eta]$ and M can be found. For the derivation of the relationship mentioned the reader is referred to the original literature.[1,2,6,7]

The comprehensive equation of this theoretical approach reads as follows:

$$[\eta] = \frac{\pi N}{440} \left(\frac{\alpha \beta \xi}{M_0^{1/2}} \right)^3 M^{1/2} \tag{6}$$

where N is Avogadro's number, $\xi = R_e/R_G$ = equivalent solid sphere radius/radius of gyration of the dissolved polymer chain, β is the effective length of the "stiff" segment in the chain, M_0 is the molecular weight of the segment, and α is the expansion factor of the dissolved polymer chain:

$$\alpha = \left(\frac{(6R_G^2/M)}{\beta^2/M_0} \right)^{1/2}$$

In principle, eq. (6) may be used for predicting the intrinsic viscosity from values of a number of polymer properties. Unfortunately, these values are generally unknown, whereas α and ξ are unknown functions of M also. So, even the dependence of $[\eta]$ on M cannot be predicted with any accuracy.

It is only for Θ-solutions that eq. (6) has proved to be valuable. In the first place, $\alpha = 1$ in this case. Furthermore, the studies of Kirk-

TABLE V
Values of K_θ for Some Polymers[a]

Polymer	$K_\theta \times 10^4$	
	Determined at $T = \theta$	Found by extrapolation
Polyethylene		25.0–23
Polypropylene		
Atactic	15.6	10.8–15.0
Isotactic		8.1–12.0
Polybutylene		
Atactic	11.3–7.5	7.5–12.3
Isotactic	10.0	7.6–12.3
Polyisobutylene	10.7	9.1–10.6
Polyisoprene		
Hevea (100% *cis*)	11.9	13.0–13.7
Polyisoprene		
cis-1,4 (anionic)		17.8–18.6
Polybutadiene		
93% *cis*-1,4		9.4–15
cis (isotactic)	18.6	19.4
70% *trans* (Alfin)		21.2
Polystyrene		
Atactic	7.0–8.7	7.4–8.3
Anionic		7.5
Isotactic		8.3–12.2
Poly-α-methylstyrene		7.0–7.4
Polyvinylcarbazole		7.4
Poly(vinyl alcohol)		16.2–22.2
Poly(vinyl acetate)	8.2–9.3	9.1–12.4?
Poly(methyl methacrylate)		
Atactic	4.8 ± 0.2–5.05	5.0–7.0
Isotactic		5.0–8.1
Syndiotactic		3.7
Poly(ethyl methacrylate)	4.75	4.0
Poly(hexyl methacrylate)	3.5–4.0	3.8
Poly(2-ethylbutyl) methacrylate	3.4	3.8
Poly(*n*-octyl methacrylate)	2.7	2.5
Poly(lauryl methacrylate)	3.5	3.3–3.75
Poly(cetyl methacrylate)		6.6
Polyacrylamide		17.7–26
Polydimethylacrylamide		7.8–8.0
Poly-4-vinylpyridine		9.4–10.1
Poly-2-vinylpyridine		13.7
Polyvinylpyrrolidone		9.0–10.8
Poly-*p*-chlorostyrene		5.0–6.0
Polychlorotrifluoroethylene		5.2–5.25
Poly-ϵ-caprolactam		19.0–36.9
Nylon 66		18–19.0
Poly-β-lactam		20.0
Poly(ethylene oxide)	13–11	9.3–11.2
Poly(propylene oxide)	10.8	10.5–11.5
Polycarbonate		8.7–21.2

[a] Based on a concentration unit of grams per 100 cc.

wood and Riseman[6] showed that ξ is constant for Θ-solutions, independently of M. This has been confirmed by the experiments of H. Kuhn,[8] in which the drag coefficients were determined for scale models of polymer molecules.

So for Θ-solutions, eq. (6) may be simplified to

$$[\eta] = K_\Theta \, M^{1/2} \tag{7}$$

where

$$K_\Theta = 4.29 \times 10^{21} \, (\beta\xi/M_0^{1/2})^3 \tag{8}$$

The predicted proportionality to the square root of M has been confirmed experimentally for Θ-solutions. The coefficient K_Θ may be regarded as a characteristic quantity for a given polymer.

The most straightforward method for the determination of K_Θ is that of performing viscosity measurements on Θ-solutions. In many cases, however, this is not possible for physical reasons. Therefore,

TABLE VI
Comparison of Values for K_Θ and κ

| Polymer	Solvent	κ	$K_\Theta \times 10^4$, g./100 cc.
Polyethylene (low pressure)	Tetralin	2.59	24
Polypropylene (atactic)	Decalin	1.05	11.6
	Isoamyl acetate	1.67	15.6
Polypropylene (isotactic)	Tetralin	0.76	10.0
Polybutene (atactic)	Ethylcyclohexane	1.01	8.7
Polybutadiene	Cyclohexane	1.78	21.2
	Benzene	1.09	12.2
Polyisobutylene	Benzene	0.85	10.4
	Toluene	0.82	10.1
Polystyrene (atactic)	Benzene	0.53	7.8
Polystyrene (isotactic)	Toluene	0.61	10.5
Polymethylstyrene	Toluene	0.52	7.2
Polychlorostyrene	Toluene	0.54	5.5
Poly(methyl methacrylate)	Acetone	0.49	7.0
	Nitroethane	0.50	7.0
Poly(ethyl methacrylate)	Isopropanol	0.66	4.8
Poly(ethylbutyl methacrylate)	Isopropanol	0.47	3.4
Poly(octyl methacrylate)	n-Butanol	0.38	2.7
Polydimethylacrylamide	Methanol	0.69	7.9
	Water	0.75	7.8
Poly(vinyl acetate)	Acetone	0.77	10.2
	Ethyl butylketone	1.31	9.2
	Ethyl isoamyl ketone	1.15	8.2
Poly(vinyl alcohol)	Water	1.74	19.6
Poly-4-vinylpyridine	Ethanol	1.38	9.8
Polyvinylpyrrolidone	Methanol	1.01	9.5
	Water	1.08	10.4
Nylon 66	Formic acid	3.35	18
Poly(ethylene oxide)	Dimethylformamide	1.17	11.2
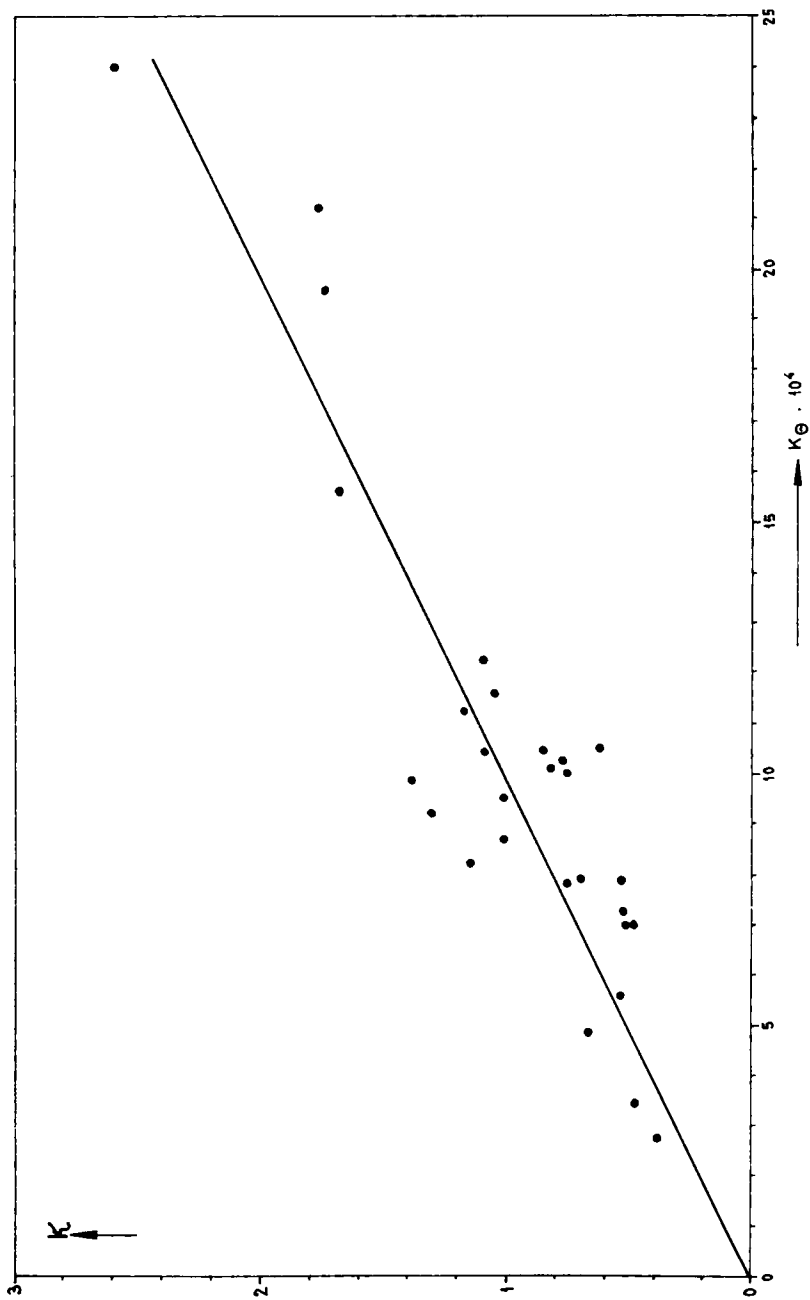
Fig. 1. Correlation between $K\theta$ and κ.

several attempts have been made to determine K_Θ from viscosity measurements at temperatures different from Θ.[7,9—11]

None of these extrapolation methods, proves to be quite satisfactory. The most promising method seems to be Stockmayer's[11] which is based on a series expansion of α as a function of M. The method can be improved by taking more terms of the series into account.

A number of values for K_Θ for several combinations of polymer and solvent may be found in an article of Bohdanecký.[12] They have been reproduced in Table V.

Relationship between K_Θ and κ

Both the quantities K_Θ [eq. (7)] and κ [eq. (5)] appear to be characteristic of the nature of the polymer. In Table VI, a number of values for K_Θ and κ for the same systems are compared. A plot of κ against K_Θ, as given in Figure 1, shows a fair correspondence with a linear relationship

$$\kappa = 1000 \, K_\Theta \tag{9}$$

Now K_Θ is a properly defined quantity, whereas the quantity κ has no fundamental basis. Therefore, K_Θ should be preferred to κ for the characterization of a polymer.

In this connection, eq. (5) could be improved by replacement of κ by K_Θ. This leads to

$$[\eta] = 32 K_\Theta \, (M/1000)^a \tag{10}$$

We propose that this equation be used for a first estimation of M from the intrinsic viscosity of polymer solutions. The value of the exponent a can be chosen in accordance with known values for polymers of related structure. As a first approximation the mean value $a = 0.7$ could be used.

A prediction of the value of K_Θ on the basis of eq. (8) is not possible, due to lack of data for the quantities β, ξ, and M_0. As K_Θ is certainly dependent on some molecular properties as stiffness and steric regularity of the polymer chain, some relationship between K_Θ and other characteristic quantities (e.g., glass transition temperature, cohesive energy density) may exist. At the moment, however, the data available are insufficient for an empirical determination of such a relationship.

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Résumé

L'équation de Mark-Houwink pour la relation entre la viscosité intrinsèque d'une solution de polymère et le poids moléculaire peut être formulée d'une façon plus générale: $[\eta] = 32K_\Theta(M/1000)^a$, la constante K_Θ ayant une signification théorique et la constante a étant approximativement égale à 0,7.

Zusammenfassung

Die Mark-Houwinksche Gleichung für die Beziehung zwischen der Viskositätszahl einer Polymerlösung und dem Molekulargewicht kann allgemeiner formuliert werden, und zwar $[\eta] = 32K_\Theta[M/1000]^a$, worin die Konstante K_Θ eine theoretische Bedeutung hat und die Konstante a annäherend gleich 0,7 ist.