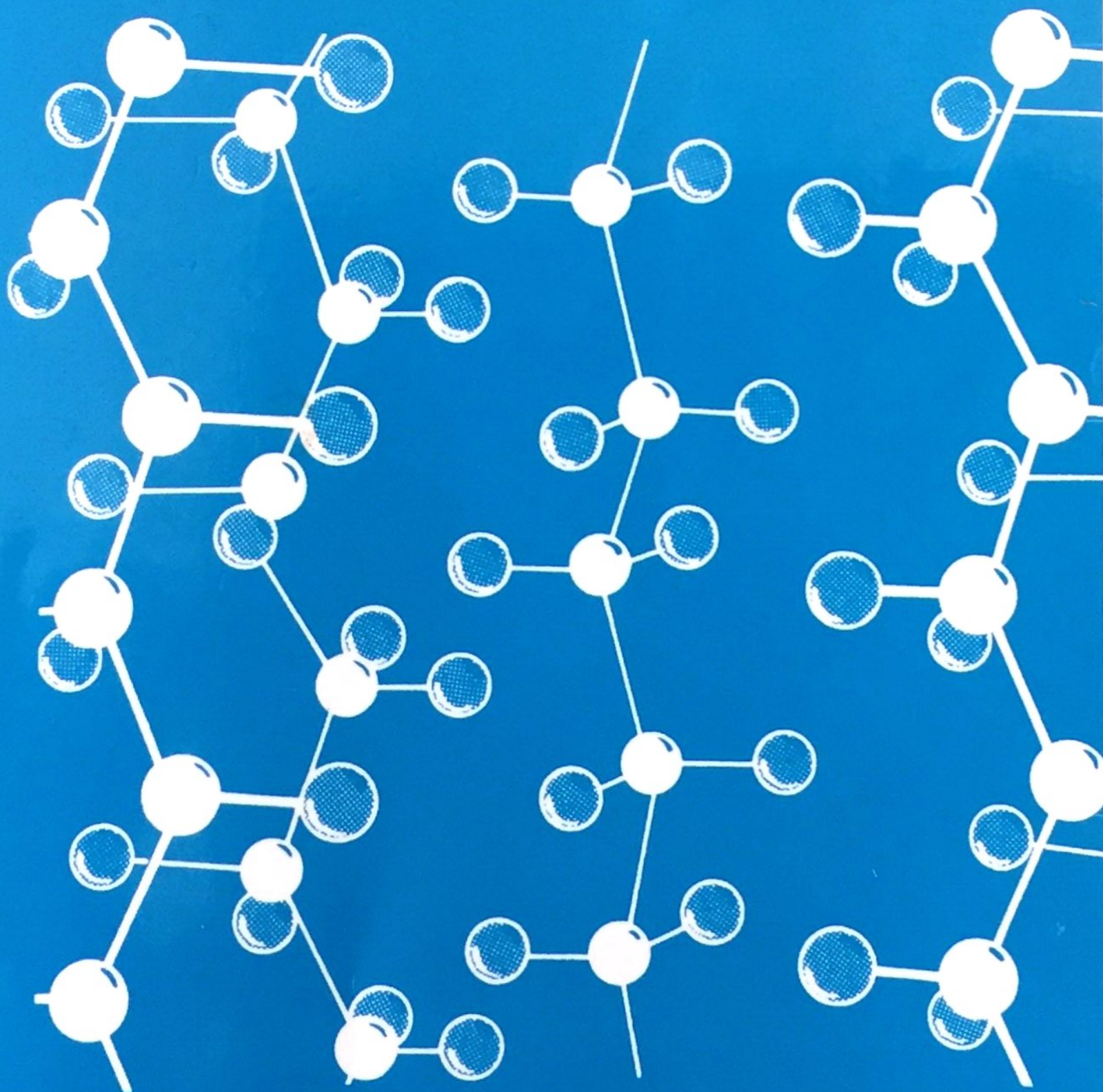


INTRODUCTION TO POLYMERS

Second Edition

R.J. YOUNG AND P.A. LOVELL



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IPR2016-01896

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CRC PRESS

Boca Raton London New York Washington, D.C.

Library of Congress Cataloging-in-Publication Data

Catalog record is available from the Library of Congress

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First edition © 1981 Chapman & Hall

Second edition 1991

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International Standard Book Number 0-7487-5740-6

Printed in the United States of America 5 6 7 8 9 0

Printed on acid-free paper

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TABLE 3.7 Quantities and terminology used in dilute solution viscometry

Common name	Name proposed by IUPAC	Symbol and definition*
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_0$
Specific viscosity	—	$\eta_{sp} = \eta_r - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \ln(\eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \lim_{c \rightarrow 0} (\eta_{red})$

* η_0 is the viscosity of the solvent and η is the viscosity of a polymer solution of concentration c (mass per unit volume).

$$\eta_{sp} = k_0[\eta]c + k_1[\eta]^2c^2 + k_2[\eta]^3c^3 + \dots \quad (3.156)$$

where k_0 , k_1 , k_2 , etc., are dimensionless constants and $k_0 = 1$. For dilute solutions, Equation (3.156) can be truncated and rearranged to the following form

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c \quad (3.157)$$

which is known as the *Huggins equation* and is valid for $[\eta]c \ll 1$. The Huggins constant $k_H (= k_1)$ is essentially independent of molar mass and has values which fall in the range 0.3 (for good polymer-solvent pairs) to 0.5 (for poor polymer-solvent pairs).

For dilute solutions with $\eta_{sp} \ll 1$

$$\ln(\eta_r) = \ln(1 + \eta_{sp}) \approx \eta_{sp} - \frac{1}{2}\eta_{sp}^2 \quad (3.158)$$

Substituting Equation (3.157) into (3.158), and retaining only the terms in c up to c^2 gives

$$\ln(\eta_r) = [\eta]c + (k_H - \frac{1}{2})[\eta]^2c^2$$

which can be rearranged into the form of the *Kraemer equation*

$$\ln(\eta_r)/c = [\eta] + k_K[\eta]^2c \quad (3.159)$$

where $k_K = k_H - \frac{1}{2}$ and so is negative (or zero).

Although there are other simplifications of Equation (3.156), the Huggins and Kraemer equations provide the most common procedure for evaluation of $[\eta]$ from experimental data. This involves a dual extrapolation according to these equations and gives $[\eta]$ as the mean intercept (Fig. 3.17).

3.14.2 Interpretation of intrinsic viscosity data

The intrinsic viscosity $[\eta]$ of a polymer is related to its viscosity-average molar mass \bar{M}_v by the *Mark-Houwink equation*

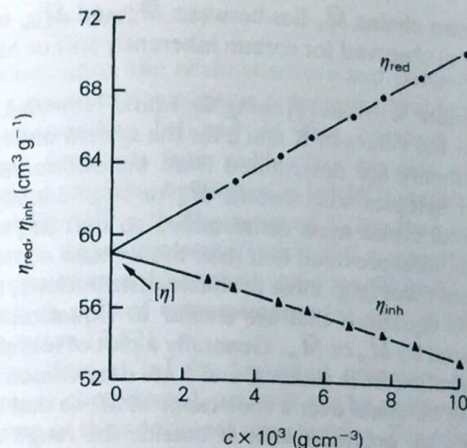


Fig. 3.17 Evaluation of $[\eta]$ for solutions in toluene of a sample of poly(*tert*-butyl acrylate) at 25°C using a dual Huggins-Kraemer plot.

$$[\eta] = K\bar{M}_v^a \quad (3.160)$$

where K and a are characteristic constants for a given polymer/solvent/temperature system. Theoretical justification for the form of this equation is presented in Section 3.4.2. For Gaussian coils, it was shown that $a = 0.5$ under theta conditions, and that a increases to a limiting value of 0.8 with coil expansion (typically $a > 0.7$ for polymers in good solvents). The value of K tends to decrease as a increases and for flexible chains it is typically in the range 10^{-3} to $10^{-1} \text{ cm}^3 \text{ g}^{-1} (\text{g mol}^{-1})^{-a}$.

The form of \bar{M}_v can be deduced on the basis that specific viscosities are additive in the limit of infinite dilution, i.e.

$$\eta_{sp} = \sum (\eta_{sp})_i$$

where $(\eta_{sp})_i$ is the contribution to η_{sp} made by the n_i moles of polymer molecules of molar mass M_i present in unit volume of a dilute polymer solution. Since $c_i = n_i M_i$, $(\eta_{sp})_i = c_i [\eta]_i$ and $[\eta]_i = K M_i^a$ then

$$[\eta] = \left(\frac{\eta_{sp}}{c} \right)_{c \rightarrow 0} = K \left(\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right)$$

Comparison of this equation with Equation (3.160) shows that

$$\bar{M}_v = \left(\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right)^{1/a} \quad (3.161)$$

Thus for Gaussian chains \bar{M}_v lies between \bar{M}_n and \bar{M}_w , but is closer to \bar{M}_w . When $a = 1$ (as observed for certain inherently stiff or highly extended chains) $\bar{M}_v = \bar{M}_w$.

In order to evaluate \bar{M}_v from $[\eta]$ using the Mark-Houwink equation, it is necessary to know the values of K and a for the system under study. These values most commonly are determined from measurements of $[\eta]$ for a series of polymer samples with known \bar{M}_n or \bar{M}_w . Ideally the samples should have narrow molar mass distributions so that $\bar{M}_n \approx \bar{M}_v \approx \bar{M}_w$. If this is not the case, then provided that their molar mass distributions are of the same functional form (e.g. most probable distribution), the calibration is valid and yields equations that are similar to Equation (3.160) but in which \bar{M}_v is replaced by \bar{M}_n or \bar{M}_w . Generally a plot of $\log[\eta]$ against $\log M$ is fitted to a straight line from which K and a are determined. Theoretically this plot should not be linear over a wide range of M , so that K and a values should not be used for polymers with M outside the range defined by the calibration samples. However, in practice such plots are essentially linear over wide ranges of M , though curvature at low M is often observed due to the non-Gaussian character of short flexible chains. Some typical values of K and a are given in Table 3.8.

For small expansions of Gaussian polymer chains the expansion parameter, α_n , for the hydrodynamic chain dimensions is given by a closed expression of the form

$$\alpha_n^3 = 1 + bz \quad (3.162)$$

where z is the excluded volume parameter defined by Equation (3.67) and b is a constant the value of which is uncertain (e.g. values of 1.55 and 1.05 have been obtained from different theories). Combining this relation with the Flory-Fox Equation (3.82) gives

$$[\eta] = K_\theta M^{1/2} + bK_\theta z M^{1/2}$$

which upon rearrangement, recognizing that from Equation (3.67) z is proportional to $M^{1/2}$, leads to

TABLE 3.8 Some typical values of the Mark-Houwink constants K and a

Polymer	Solvent	$T/^\circ\text{C}$	K^*	a
Polyethylene	Decalin	135	6.2×10^{-2}	0.70
Polystyrene	Toluene	25	7.5×10^{-3}	0.75
Polystyrene	Cyclohexane	34 [†]	8.2×10^{-2}	0.50
Poly(vinyl acetate)	Acetone	30	8.6×10^{-3}	0.74
Cellulose triacetate	Acetone	20	2.38×10^{-3}	1.0

* The units of K are $\text{cm}^3 \text{g}^{-1} (\text{g mol}^{-1})^{-a}$.

[†] Theta conditions, $T = \theta$.

$$[\eta]M^{1/2} = K_\theta + BM^{1/2} \quad (3.163)$$

where B depends upon the chain structure and polymer-solvent interactions, and is a constant for a given polymer/solvent/temperature system. Thus the corresponding $[\eta]$ and M data obtained for evaluation of Mark-Houwink constants from calibration samples with narrow molar mass distributions, can also be plotted as $[\eta]M^{1/2}$ against $M^{1/2}$ to give K_θ as the intercept at $[\eta]M^{1/2} = 0$. The value of K_θ can then be used to evaluate for the polymer to which it relates: (i) $\langle s^2 \rangle_0^{1/2}$ (i.e. unperturbed dimensions) for any M by assuming a theoretical value for Φ_0^* in Equation (3.83), and (ii) α_n for a given pair of corresponding $[\eta]$ and M values by using the Flory-Fox Equation (3.82).

The interpretation of $[\eta]$ for branched polymers and copolymers is considerably more complicated, and will not be dealt with here other than to highlight some of the additional complexities. The effect of branching is to increase the segment density within the molecular coil. Thus a branched polymer molecule has a smaller hydrodynamic volume and a lower intrinsic viscosity than a similar linear polymer of the same molar mass. For copolymers of the same molar mass, $[\eta]$ will differ according to the composition, composition distribution, sequence distribution of the different repeat units, interactions between unlike repeat units, and degree of preferential interaction of solvent molecules with one of the different types of repeat unit.

3.14.3 Measurement of solution viscosity

The viscosities of dilute polymer solutions most commonly are measured using capillary viscometers of which there are two general classes, namely U-tube viscometers and suspended-level viscometers (Fig. 3.18). A common feature of these viscometers is that a measuring bulb, with upper and lower etched marks, is attached directly above the capillary tube. The solution is either drawn or forced into the measuring bulb from a reservoir bulb attached to the bottom of the capillary tube, and the time required for it to flow back between the two etched marks is recorded.

In U-tube viscometers, the pressure head giving rise to flow depends upon the volume of solution contained in the viscometer, and so it is essential that this volume is exactly the same for each measurement. This normally is achieved after temperature equilibration by carefully adjusting the liquid level to an etched mark just above the reservoir bulb.

Most suspended-level viscometers are based upon the design due to Ubbelohde, the important feature of which is the additional tube attached just below the capillary tube. This ensures that during measurement the solution is suspended in the measuring bulb and capillary tube, with