

Practical Evaluation of the $[\eta]$ - M Relationship. II. Estimation of K_θ Values of Polymer Solutions

D. W. VAN KREVELEN and P. J. HOFFTYZER,
Algemene Kunstzijde Unie N.V. (AKU), Arnhem, The Netherlands

Synopsis

A method is proposed for the prediction of the intrinsic viscosity of θ solutions, based upon the constitution of the dissolved polymer. The method makes use of additive values for constitutional groups to calculate a quantity that represents the specific chain stiffness per main chain atom.

Introduction

The well-known Mark-Houwink equation¹ gives the empirical relation between the intrinsic viscosity of polymer solutions and the molecular weight:

$$[\eta] = KM^a \quad (1)$$

Many studies have already been devoted to the theoretical interpretation of this equation. A statistical consideration of possible conformations^{2,3} has led to a result the validity of which is strictly limited to so-called θ solutions, i.e., solutions in which the partial molar free energy due to polymer-solvent and polymer-polymer interaction is equal to zero. This result reads:

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

In this equation K_θ is a fundamental quantity which is dependent only on the constitution (i.e., structure) and conformation of the polymer. According to theory,

$$K_\theta = 4.3 \times 10^{21} \xi_\theta^3 (\beta/M_0^{1/2})^3 \quad (3)$$

where ξ_θ is the ratio of the equivalent hydrodynamic radius to the radius of gyration of the polymer particle, β is the effective length of a rigid chain segment, and M_0 is molecular weight of this segment.

For non-ideal solutions, i.e., non- θ solutions, the theory leads to the relation:

$$[\eta] = [\eta]_\theta \alpha_\eta^3 = K_\theta \alpha_\eta^3 M^{1/2} \quad (4)$$

where α_η is the so-called expansion factor of the radius of gyration. This factor depends, among other things, on the molecular weight. A procedure to calculate α_η theoretically has not been found.

Recently we have subjected the known empirical data concerning eq. (1) to a renewed analysis⁴ and demonstrated that eq. (1) can be approximated reasonably well by

$$[\eta] = 32K_\theta(M/1000)^a \quad (5)$$

Equation (5) obviates the drawback of eq. (1) that K and a are interdependent: disregarding a slight influence of the nature of the solvent in θ solutions, every polymer has only one K_θ value and only a is determined by the interaction of polymer and solvent. Furthermore, eq. (5) automatically goes over into eq. (2) when $a = 1/2$.

For a number of polymers the literature gives values of K_θ . Although the values found by various investigators differ appreciably, the variation is less than for the quantities K and a in eq. (1).

It is clear that it is of particular importance to know the relation between the fundamental quantity K_θ and the polymer constitution. The fact is that in eq. (5) K_θ is the main factor on which $[\eta]$ depends; in turn, $[\eta]$ itself is of great importance for the knowledge of the viscosity of polymer solutions in general.

The object of this article is to develop a method enabling us to calculate K_θ from the structure.

Relation Between K_θ and Polymer Structure

In deriving a relation between K_θ and the polymer structure we have been guided by the theoretical equation

$$K_\theta = \text{const. } \xi_\theta^3 (\beta/M_0^{1/2})^3 \quad (3)$$

There are indications that the factor ξ_θ^3 is practically constant.⁵ The obvious approach was to investigate whether there is a direct relation between K_θ and the molecular weight per structural unit. Naturally this had to be done for a specific family of polymers with fundamentally the same β values. K_θ values were derived from the data of Bohdanecky⁶ and Brandrup and Immergut.⁷ In doing this for the vinyl polymers (Fig. 1) it appears that there is no question of a simple relationship. Excluding the polymers with strong hydrogen bonds (indicated by symbol \times in Fig. 1), one finds a very superficial relation, viz.

$$K_\theta \sim (M_{\text{unit}})^{-1}$$

This relation deviates considerably from the theoretical relation. Moreover, the scatter is appreciable.

When other polymer families are drawn into the relation, β also changes, and a universally valid significant relationship is very difficult to find.

We therefore decided to follow a completely different route.

On the analogy of eq. (3) we have assumed the relation:

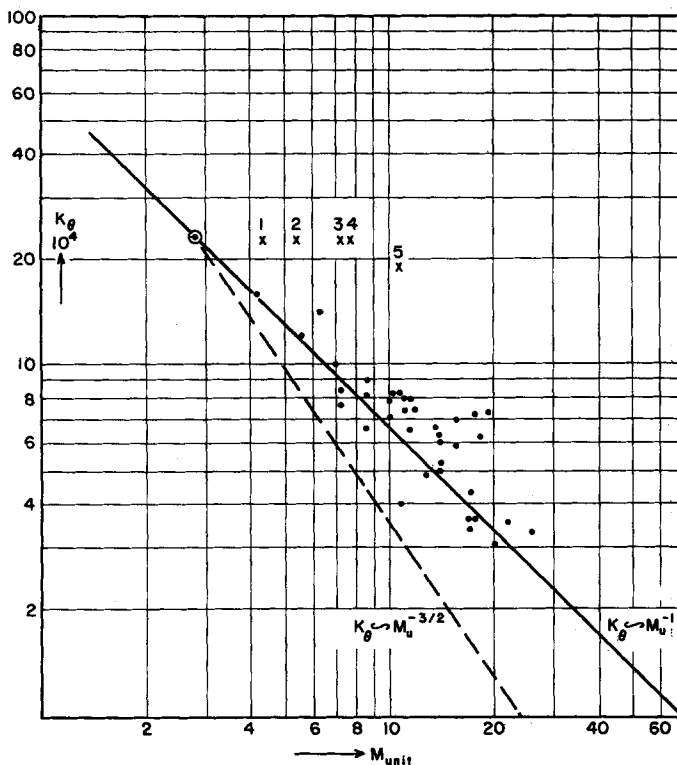
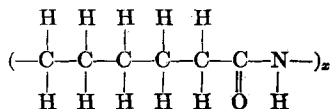


Fig. 1. K_θ as a function of M_{unit} for vinyl polymers: (\odot) polyethylene; (1) poly(vinyl alcohol); (2) polyacrylonitrile; (3) polyacrylamide; (4) polymethacrylonitrile; (5) poly(vinylsulfonic acid).

$$K_\theta = (S_*/M_*^{1/2})^3 \quad (6)$$

where M_* is the molecular weight per main chain atom, and S_* a quantity connected with the specific chain stiffness per main-chain atom. The concept "main-chain atom" requires some elucidation. By main chain we understand the polymer chain proper, without its side groups and branches. In polyethylene all the carbon atoms are main-chain atoms; in polypropylene this is the case with two out of three carbon atoms. In nylon 6 all the carbon atoms and nitrogen atoms are main-chain atoms, as is evident from the structural formula:



but in this case oxygen atoms are not main chain atoms. Hydrogen atoms are never counted among the chain atoms. When the main chain contains rings, all the atoms in the ring skeleton proper are considered to be main-chain atoms.

TABLE I
 Experimental and Calculated K_{θ} Values

Polymer	Experimental values of		Calculated values				
	$K_{\theta} \times 10^6$ (range)	M_{unit}	η	M^*	$\Sigma S_i \times 10^2$	$S^* \times 10^2$	$K_{\theta} \times 10^6$
Polyethylene	2300 \pm 300	28	2	14	100	50	2380
Polypropene	1500 \pm 300	42	2	21	105	52.5	1500
Poly- <i>n</i> -butene	1200 \pm 100	56	2	28	110	55	1120
Poly- <i>isobutene</i>	1000 \pm 150	56	2	28	110	55	1120
Poly- <i>n</i> -pentene	1200 \pm 300	70	2	35	115	57.5	920
Poly(vinyl chloride)	1250 \pm 300	62.5	2	31.25	120	60	1240
Poly(vinyl bromide)	\sim 400	107	2	53.5	110	55	425
Poly(vinylsulfonic acid)	820 \pm 140	108	2	54	140	70	870
Poly(vinyl alcohol)	2200 \pm 300	44	2	22	120	60	2090
Poly(vinyl acetate)	900 \pm 130	86	2	43	120	60	770
Poly(vinyl <i>n</i> -butyrate)	800 \pm 100	114	2	57	131	65.5	650
Poly(vinyl benzoate)	620 \pm 80	148	2	74	150	75	660
Poly(acrylic acid)	\sim 760	72	2	36	110	55	770
Poly(methyl acrylate)	810 \pm 100	86	2	43	120	60	770
Poly(ethyl acrylate)	900 \pm 200	100	2	50	125.5	62.8	700
Poly(methacrylic acid)	\sim 660	86	2	43	115	57.5	670
Poly(methyl methacrylate)	650 \pm 250	100	2	50	125	62.5	690
Poly(ethyl methacrylate)	480 \pm 40	114	2	57	130	65	640
Poly(octyl methacrylate)	300 \pm 50	198	2	99	160	80	520
Poly(methyl methacrylate)	650 \pm 30	114	2	57	130	65	640
Polystyrene	800 \pm 100	104	2	52	135	67.5	820
Poly- α -methylstyrene	740 \pm 100	118	2	59	135	67.5	680

Poly- <i>p</i> -methylstyrene	660	118	2	59	135	67.5	680
Poly- <i>p</i> -cyclohexylstyrene	520 ± 100	186	2	93	155	77.5	520
Poly- <i>p</i> -chlorostyrene	500 ± 300	138.5	2	69	135	67.5	540
Polyvinylcyclohexane	~800	110	2	55	135	67.5	750
Polyvinylpyridine	820 ± 100	105	2	52.5	135	67.5	810
Polyvinylpyrrolidone	900 ± 250	111	2	55	135	67.5	750
Polyvinylcarbazole	~740	193	2	96.5	175	87.5	700
Polyacrylonitrile	2250 ± 250	53	2	26.5	140	70	2510
Polyacrylamide	2600 ± 400	71	2	35.5	150	75	1990
Polydimethylacrylamide	780 ± 150	99	2	49.5	130	65	790
Polyacrylomorpholide	700 ± 100	141	2	70.5	145	72.5	640
Polyacrylopiiperidide	580 ± 100	139	2	69.5	145	72.5	660
Polymethacrylonitrile	~2200	67	2	33.5	145	72.5	1960
Polybutadiene (<i>cis</i>)	1700 ± 150	54	4	13.5	175	43.8	1690
Polybutadiene (<i>trans</i>)	2000 ± 500	54	4	13.5	200	50	2520
Polyisoprene (<i>cis</i>)	1300 ± 200	68	4	17	180	45	1300
Polyisoprene (<i>trans</i>)	~2320	68	4	17	205	51.5	1950
Polychloroprene	1150 ± 200	88.5	4	22.1	195	49	1130
Poly(ethylene oxide)	1500 ± 200	44	3	14.7	135	45	1610
Poly(propylene oxide)	1150 ± 100	58	3	19	140	46.8	1240
Polytetrahydrofuran	1800 - 3300	72	5	14.4	235	47	1900
Polyformaldehyde	1320 - 3800	30	2	15	85	42.5	1320
Polydimethylsiloxane	900 ± 160	74	2	37	115	57.5	840
Poly(hexamethylene fumarate)	1800 ± 200	198	12	16.5	600	50	1870
Poly(hexamethylene maleate)	1350 ± 200	198	12	16.5	575	47.9	1640
Poly(hexamethylene succinate)	1650 ± 200	200	12	16.7	600	50	1850
Poly(hexamethylene sebacate)	2150 ± 600	284	18	15.8	900	50	1990
Poly(hexamethylene α,α' -dibutyl sebacate)	1550 ± 250	396	18	22.0	940	52.2	1380

(continued)

TABLE I (continued)

Polymer	Experimental values of		Calculated values				
	$K_g \times 10^6$ (range)	M_{unit}	n	M_*	$\Sigma S_i \times 10^2$	$S_* \times 10^3$	$K_g \times 10^6$
Poly(decamethylene adipate)	1000 ± 100(?)	284	18	15.8	900	50	1990
Poly(decamethylene sebacate)	2200 ± 300	340	22	15.4	1100	50	2070
Poly(hexadecamethylene sebacate)	2700 ± 500	424	28	15.1	1400	50	2130
Polyhexadecanoate	1850 ± 600	184	12	15.3	600	50	2090
Poly(<i>cis</i> -1,4-cyclohexene sebacate)	1400 ± 200	282	18	15.7	800	44.5	1420
Poly(<i>trans</i> -1,4-cyclohexene sebacate)	1600 ± 200	282	18	15.7	830	46.2	1500
Poly(octamethylene hexahydroterephthalate)	1600 ± 200	282	18	15.7	830	46.2	1590
Poly(ethylene terephthalate)	1750 ± 250	192	12	16	600	50	1950
Polycarbonate	1800 ± 200	254	16	16	795	49.8	1930
Poly-ε-aminocaproate (nylon 6)	≥ 1900	113	7	16.2	375	53.6	2360
Poly(hexamethylene adipamide)	1900 - 2530	226	14	16.2	750	53.6	2360
(nylon 66)	~2500	157	10	15.7	510	51	2130
Poly(heptamethylene urethane)							

In Table I a survey is given of a number of fairly reliable K_θ values. Table I also gives the values of M_* for the polymers concerned.

It has now been found that there is a significant relation between S_* and the polymer structure. It appears that S_* can be calculated from group contributions according to the formula

$$S_* = \sum_i S_i/n$$

where n is the number of main chain atoms per structural unit.

The S_i values concerned, which are contributions of certain chain segments, have been calculated from some standard structures.

Thus, the value of S_{-CH_2-} was derived from the S_* value of polyethylene, that of S_{-O-} from the S_* values of poly(ethylene oxide) and polytetrahydrofuran (in combination with S_{-CH_2-}), that of $S_{-NH-CO-}$ from the S_* value of nylon 66, etc.

The details of the derivation will not be discussed here. Table II gives the results of these derivations for main and side chain elements. Finally Table I, in the column on the extreme right, gives the calculated S_* and K_θ values of the polymers investigated. On the whole the result may be considered quite satisfactory.

Side chains increase the S_* value of a polymer; generally the increase is greater according as the side chain is more voluminous.

According to eq. (6) the calculated value for K_θ will go through a minimum at increasing length of the side chain, i.e., with increasing number of CH_2 groups. The fact is that when the structural unit contains m CH_2 groups in the side chain and n atoms in the main chain, then

$$S_* = \sum S_i/n = (A + 5m)/n$$

$$M_* = (B + 14m)/n$$

The values of A and B can be derived directly from the structure. Substitution gives:

$$K_\theta^{1/3} = n^{-1/2}(A + 5m)/(B + 14m)^{1/2}$$

In dependence on the values of A and B this function can show a minimum at a certain value of m . However, the number of available values of K_θ is not sufficient, and the values scatter too much to permit verification of this phenomenon.

From the foregoing it will be clear that a very large number of K_θ values can already be calculated with the available S_i values for main-chain and side-chain elements.

It stands to reason that the method developed here is tentative and open to objections. However, the remarkable agreement of the relationship with the experimental data does indicate that this approach is a useful one.

TABLE II
 S_i Group Contributions

Bifunctional elements	$S_i \times 10^2$		Monofunctional elements	$S_i \times 10^2$ on main or side chain
	In main chain	In side chain		
	50	5	H	0
	65	10	$-\text{CH}_3$	5
	75			35
	100			50
	300	30		75
	(200)	(20)	$-\text{COOH}$	10
	(230)	(25)	$-\text{SO}_3\text{H}$	(40)
$-\text{O}-$	35	5	$-\text{CN}$	(40)
$-\text{N}-$	60	(10)	$-\text{OH}$	(20)
$-\text{Si}-$	(70)		$-\text{NH}_2$	(40)
			$-\text{Cl}^{\text{a}}$	20
			$-\text{Br}^{\text{d}}$	(10)

^a Also other one-ring systems (appr.).

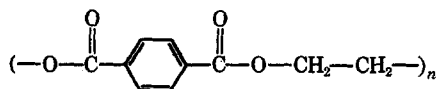
^b Also other two-ring systems (appr.).

^c Also other three-ring systems (appr.).

^d Only when in main chain (when substituted in side-chain effect is small).

Examples

To elucidate the foregoing some examples are given.
Poly(ethylene Terephthalate). The structural unit is



The number of chain atoms is 12; the molecular weight per structural unit is 192; the molecular weight per chain atom is 16. The calculation of $\sum S_i$ per structural unit is as follows:

—C ₆ H ₄ —	300 × 10 ⁻²
2 —CH ₂ —	100
2 —CO—	130
2 —O—	70
$\sum S_i$	600 × 10 ⁻²

$$S_* = 600 \times 10^{-2}/12 = 50 \times 10^{-2}$$

$$K_\theta = (S_*/M_*^{1/2})^3 = (50 \times 10^{-2}/4)^3 = (12.5 \times 10^{-2})^3 = 20 \times 10^{-4}$$

From the literature it is known that

$$[\eta] = 2.1 \times 10^{-4} M^{0.81}$$

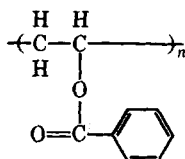
It follows that

$$K_\theta = 2.1 \times 10^{-4} \times 1000^{0.81} \approx 20 \times 10^{-4}$$

In view of the considerable extrapolation of the experimental data the result is satisfactory. The *Polymer Handbook*⁷ gives the value

$$K_\theta \times 10^5 = 160 \pm 15$$

Poly(vinyl Benzoate). The structural unit is



The number of chain atoms is 2; the molecular weight per structural unit is 148; the molecular weight per main chain atom is 74; thus $\sum S_i$ per structural unit ($\times 10^2$) is calculated as follows:

Main chain: 2 —C—	100
Side chain: —O—	5
—C=O	10
C ₆ H ₅	35
	50
	150

$$S_* \text{ per main chain atom: } 75 \times 10^{-2}$$

$$K_\theta = (S_*/M_*^{1/2})^3 = (75 \times 10^{-2}/8.6)^3 = 6.6 \times 10^{-4}$$

The value of K_θ given in the literature is 6.2×10^{-4} .

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Résumé

Les auteurs proposent une méthode pour prédire la viscosité intrinsèque de solutions θ sur la base de la constitution du polymère dissous. Cette méthode utilise des valeurs additives pour les groupes constitutifs afin de calculer une grandeur représentant la rigidité de chaîne spécifique par atome de la chaîne principale.

Zusammenfassung

Es wird eine Methode vorgeschlagen, die es ermöglicht, die Eigenviskosität von θ -Losungen vorherzusagen; diese Vorhersage ist auf der Konstitution des gelösten Polymeren basiert. Die Methode verwendet additive Werte für Struktureinheiten zur Berechnung einer Grösse, welche die spezifische Kettensteifigkeit pro Atom der Hauptkette vertritt.

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