

A Novel Approach to Viscometric Parameters of Polymer Solutions

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Synopsis

A three-parameter equation is put forward to evaluate the $[\eta]$ of polymer solution from a wide range of concentrations, up to a relative viscosity of 100. The equation is tested by viscometric data of polystyrene, poly(vinyl chloride), poly(1-vinylnaphthalene), poly(2-vinylnaphthalene), and poly(4-vinylbiphenyl) at different temperatures and in a variety of solvents including mixed solvents. A statistical method is employed to analyze the experimental data. It is found that the values of $[\eta]$ obtained by the new equation are consistently lower than those derived from the Huggins equation. However, the discrepancy is not more than 3% on average, and it does not affect the values of Mark-Houwink constants significantly. Other parameters of the equation are also computed.

INTRODUCTION

Intrinsic viscosity measurement serves as a simple and reliable tool for polymer characterization. It is widely used and is conventionally accessible by graphic extrapolation methods which are based on the equations proposed by Huggins,¹ Kraemer,² Martin,³ and Schulz-Blaschke,⁴ given respectively as

$$\eta_{sp}/c = [\eta]_H + k_H[\eta]_H^2 c \quad (1)$$

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

$$\ln (\eta_{sp}/c) = \ln [\eta]_M + k_M[\eta]_M c \quad (3)$$

$$\eta_{sp}/c = [\eta]_S + k_S[\eta]_S \eta_{sp} \quad (4)$$

where $\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta_r - 1$, with η being the zero-shear Newtonian viscosity of the polymer solution; η_0 is the zero-shear Newtonian viscosity of the pure solvent; and $\eta_r = \eta/\eta_0$, the relative viscosity. The parameters $[\eta]_H$, $[\eta]_K$, $[\eta]_M$, and $[\eta]_S$ are intrinsic viscosities and k_H , k_K , k_M , and k_S are empirical constants defined by the respective equations for a polymer solution of concentration c . The first three equations are in fact the simplified versions of the last one. In the limit of $(k_S[\eta]_S c)^2 < 1$, eq. (4) is reduced to eqs. (1) and (3), whereas when $([\eta]_S^2 c^2 + 2k_S[\eta]_S c) < 1$, it is truncated to eq. (2).

The orthodox procedure for determination of the intrinsic viscosity $[\eta]$ involves a highly accurate timing of the efflux times of dilute polymer solutions and a proper choice of viscometer to minimize both the end effects as well as the kinetic energy correction effects effectively. It also demands a judicious selection of concentration, usually with $\eta_r < 2$, to start with the measurements, for at most practical concentrations the above equations are invalid. The Huggins plot shows an upturn if the solutions are either too dilute⁵ or too concentrated, hence it makes the extrapolation impossible. In the event the experimental data are

collected over a range of concentrations that extends to a curvilinear region, then spurious results may result if they are forced into rectilinear form by the above equations. In this sense, it could be a tedious and erroneous method.

This article suggests a new equation by which the $[\eta]$ can be determined from viscometric data of polymer solutions over a wide range of concentrations. The validity of the equation is examined by several vinyl polymer systems which differ considerably in chemical structure, molecular weight distribution, solvent, and temperature.

THE EQUATION

The constant k_S in eq. (4) is generally treated as a constant under the conditions at which there are short-range and long-range interactions in dilute polymer solution. However, as the concentration of the polymer solution increases, the polymer-polymer contacts become increasingly important. As consequence the foregoing assumption will not be able to tolerate the drastic changes in solution viscosity and other related parameters with concentration. In order to overcome these difficulties, a power function for k_S is proposed as

$$k_S = k_C \eta_{sp}^{n-1} \quad (5)$$

where k_C and n are the new empirical constants.

Introducing eq. (5) into (4) yields

$$\eta_{sp}/c = [\eta]_C [1 + k_C \eta_{sp}^n] \quad (6)$$

in which $[\eta]_S$ is replaced by $[\eta]_C$ as a result of the substitution. Accordingly, they are defined as

$$[\eta]_S = \lim_{\eta_{sp} \rightarrow 0} (\eta_{sp}/c) \quad (7)$$

and

$$[\eta]_C = \lim_{\eta_{sp}^n \rightarrow 0} (\eta_{sp}/c) \quad (8)$$

RESULTS

The experimental data were fitted to eq. (6) and processed by a linear least-squares computer program. In this particular case, the η_{sp}^n in eq. (6) was taken as the independent variable and η_{sp}/c as the dependent variable. The value of n was adjusted until the minimum standard deviation (S.D.) was obtained. The corresponding viscometric and statistical parameters $[\eta]_C$, k_C , n , S.D., and the confidence limit according to the t distribution of both $[\eta]_C$ and k_C ,⁶ together with the total population of variables, N , and the highest concentration of the solution used for analysis, C_h , are tabulated in Tables I through IV. The $[\eta]_H$ and k_H values are quoted directly from the original papers⁷⁻¹⁰ for comparison. The footnote finds the limiting value of η_r allowed by the computer program. The confidence interval is 0.95. The correlation coefficient r was also computed and will be reported when necessary.¹¹

TABLE I
 Viscometric and Statistical Parameters for Polystyrenes Reported in Reference 7

Solvent	$M_n \times 10^{-5}$	$[\eta]_C$, dl/g	k_C	n	S.D., dl/g	N	C_h^a , g/dl	$[\eta]_H$, dl/g	k_H
At $T = 30^\circ\text{C}$									
Toluene	6.00	1.994 $\pm 0.001^b$	0.325 $\pm 0.002^b$	0.712	0.020	26	3.394	2.040	0.382
	1.46	0.688 ± 0.001	0.322 ± 0.0003	0.724	0.004	30	9.328	0.704	0.379
	0.58	0.363 ± 0.001	0.295 ± 0.001	0.798	0.002	25	5.927	0.369	0.322
Butanone	6.00	0.986 ± 0.006	0.439 ± 0.001	0.748	0.012	17	4.952	1.020	0.499
	1.46	0.430 ± 0.003	0.388 ± 0.001	0.774	0.006	27	8.831	0.445	0.415
90% Butanone + 10% isopropyl alcohol	6.00	0.782 ± 0.007	0.479 ± 0.004	0.800	0.006	9	1.995	— ^c	— ^c
	1.46	0.315 ± 0.002	0.460 ± 0.001	0.780	0.004	27	8.562	0.323	0.572
At $T = 48.2^\circ\text{C}$									
Toluene	6.00	1.900 ± 0.005	0.326 ± 0.001	0.716	0.017	12	3.797	1.950	0.381
	1.46	0.593 ± 0.003	0.327 ± 0.001	0.716	0.006	25	9.176	0.623	0.304
	0.58	0.318 ± 0.001	0.346 ± 0.001	0.754	0.002	18	4.973	0.325	0.414
Butanone	6.00	0.932 ± 0.006	0.481 ± 0.001	0.738	0.009	12	5.262	0.977	0.559
	1.46	0.369 ± 0.003	0.407 ± 0.001	0.780	0.006	20	7.077	— ^c	— ^c
90% Butanone + 10% isopropyl alcohol	6.00	0.842 ± 0.014	0.387 ± 0.008	0.860	0.010	8	2.031	— ^c	— ^c
	1.46	0.346 ± 0.003	0.370 ± 0.001	0.824	0.006	25	8.386	0.351	0.464

^a $\eta_r < 45.0$.

^b The confidence limit according to the t distribution.

^c No observed linear portion.

Table I shows the results obtained from three polystyrene fractions with the indicated number-average molecular weight M_n ,⁷ in three different solvents at 30 and 48.2°C. The data for the $M_n = 1.46 \times 10^5$ fraction are particularly chosen to demonstrate the linearity of the plot of η_{sp}/c versus η_{sp}^n , i.e., eqs. (6), as shown in Figure 1. The figure also includes the plots of eqs. (1)–(4). It is obvious that none is linear over the entire concentration range except curve V, which is constructed according to eq. (6). Nevertheless, two linear portions are noted, namely, curve I at $c < 3$ g/dl and curve III at $c > 3$ g/dl. The insert is the magnification of curve V at the dilution region. Curves I, II, IV, and V produce a common intercept of 0.70 dl/g at infinite dilution by graphic extrapolation. However, curve III yields $[\eta]_M = 0.71$ dl/g at $c = 0$, and its linear portion stretches to a much higher value of 0.82 dl/g. Statistical treatment reveals that $[\eta]_C = 0.688$

TABLE II
 Viscometric and Statistical Parameters for Polystyrene with $M_w = 370,000$ at 25°C^a

Solvent	$[\eta]_C$, dl/g	k_C	n	S.D., dl/g	N	C_h^b , g/dl	$[\eta]_H$, dl/g	k_H
Benzene	1.294 ± 0.008	0.283 ± 0.01	0.726	0.010	8	8.000	1.360	0.225
Chloroform	1.236 ± 0.003	0.339 ± 0.002	0.690	0.002	5	2.000	1.290	0.353
Toluene	1.191 ± 0.011	0.320 ± 0.001	0.712	0.013	8	8.000	1.240	0.345
Tetralin	1.146 ± 0.015	0.297 ± 0.009	0.772	0.012	5	2.000	1.160	0.326
Ethylbenzene	1.100 ± 0.005	0.310 ± 0.001	0.732	0.007	8	8.000	1.140	0.320
Dioxane	1.106 ± 0.005	0.301 ± 0.005	0.732	0.005	8	8.000	1.130	0.356
<i>o</i> -Dichloro- benzene	1.072 ± 0.030	0.355 ± 0.003	0.708	0.026	8	8.000	1.110	0.387
<i>x</i> -Dichlorodi- ethylbenzene ^c	0.880 ± 0.004	0.347 ± 0.003	0.764	0.002	5	2.000	0.898	0.427
<i>x</i> -Chlorotri- ethylbenzene ^c	0.837 ± 0.003	0.332 ± 0.002	0.808	0.002	5	2.000	0.848	0.421
Methyl <i>n</i> -amyl ketone	0.668 ± 0.002	0.362 ± 0.002	0.846	0.001	5	2.000	0.675	0.461
Butanone	0.638 ± 0.006	0.415 ± 0.0005	0.758	0.007	9	10.000	0.663	0.475
Ethyl acetate	0.586 ± 0.004	0.469 ± 0.0004	0.758	0.005	8	10.000	0.616	0.529
Decalin	0.533 ± 0.009	0.503 ± 0.001	0.780	0.010	8	8.000	0.564	0.529
Ethyl laurate	0.477 ± 0.008	0.530 ± 0.010	0.802	0.005	5	2.000	0.502	0.596

^a From reference 8.

^b $\eta_r < 100.0$.

^c A mixture of isomers with different *x*'s.

dl/g, in comparison with $[\eta]_H = 0.704$ dl/g reported by Weissberg et al.⁷ A total of 30 concentrations, with the highest of 9.328 g/dl, are entered into the computer program to get S.D. = 0.004 dl/g at $n = 0.724$. The confidence limits are found to be ±0.001 for $[\eta]_C$ and ±0.0003 for k_C . Other polystyrene fractions are likewise examined. They follow eq. (6) satisfactorily as justified by their S.D. values shown in Table I. Although some systems do not show linear behavior at all in the Huggins plot, they do exhibit reasonable linearity in the present analysis.

The $[\eta]$ of a polymer solution is related to its viscosity-average molecular weight M_v by the Mark-Houwink equation given as

$$[\eta] = KM_v^a \quad (9)$$

where K and a are the characteristic constants for a particular polymer-solvent system. At 30°C, statistical computation gives $K = 1.18 \times 10^{-4}$; $a = 0.73$, with S.D. = 0.016; and $r = 0.9997$ for polystyrene in toluene if the data of $[\eta]_C$ are used for analysis. These values are consistent with $K = 1.17 \times 10^{-4}$; $a = 0.73$, with S.D. = 0.014; and $r = 0.9998$ when values of $[\eta]_H$ are employed instead. The parallelism is observed for the same system at 48.2°C if $K = 0.66 \times 10^{-4}$; $a = 0.77$,

TABLE III
 Viscometric and Statistical Parameters for Vinyl Aromatic Polymers in Benzene at 30°C^a

Polymer	M_w $\times 10^{-5}$	$[\eta]_C$, dl/g	k_C	n	S.D., dl/g	N	C_h , ^b dl/g	$[\eta]_H$, dl/g	k_H
Poly(1-vinyl-naphthalene)	0.522	0.154 ± 0.001	0.424 ± 0.0001	0.816	0.002	17	26.528	0.156	0.50
	1.034	0.268 ± 0.003	0.347 ± 0.001	0.798	0.005	14	12.276	0.270	0.46
	1.473	0.359 ± 0.003	0.351 ± 0.0006	0.770	0.006	22	15.414	0.372	0.40
	1.553	0.370 ± 0.004	0.382 ± 0.001	0.740	0.006	16	14.516	0.387	0.43
Poly(2-vinyl-naphthalene)	0.489	0.203 ± 0.004	0.374 ± 0.002	0.758	0.005	10	14.498	0.204	0.50
	0.640	0.226 ± 0.002	0.394 ± 0.003	0.790	0.002	9	5.059	0.229	0.49
	1.825	0.436 ± 0.003	0.380 ± 0.001	0.730	0.004	12	10.395	0.453	0.42
	3.060	0.615 ± 0.010	0.383 ± 0.003	0.698	0.016	15	9.310	0.662	0.36
	5.634	0.855 ± 0.008	0.323 ± 0.003	0.724	0.010	13	5.478	0.880	0.36
	7.361	1.015 ± 0.008	0.341 ± 0.002	0.710	0.013	14	5.924	1.072	0.33
Poly(4-vinyl-biphenyl)	0.105	0.0699 ± 0.0001	0.608 ± 0.00004	0.864	0.0001	8	24.901	0.070	0.85
	0.808	0.227 ± 0.001	0.350 ± 0.0003	0.804	0.002	14	20.925	0.234	0.36
	1.030	0.243 ± 0.001	0.364 ± 0.0004	0.784	0.003	21	16.598	0.248	0.40
	1.694	0.375 ± 0.003	0.309 ± 0.001	0.784	0.005	18	12.143	0.381	0.33
	7.065	0.917 ± 0.013	0.303 ± 0.002	0.714	0.030	23	11.132	0.940	0.33
	11.040	1.246 ± 0.012	0.319 ± 0.003	0.710	0.018	16	5.058	1.281	0.36

^a From reference 9.^b $\eta_r < 100.0$.

with S.D. = 0.039; $r = 0.9986$ from the $[\eta]_C$ data, compared with $K = 0.68 \times 10^{-4}$; $a = 0.77$, with S.D. = 0.027; and $r = 0.9993$ from the $[\eta]_H$ values.

The results of another polystyrene fraction with $M_w = 370,000$ in 14 solvents at 25°C are listed in Table II.⁸ The data are also well fitted to eq. (6), with S.D. less than 0.03 dl/g for all systems investigated.

Utracki and co-workers⁹ have studied the viscosity of three vinyl aromatic polymers—poly(1-vinyl-naphthalene), poly(2-vinyl-naphthalene), and poly(4-vinylbiphenyl)—in benzene at 30°C over a wide range of concentrations. The results obtained from the present approach are shown in Table III. The values of $[\eta]_C$ agree well with those of $[\eta]_H$ reported in the original paper. Since there are remarkable discrepancies between the molecular weights measured by GPC and those measured by other absolute methods,¹² no effort is made to compare the values of Mark-Houwink and short-range interaction and long-range in-

TABLE IV
Viscometric and Statistical Parameters for Poly(vinyl Chloride) in Cyclohexanone at 30°C^a

$M_w \times 10^{-5}$	$[\eta]_C$, dl/g	k_C	n	S.D. dl/g	N	C_h , ^b g/dl	$[\eta]_H$, dl/g	k_H
2.30	1.993 ± 0.050	0.262 ± 0.004	0.778	0.054	8	4.538	2.053	0.300
1.74	1.476 ± 0.010	0.361 ± 0.001	0.742	0.010	7	5.412	1.524	0.427
1.51	1.405 ± 0.078	0.281 ± 0.006	0.766	0.086	9	6.272	1.409	0.333
1.12	1.013 ± 0.019	0.340 ± 0.001	0.756	0.019	9	7.967	0.987	0.499
1.10	1.013 ± 0.041	0.337 ± 0.004	0.754	0.051	10	7.127	1.053	0.378
1.00	0.927 ± 0.018	0.358 ± 0.001	0.742	0.018	10	8.792	0.984	0.393
0.80	0.861 ± 0.022	0.297 ± 0.002	0.776	0.030	10	8.792	0.851	0.435
0.70	0.664 ± 0.006	0.351 ± 0.001	0.752	0.008	11	11.213	0.684	0.397

^a From reference 10.

^b $\eta_r \leq 100.0$.

teraction parameters resulting from the two different analyses. It can be seen that the exponent n tends to increase slightly as the weight-average molecular weight M_w decreases. Poly(4-vinylbiphenyl), which has the lowest M_w of 10,500, displays exceptionally high values of n , k_C , and k_H .

Samples of whole poly(vinyl chloride) were produced by the suspension

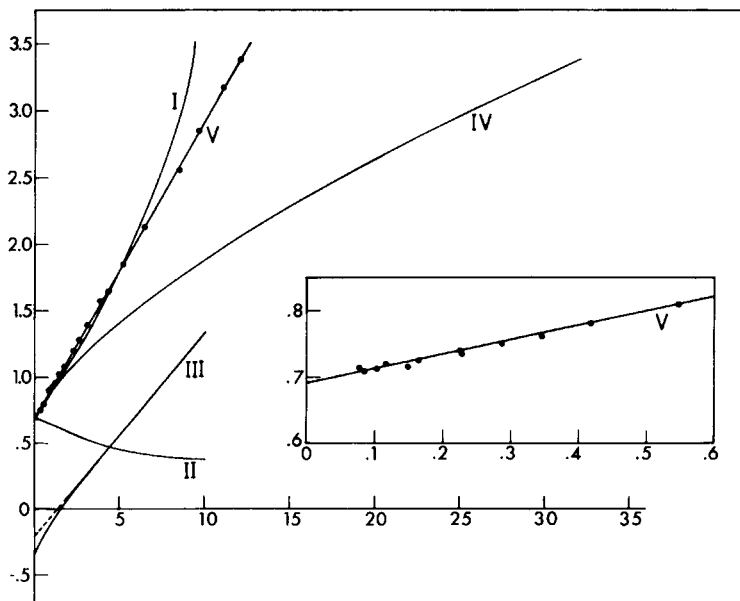


Fig. 1. Plots of eqs. (1)–(4) and (6) for polystyrene ($M_w = 146,000$) in toluene at 30°C. Curve I: η_{sp}/c vs. c , eq. (1); curve II: $\ln(\eta_r/c)$ vs. c , eq. (2); curve III: $\ln(\eta_{sp}/c)$ vs. c , eq. (3); curve IV: η_{sp}/c vs. η_{sp} , eq. (4); curve V: (●) η_{sp}/c vs. $\eta_{sp}^{0.724}$, eq. (6); insert: enlarged scale of curve V.

polymerization method.¹⁰ The viscosities of these unfractionated polymers were studied as functions of concentration and shear rate. The zero-shear Newtonian viscosities were derived and applied for our present purposes. The results demonstrated in Table IV show that $[\eta]_C$ and $[\eta]_H$ are again comparable. The S.D.'s are rather high in comparison with those of the fractionated samples. However, the variation in the n values for these samples is surprisingly low considering their substantial diversity in molecular weight distributions.

CONCLUSIONS

The viscometric data of moderately concentrated vinyl polymer solutions are satisfactorily described by eq. (6) in the sense that the r values are not smaller than 0.9990 in any instance. The accuracy of $[\eta]_C$ is expressed by the 95% confidence limit of the t distribution with $N-2$ degrees of freedom.⁶

The values of $[\eta]_C$ are almost consistently smaller than those of $[\eta]_H$, in particular for sharp polymer fractions. This is because $[\eta]_H$ is estimated by eq. (1) in which the higher concentration terms are neglected. The two parameters are empirically correlated by

$$[\eta]_C = 0.972[\eta]_H \quad (10)$$

with S.D. = 0.0151 dl/g and $r = 0.9995$ for these series of polymers. The average deviation is less than 3%. However, the constant k_C is not a simple function of k_H as reflected by $r = 0.8947$. This is not unexpected when referring to eq. (5).

The exponent n varies from 0.69 to 0.86 depending on the system. The upper limit of concentration is arbitrarily set at $\eta_r < 100.0$, and it is not unlikely that it can be extended to a somewhat higher level. This investigation covers molecular weights ranging from 1.1×10^6 to 1.0×10^4 . Low molecular weight species of poly(vinyl chloride) of $M_v = 1.05 \times 10^4$ and 2.6×10^4 reported in reference 10 result in $[\eta]_C = 0.204$ and 0.365 dl/g, respectively. These figures are distinctly higher than the Huggins values probably because the density recommended is too low for these two entities.

The Martin equation, which was particularly devised to deal with fairly concentrated polymer solutions, does not seem to produce acceptable $[\eta]$ values⁸ in this particular study. It is obvious that eq. (6) would definitely cover a wider range of concentrations than any other forms discussed. More important, it leads to reliable results as far as the $[\eta]$ determination is concerned. These findings will make the $[\eta]$ measurement method more workable by providing more room to select an appropriate initial concentration to start the experiment.

The $[\eta]$ has also been evaluated from moderately concentrated solutions by the Baker equation¹³ or the extended power series expressions of Huggins and Kraemer.^{7,14,15} However, eq. (6) seems to be the only three-parameter equation that can estimate $[\eta]$ from concentrated polymer solutions of η_r as high as 100.0 without loss of accuracy.

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