One-Point Determination of Intrinsic Viscosity for Polycarbonate, Poly(phenylene Oxide), and Polyetherimide

JOHN R. NERO and SUBHAS K. SIKDAR, *General Electric Research and Development Center, Schenectady, New York 12301*

Synopsis

Intrinsic viscosity determination for polymers can be simplified and considerable time and effort saved via a single measurement of relative viscosity at a known concentration. Several workers have proposed one-point intrinsic viscosity methods. Of the methods in the literature, two one-point methods were found to be as accurate as the multiple-point graphical extrapolation procedure. These two methods, one due to Solomon and Ciuta and a nomographic technique due to Khan and Bhargava, were successfully applied for the intrinsic viscosity determination of three polymers: polycarbonate, poly(phenylene oxide) and polyetherimide.

INTRODUCTION

Intrinsic viscosity $[\eta]$ is generally determined by the manipulation of dilute solution viscosities of a polymer in a given solvent using an appropriate relationship which describes $[\eta]$ in terms of specific viscosity η_{sp} or relative viscosity η_r. Two commonly used relationships are the equations of Huggins and of Kraemer.

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c, \quad \text{Huggins equation} \tag{1}$$

$$\ln \eta_r/c = [\eta] - k''[\eta]^2 c, \quad \text{Kraemer equation} \tag{2}$$

These equations are actually truncated versions of virial expressions in concentration c, where k' and k'' are constants for a given polymer–solvent system. The intrinsic viscosity is determined by measuring relative viscosities (or specific viscosities) at a series of different concentrations and extrapolating this data to infinite dilution. An example of intrinsic viscosity determination for a bisphenol-A polycarbonate–chloroform system at 25°C via Huggins plot and Kraemer plot is shown in Figure 1.

The time and effort involved in this method can be drastically reduced by requiring only one relative viscosity measurement for $[\eta]$ determination. Using a single point method, it is possible to obtain accurate and quick intrinsic viscosity data.

Numerous single point methods are found in the literature (Solomon and Ciuta,[1] Deb and Chatterjee,[2] Elliot et al.[3]). Most of these equations are derivable from Huggins' or Kraemer's equation. These equations are successful in particular cases in predicting intrinsic viscosity with varying degrees of accuracy. Another approach via a single specific viscosity measurement has been proposed recently by Khan and Bhargava,[4] who tried a nomographic technique.
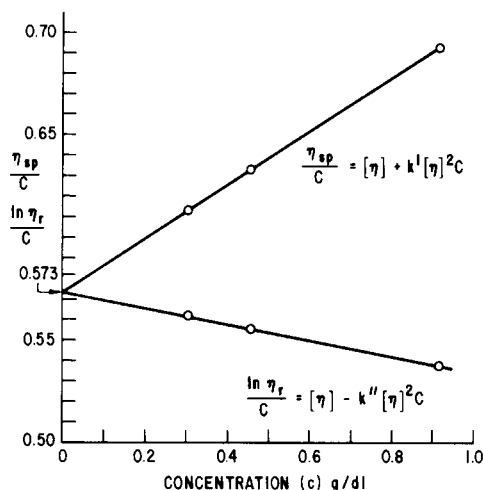
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Fig. 1. Correlations for viscosity of dilute solutions for polycarbonate/chloroform system at 25°C.

In this paper we present an analysis of dilute solution viscosity data for common intrinsic viscosity ranges of three polymers in chloroform: bisphenol-A polycarbonate, poly(2,6-dimethyl-1,4-phenylene oxide), and a polyetherimide.[5] The purpose of this paper is to evaluate two one-point methods in terms of intrinsic viscosities of these polymers. The two methods, an equation due to Solomon and Ciuta and a nomographic technique of Khan and Bhargava, were selected after screening the methods in the literature for accuracy and convenience.

DISCUSSION

Solomon and Ciuta have proposed a fairly accurate single point equation for flexible polymers. Solomon and Ciuta's formula for one-point intrinsic viscosity,

$$[\eta] = \sqrt{2}/c \sqrt{\eta_{sp} - \ln \eta_r} \qquad (3)$$

is derived by combining the Huggins and Kraemer equations, noting that as $c \rightarrow 0$, $k' + k'' = \frac{1}{2}$. Palit and Kar[6] have also derived eq. (3), showing that it follows directly from the definition of intrinsic viscosity and is not dependent on the Huggins or Kraemer equations.

The Solomon and Ciuta equation, for good polymer–solvent systems, will give accurate $[\eta]$ results at low concentrations if a single measurement of relative viscosity is made at a known concentration. The authors suggest concentrations of 0.2% for use with eq. (3); higher concentrations will increase the error in this method. The prime condition of validity for Solomon and Ciuta's equation is $\eta_{sp} \ll 1$.

Gillespie and Hulme[7] have shown that the Solomon and Ciuta equation should give results in agreement with the Huggins' equation when $k' = \frac{1}{3}$. Therefore, the correctness of the single point $[\eta]$ value can be determined. In addition, Shroff[8] has proposed that, for k' values in the range of 0.3–0.4, good agreement

TABLE I
Comparison of Intrinsic Viscosity Values Determined by Extrapolation and Those Calculated
From Solomon and Ciuta's Equation

Polymer–solvent system	Concentration[a]	Extrapolation	Solomon–Ciuta	k	$\Delta[\eta]$
Polyetherimide/chloroform at 250°C					
	1.0264	0.518	0.516	0.348	0.002
	0.342	0.518	0.513	0.344	0.005
	0.8529	0.325	0.327	0.340	0.002
	0.2843	0.325	0.321	0.341	0.004
	0.9753	0.431	0.423	0.344	0.008
	0.3251	0.431	0.423	0.343	0.008
	0.1172	0.284	0.279	0.340	0.005
	0.586	0.284	0.282	0.365	0.002
Polyphenylene oxide/ chloroform at 25°C					
	1.3291	0.429	0.414	0.348	0.015
	0.4430	0.429	0.421	0.338	0.008
	1.4280	0.655	0.585	0.351	0.30
	0.4160	0.655	0.583	0.342	0.28
	0.7140	0.280	0.275	0.328	0.005
	0.4160	0.280	0.274	0.328	0.006
	1.7567	0.344	0.341	0.346	0.003
	0.5855	0.344	0.341	0.339	0.003
Polycarbonate/chloroform at 25°C					
	0.9865	0.493	0.497	0.349	0.004
	0.329	0.493	0.484	0.350	0.011
	1.0232	0.638	0.633	0.351	0.005
	0.5116	0.638	0.627	0.343	0.011
	0.9558	0.341	0.341	0.342	0.00
	0.3186	0.341	0.342	0.348	0.001
	1.0991	0.239	0.236	0.343	0.003
	0.3663	0.239	0.235	0.395	0.004

[a] The Huggins relation is obeyed for all examples at least up to the concentration cited.

can be expected between the single-point and multipoint extrapolation method.

When examined against intrinsic viscosity data of polycarbonate, poly(phenylene oxide), and polyetherimide, Solomon and Ciuta's equation has been found to be fairly accurate, even up to concentrations of 1%. Table I illustrates the accuracy of this technique for these polymers. Huggins constant k' values are included in this table for comparison. As expected, good agreement with the multipoint method is exhibited by the k' values falling in the range 0.3–0.4.

Another single point method, chosen for use with these polymers because of its convenience and accuracy, is a graphical solution proposed by Khan and Bhargava.[4] This method has been found to be of more general use than other single-point techniques found in the literature.

The graphical solution employs the theory of parallel axes and the relationship between $[\eta]$ and η_{sp}/c, as given by the Huggins equation, as a basis for the single-point determination of $[\eta]$. Thus eq. (1) can be written as

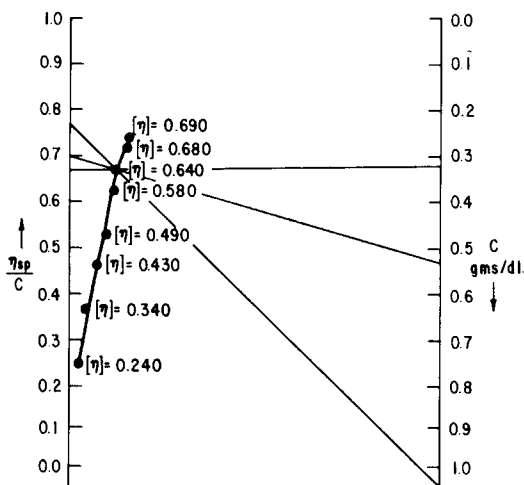$$[\eta] = \eta_{sp}/c - KC \quad (K = k'[\eta]^2) \tag{4}$$

Fig. 2. Locus of [η] for a polycarbonate/chloroform system at 25°C.

By plotting reduced viscosity η_{sp}/c and concentration data from a given polymer–solvent system on parallel and opposite axes, a standard locus for that system is formed, as exemplified by the polycarbonate/chloroform data in Figure 2. This locus is used to find [η] of a polymer fraction if one specific viscosity measurement is made.

The curve is set up by using data from several [η] values (multipoint method) of different polymer molecular weight fractions. For each fraction, η_{sp}/c and c values are plotted and joined by a straight line on parallel and opposite axes of a graph. The lines formed for each value of [η] will intersect. Intersecting points from several [η] values will lie on a nonlinear curve, which can be termed the locus of [η].

Given the locus, the value of [η] for the polymer sample can be determined by knowing one specific viscosity measurement. By plotting the values of η_{sp}/c and
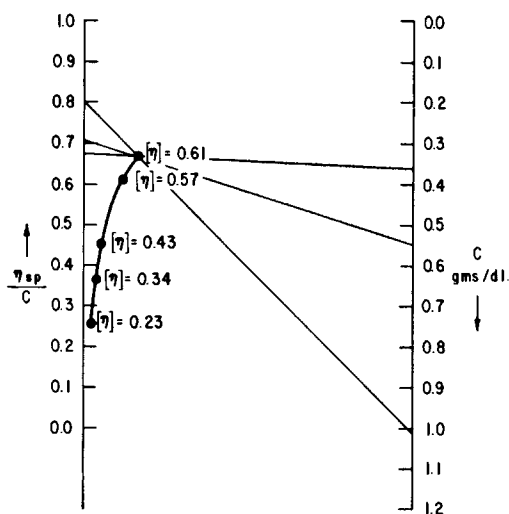

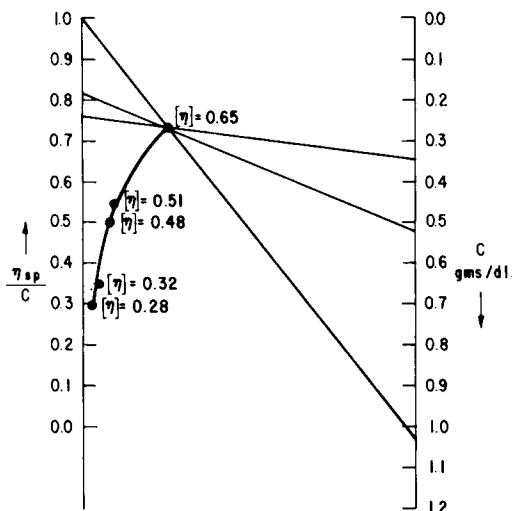Fig. 3. Locus of [η] for a polyphenylene oxide/chloroform system at 25°C.

Fig. 4. Locus of $[\eta]$ for a polyetherimide/chloroform system at 25°C.

c from one specific viscosity measurement and joining the points, the line formed will intersect the locus of $[\eta]$. When this intersecting point is connected to the zero of the c axis and extrapolated to the η_{sp}/c axis, the value of $[\eta]$ is given on η_{sp}/c axis.

This graphical solution can easily be determined for good polymer–solvent systems. Figures 3 and 4 display loci of $[\eta]$ for a common range of $[\eta]$ values for poly(phenylene oxide)/chloroform and polyetherimide/chloroform systems at 25°C. Table II illustrates the accuracy of the one-point graphical method for polycarbonate/chloroform and poly(phenylene oxide)/chloroform systems at 25°C.

CONCLUSIONS

It is the authors' recommendation that the single-point methods of Solomon and Ciuta and the nomographic technique of Khan and Bhargava are accurate

TABLE II
Comparison of Extrapolation and Graphical Determination of $[\eta]$

Polymer–solvent system at 25°C	$[\eta]$ Extrapolation	$[\eta]$ Graphical	$\Delta[\eta]$
Polyphenylene oxide/chloroform	0.232	0.228	0.004
	0.323	0.285	0.038
	0.394	0.390	0.004
	0.505	0.515	0.01
	0.538	0.512	0.026
	0.638	0.623	0.015
Polycarbonate/chloroform	0.262	0.270	0.008
	0.341	0.350	0.009
	0.389	0.375	0.014
	0.419	0.443	0.024
	0.477	0.475	0.002
	0.648	0.630	0.018

and most easy to use. When compared to other methods found in the literature, Solomon and Ciuta's formula is preferred because it has a means of testing the correctness of the single point $[\eta]$ value. The graphical method is not limited by intrinsic viscosity or concentration and will be valid when other methods fail. The results given indicate both methods yield acceptable and reliable $[\eta]$ values for polycarbonate, poly(phenylene oxide) and polyetherimide–chloroform systems.

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