Estimation of Unperturbed Parameter K_θ by Gel Permeation Chromatography and Viscometry

INTRODUCTION

The unperturbed chain dimension is an important parameter of a polymer directly related to the conformations of the chains in solutions. They are determined either by direct measurements in the theta, θ, solvents or by measuring the perturbed dimensions in good solvents and then extrapolating to the unperturbed state using one of the several existing theories. When determined directly by light scattering and viscometric methods from dilute solutions in θ solvents, introduction of some errors due to poor solubility of polymers in the vicinity of θ temperatures is very likely. On the other hand, indirect methods require the determinations of intrinsic viscosities and measurements of molecular masses of a number of fractions in thermodynamically good solvents. These methods are also rather time-consuming. Both methods, however, have been widely used and a good agreement between the results obtained by these two procedures has been reported.

In this communication we propose a simple method for the determination of unperturbed chain parameter, K_θ, from a single viscometric measurement and a gel permeation chromatography (GPC) chromatogram. This is actually an extension of the application of the method of Weiss and Cohn-Ginsberg[1] for the measurement of Kuhn–Mark–Houwink–Sakurada (KMHS) constants.

THEORY

In GPC work, the universal calibration parameter J is defined as

$$J_i = [\eta]_i M_i \tag{1}$$

where $[\eta]_i$ and M_i represent the intrinsic viscosity and the molecular mass of ith species. The KMHS equation for the same species is written as

$$[\eta]_i = K M_i^a \tag{2}$$

By substituting the M_i value from eq. (1) into eq. (2) one obtains for $[\eta]_i$

$$[\eta]_i = K^{1/(1+a)} J_i^{a/(1+a)} \tag{3}$$

It is known that the conventional determination of intrinsic viscosity yields the weight average intrinsic viscosity,[2] which means

$$[\eta] = [\eta]_{av} = \sum_i w_i [\eta]_i \equiv [\eta]_w \tag{4}$$

where w_i is the weight fraction of ith species. Combination of eqs. (4) and (3) gives the following:

$$[\eta] = K^{1/(1+a)} \sum_i w_i J_i^{a(1+a)} \tag{5}$$

If the KMHS constants K and a for the GPC conditions, i.e., for that particular GPC solvent and temperature, are available and the w_i and J_i values can be obtained from a GPC chromatogram and calibration curve, the $[\eta]$ value for that polymer can be calculated from eq. (5) by the method of Weiss and Cohn-Ginsberg.[1] This method requires the establishment of a universal calibration curve and the availability of KMHS constants for the conditions and solvents employed in GPC measurements.

At this point its use can be easily extended for the determination of molecular mass of polymers in θ conditions. For a solvent other than that used in GPC measurements, following the similar

arguments leading to eq. (5), one can write for the intrinsic viscosity of a polymer in a non-GPC solvent

$$[\eta]_2 = K_2 K_1^{-a_2/(1+a_1)} \sum_i w_i J_{i,1}^{a_2/(1+a_1)} \tag{6}$$

where the subscripts 1 and 2 refer to GPC and non-GPC solvents, respectively. A slightly different form of eq. (6) has been used recently by Dobbin et al.[3] to determine the KMHS constants for a polymer having broad molecular mass distribution.

If the non-GPC solvent is a θ solvent, however, one can make the following substitutions in eq. (6): $[\eta]_\theta = [\eta]_2, a_2 = 0.5$, and $K_\theta = K_2$

$$[\eta]_\theta = K_\theta K_1^{-0.5/(1+a_1)} \sum_i w_i J_{i,1}^{0.5/(1+a_1)} \tag{7}$$

or

$$[\eta]_\theta / K_\theta = K_1^{-0.5/(1+a_1)} \sum_i w_i J_{i,1}^{0.5/(1+a_1)} \tag{8}$$

The left-hand side of eq. (8) is nothing but the square root of the viscosity average molecular mass of the polymer under θ conditions. In other words,

$$M_{\eta,\theta} = K_1^{-1/(1+a_1)} \left(\sum_i w_i J_{i,1}^{0.5/(1+a_1)} \right)^2 \tag{9}$$

The above equation provides a simple and direct way of estimating the viscosity average molar mass of polymers at θ state from a single GPC chromatogram in good solvents. The terms in large parentheses can be easily obtained from the chromatogram of that specific polymer and the universal calibration curve.

Once $M_{\eta,\theta}$ is obtained in this way, it can be used to calculate the K_θ value directly from KMHS equation,

$$[\eta]_\theta = K_\theta M_{\eta,\theta}^{0.5} \tag{10}$$

by inserting the experimentally determined intrinsic viscosity value $[\eta]_\theta$ (at any θ solvent and temperature). This K_θ value can then be used to calculate the unperturbed dimension through the expression $(K_\theta/\phi)^{1/3}$, where ϕ is the Flory constant.

EXPERIMENTAL

In this study two polymers, namely, poly(ethyl methacrylate) (PEMA) and poly(n-butyl methacrylate) (PBMA), were used to check the validity of the proposed method. A Waters Model 244 GPC/ALC instrument was used throughout the study. GPC was operated on THF at room temperature. The chromatograph was equipped with four μ-styragel columns of 10^6, 10^5, 10^4, 10^3 Å pore dimensions. The columns were calibrated with a series of narrow molecular mass distribution polystyrene standard samples obtained from Polysciences, Inc. Using the KMHS constants of PEMA and PBMA in THF at room temperature[4] and the universal calibration curve and the chromatograms of the polymer samples, the average molecular masses and molecular mass distribution of the samples are determined and given in Table I. The intrinsic viscosities of the polymer samples listed in Table II were determined under θ conditions by using an Ubbelohde type viscometer.

TABLE I
Characteristics of Polymers Used in This Work

Polymer	M_w/M_n	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	$M_\eta \times 10^{-5}$ [a]	$M_{\eta,\theta} \times 10^{-5}$ [b]
PEMA	2.14	11.0	5.1	9.4	8.7
PBMA	3.04	12.0	4.0	1.04	8.8

[a] Viscosity average molecular mass determined in THF at 25°C by using $[\eta] = 15.49 \times 10^{-5} M^{0.679}$ for PEMA[4] and $[\eta] = 5.23 \times 10^{-5} M^{0.758}$ for PBMA.[4]

[b] Computed from corresponding GPC chromatograms and universal calibration curve according to eq. (9).

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TABLE-II

Intrinsic Viscosities and Unperturbed Parameters of PEMA and PBMA

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Polymer	Solvent(s)	θ (°C)	$[\eta]_\theta$ (cc/g) measured	$K_\theta \times 10^3$ (cc/g) This work	Literature	References
PEMA	Isopropanol	36.9	43.6	46.8	47.5	8
	Isopropanol	36.9			64.0	9
	Butanone/ Isopropanol (1:7)	23.0	49.2	52.5	47.3	8
PBMA	Isopropanol	20.9			38.8	7
	Isopropanol	23.0	34.3	36.6	34 ± 5	8
	Isopropanol	25.0			42.0	10

RESULTS

To assess the accuracy of the proposed method, first the intrinsic viscosities of PEMA in single and binary solvent mixtures were determined under θ conditions. $M_{\eta,\theta}$ of the same polymer was computed from its GPC chromatogram according to eq. (9). The calculated K_θ values using these two quantities are listed in Table II together with some literature values. Although K_θ should be constant for a given polymer independent of solvent and temperature, there are almost always inconsistencies in the K_θ values of a specific polymer reported in the literature. The literature K_θ values given for these two polymers in Table II are not exhaustive; only those values obtained by direct measurements under θ conditions are listed. Even the values reported for PEMA in the same solvent and at the same temperature differ by about 25%. So it is not easy to make a reliable comparison of our values with those reported in the literature. We can, however, say that the values given in Ref. 8 and our K_θ values are in good agreement both for PEMA and PBMA.

Several studies[5,6] showed that both solvent and temperature have a combined effect on K_θ. For PBMA such an effect has been reported.[7] As can be seen from Table II, even different θ temperatures have been reported for PBMA in isopropanol. Consequently, uncertainty in θ temperature will result in different K_θ values. K_θ determined for PBMA by the method proposed here using the measured value of $[\eta]_\theta$ at 23°C in isopropanol agrees very well with the value given in Ref. 8. The K_θ's obtained in this study are also in good agreement with those obtained by extrapolation procedures in good solvents.[7-10].

In conclusion, the GPC analysis of a polymer in a solvent whose KMHS constants are known can be used to estimate the viscosity average molar mass in θ conditions and the unperturbed parameter K_θ, provided that the intrinsic viscosity in θ state is determined. This procedure of determining K_θ is more practical than the conventional methods which require either fractionation of polymers and measurements of intrinsic viscosities and molar masses of each fraction in good solvents or determination of intrinsic viscosity and molar mass of whole polymers in θ conditions. The proposed method, however, is limited by the availability and reliabilities of KMHS constants. The strong dependence of viscosity on temperature in the vicinity of θ temperature remains to be a possible source of error as it is in the conventional methods.

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