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Study on the concentration effects in size exclusion chromatography VII. A quantitative verification for the model theory of concentration and molecular mass dependences of hydrodynamic volumes for polydisperse polymers

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Abstract

A model theory of concentration effects for polydisperse polymers was proposed in 1988. It is successful in relating the concentration of the injected solution to the effective hydrodynamic volumes of peak, the retention volumes of peak and the polydispersity index ($D_c = \langle V_{\text{new}} \rangle / \langle V_{\text{hen}} \rangle$) of hydro-dynamic volume distribution for polydisperse polymers at a given concentration. The dependence of the concentration of injected polymer solution on the effective hydrodynamic volumes, the retention volumes of peak and the polydispersity index of hydrodynamic volume distribution for narrow disperse and polydisperse polystyrene, poly(dodecyl methacrylate), poly(tridecyl methacrylate) and poly(methyl methacrylate) in tetrahydrofuran solvent were studied. The proposed theory was verified by these experimental data. Results show that the proposed theory can predict the concentration effects in GPC for polydisperse polymers quantitatively and can provide a theoretical foundation for the two methods of calibrating the universal calibration curves with polydisperse polymers and of determining the second virial coefficients (A_2) of polymers. It is found that the determined values of A_2 for narrow disperse and polydisperse polymers by the proposed method are in agreement with those obtained by the LALLS method, and the two universal calibration curves with narrow disperse and polydisperse polymers are in excellent agreement. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Concentration effects; Molecular mass dependence; Hydrodynamic volume; Second virial coefficients; Universal calibration; Polydisperse polymers; Polymers

1. Introduction

The effects of sample concentration on the gel permeation chromatography (GPC) retention volumes and the hydrodynamic volumes of polymers with narrow molecular mass distribution are well

established [1–6] and have been characterized by a simple model theory [7]. The effective concentration of the narrow distribution polymers in GPC separation process may be taken to be equal to the respective concentration of the solutes which are injected into the columns, since the volume contraction coefficients (β) for each kind of macromolecules approximately have the same value, so that it

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did only lead to the same dilution or the same concentration effects for each kind of macromolecule. Thus a narrow disperse specimen travels through the columns in the absence of spreading and skewing resulting from the same concentration effects for each kind of macromolecule. Thus only the retention volumes of the peak tend to increase with increasing concentration in the sample.

For a specimen with broad molecular mass distribution and at higher concentration, the effects of concentration on the shift of retention volumes, the axial spreading and the skewing must be taken into account at the same time. As given by Blasdon [8], Tung [9], Dawkins [10] and Hamielec [11], the higher concentration solution of high polymers with broad distribution dissolving in a good solvent can cause distortion of chromatograms and shows a marked axial spreading, skewing and tailing. Therefore in the second paper [12] we had proposed a new model theory of concentration effects for polydisperse polymers, which can predict the shift of retention volumes, the axial spreading and the skewing of the chromatograms resulting from the concentration effects. In this paper a quantitative verification for the model theory of concentration effects for polydisperse polymers in size exclusion chromatography will be provided.

2. Model theory of concentration effects [12]

2.1. Characteristics of chromatograms by hydrodynamic volumes

According to Tung [13] the chromatogram of the polymers is the convolution of two distributions. One is the distribution $C(v)$ of the polymers as a function of retention volume v , $C(v)d(v)$ is the amount of polymers with retention volume between v and $v + d(v)$, and $G(v - v_e)$ is the axial dispersion function of the column plus the instrument. It represents the shape of the chromatogram for a monodisperse sample with exclusion volume v_e and normalization at unity of the area between the curve and the retention volume axis.

This chromatogram, then, has the following equation:

$$F(v) = \int_0^{\infty} C(v)G(v - v_e) dv \quad (1)$$

Where $F(v)$ is the response of a detector sensitive to the concentration and $\int_0^{\infty} F(v) dv$ is the total amount of polymer injected.

It is usually assumed that $G(v - v_e)$ is a Gaussian distribution and has the following form:

$$G(v - v_e) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left\{-\frac{(v - v_e)^2}{2\sigma^2}\right\} \quad (2)$$

Where σ is the axial dispersion parameter. This assumption is not limiting the generality of our solution, since when the chromatographic measurement is performed on a good apparatus with a highly effective separating column and is performed in an excellent working condition, thus the resulting distribution curve for a narrow disperse polymer may be approximate to the Gaussian distribution function.

Another approximation is related to the calibration curve. It is better to use the universal calibration and the effective hydrodynamic volume V_h to characterize the set of columns.

According to the universal calibration curves the dependences of retention volumes (v) or exclusion volumes—retention volumes of peak (or v_e) on the effective hydrodynamic volumes (V_h) or the effective hydrodynamic volumes of peak (or \hat{V}_h) may be characterized as follows:

For the effective hydrodynamic volumes of peak for the solvated macromolecules in monodisperse polymers at infinitive dilution:

$$\ln[\eta]M = \ln \hat{V}_{\text{hop}} = a - bv_{e0} \quad (3.1)$$

where $[\eta]M = V_{\text{ho}}$ (by Benoit equation); $[\eta] = KM^\alpha$ (by the Mark–Houwink equation); K and α are constants of the Mark–Houwink equation.

For the effective hydrodynamic volumes of the peak for the solvated macromolecule in monodisperse polymers at a given concentration (C):

$$\ln \hat{V}_{\text{hcp}} = a - bv_{ec} \quad (3.2)$$

For the effective hydrodynamic volumes of the peak for the solvated macromolecule in polydisperse polymers at a given concentration (C):

$$\ln \hat{V}_{\text{hcp}} = a - bv_{ec} \quad (3.3)$$

For the hydrodynamic volumes of any kind of solvated macromolecules in polydisperse polymers at a given concentration (C):

$$\ln \hat{V}_{hc} = a - bv_c \quad (3.4)$$

From the above relations it is easy to show that the difference between the retention volumes (v) and the retention volumes of the peak (v_e) for the two kinds of solvated macromolecules in polydisperse polymers at a given concentration (C) may be expressed as:

$$\begin{aligned} v_c - v_{ec} &= (-1/b)(\ln V_{hc} - \ln \hat{V}_{hcp}) \\ &= A(\ln \hat{V}_{hc} - \ln \hat{V}_{hcp}) \end{aligned} \quad (3.5)$$

Dropping out C , we have:

$$v - v_e = (A) \ln(V_h / \hat{V}_{hp}) \quad (3)$$

Where $A = 1/(-b)$, it is a constant, a and b are constants for the universal calibration curve, \hat{V}_{hcp} and \hat{V}_{hop} are the effective hydrodynamic volumes of the peak at a given concentration (C) and infinitive dilution, V_{hc} and V_{ho} are the effective hydrodynamic volumes for any kind of solvated macromolecules at a given concentration and infinitive dilution.

If we use these relations $V_{ho} = [\eta] \cdot M$ and $[\eta] = K \cdot M^\alpha$, it is possible to change the variable v to the quantities V_h , the concentration of polymers with retention volumes $C(v)dv$ is transformed to $C(V_h) dV_h$, thus we have:

$$\begin{aligned} F(V_h) &= \frac{1}{\sqrt{2\pi}} \frac{A}{\sigma} \left(\frac{1}{V_h} \right) \int_{-\infty}^{\infty} C(V_h) \\ &\cdot \exp \left\{ -\frac{A^2}{\sigma^2} \ln^2 \left(\frac{V_h}{\hat{V}_{hp}} \right) \right\} dV_h \end{aligned} \quad (4)$$

The quantity under the integral is the contribution of polymers with the effective hydrodynamic volumes between V_h and $V_h + dV_h$. $C(V_h)$ represents the true or theoretical chromatogram of the sample. $F(V_h)$ is the observed or experimental chromatogram which has broadened by the chromatographic column dispersion process. For the narrow disperse polymers the function of $F(V_h)$ usually has the Wesslau type of distribution [14].

2.1.1. Concentration dependence of hydrodynamic volumes

According to our model theory [7] the effective hydrodynamic volumes, V_{hc} , of a monodisperse solvated macromolecule at a given concentration, C , is defined as follows:

$$V_{hc} = V_{ho} \beta = \beta_0 \exp - \left\{ \frac{\eta_{sp}}{[C]} \right\} \cdot V_{ho} \quad (5)$$

It is evident that Eq. (5) is distinguished from the Eizner and Yamakawa relations [6] in characterizing the concentration effect on macromolecular dimension.

For the hydrodynamic volume [6]:

$$V_{hc}^E = V_{ho} (1 - A_2 M F_E C - \dots)^3 \quad (\text{for Eizner}) \quad (5.1)$$

and

$$V_{hc}^Y = V_{ho} \exp(-3A_2 M F_Y C) \quad (\text{for Yamakawa}) \quad (5.2)$$

The former relation is based on the conception of contraction coefficients (β) for effective hydrodynamic volumes at infinitive dilution. Thus it can be successful in separately estimating the contributions of concentration effects resulting from the concentration (C) and the molecular mass (M) in a given solvent with the term of $\beta = \beta_0 \exp - \{ \eta_{sp} / C / [\eta] \}$ and $V_{ho} = K(M)^{1+\alpha}$ in Eq. (5), but the latter relations in Eqs. (5.1) and (5.2) are derived from the conception of the expansion factor for radius of gyration (α_s^2), and the parameters (Z) or (F) in the expression of the expansion factor is not directly experimentally accessible, it can only be determined from experimental data with the aid of different theories. Therefore there are two different equations, (5.1) and (5.2), for characterizing the concentration effects on macromolecular dimension.

Where F_E and F_Y are the parameters of excluded volume effects, A_2 and M are the second virial coefficient and molecular mass, β is the volume contraction coefficient, it decreases with increasing concentration, C , the specific viscosity, η_{sp} , and the intrinsic viscosity, $[\eta]$, and $\beta_0 = e$ is a constant. In the polydisperse polymer system the term of ($\eta_{spj} /$

$c_j)/[\eta]_j$ for j -th kind of monodisperse polymer chain may be expressed by the following relation [12]:

$$\frac{\eta_{spj}}{C_j} = 1 + K_H[\eta]_j C_j + K'[\eta]_j^2 C_j^2 \quad (6)$$

where K_H is the Huggins constant which reflects the polymer–solvent interaction, K' is a constant. If in the polymer system there are j kinds of macromolecules with different effective hydrodynamic volumes, V_{hcj} . At a given concentration the weight-average effective hydrodynamic volume which has been corrected by the axial dispersion may be calculated by the following equation:

$$\langle V_{hcw} \rangle = \sum_{j=1}^{\infty} \bar{W}_j V_{hcj} \quad (7)$$

where V_{hcj} is the effective hydrodynamic volume of the solvated molecule for the j -th kind; \bar{W}_j is the weight fraction of macromolecules for the j -th kind.

Substituting Eqs. (5) and (6) into Eq. (7) yields:

$$\langle V_{hcw} \rangle = \sum_{j=1}^{\infty} V_{hoj} \bar{W}_j \exp - \{K_H[\eta]_j C_j + K'[\eta]_j^2 C_j^2\} \quad (8)$$

In Eq. (8) the summation is with respect to the j of \bar{W}_j , C_j and $[\eta]_j$. But the average values to be calculated is the weight-average of hydrodynamic volumes, therefore it is necessary to change the $C_j[\eta]_j$ to the effective hydrodynamic volume, V_{hcj} , by the relation:

$$C_j[\eta]_j = [\eta]_j \frac{C_j M_j}{M_j} = V_{hcj} C_{jm}$$

Where $C_{jm} = C_j/M_j$, it represents the mole concentration of molecules for the j -th kind, substituting this relation into Eq. (8) and taking the average we have:

$$\langle V_{hcw} \rangle = \langle V_{how} \rangle \exp - \{K_H \langle V_{how} \rangle C_M + K' \langle V_{how} \rangle^2 C_M^2\} \quad (9)$$

Where C_M is the mole concentration for all the polymer molecules; $\langle V_{how} \rangle$ is the weight-average hydrodynamic volume at infinitive dilution, it is independent on the concentration, but it is only determined by the molecular mass, its distribution of the sample and the polymer–solvents system. It is

usually assumed [14] that the distribution of the studied polymers obeys logarithmic normal function. Then $\langle V_{how} \rangle$ may be expressed by the relation [12]:

$$\langle V_{how} \rangle = [\bar{\eta}] \bar{M}_w Q_{1w} \quad (10)$$

Where Q_{1w} represents a correct factor for the polydispersity index of molecular mass distribution obtained by the method of weight-average of hydrodynamic volume, it is the function of the polydispersity index of molecular mass distribution and polymer–solvent systems.

Substituting this relation into Eq. (9) yields:

$$\langle V_{hcw} \rangle = [\bar{\eta}] \bar{M}_w Q_{1w} \exp - \{K_H [\bar{\eta}] Q_{1w} C + K' [\bar{\eta}]^2 Q_{1w}^2 C^2\} \quad (11)$$

At relatively low concentration, Eq. (11) may be simplified to:

$$\langle V_{hcw} \rangle = [\bar{\eta}] \bar{M}_w Q_{1w} \exp - \{K_H [\bar{\eta}] Q_{1w} C\} \quad (12)$$

Where C is the weight concentration for the whole polymer.

2.1.2. Concentration dependence of GPC retention volumes

It is known that the average effective hydrodynamic volumes of polydisperse polymers is not a unique function of the retention volumes of the peak. For establishing this relation between them we had proposed a corrected method [15], in which a correct factor Q_{2w} was derived. It is shown that Q_{2w} is the function of the polydispersity index of molecular mass distribution, the intrinsic viscosity, the concentration and the polymer–solvent systems. Introducing the above correct factor into Eqs. (11) and (12), the effective hydrodynamic volume of peaks, \hat{V}_{hcp} , may be written in this form:

$$\hat{V}_{hcp} = [\bar{\eta}] \bar{M}_w \left(\frac{Q_{1w}}{Q_{2w}} \right) \exp - \{K_H [\bar{\eta}] Q_{1w} C + K' [\bar{\eta}]^2 Q_{1w}^2 C^2\} \quad (13)$$

and

$$\hat{V}_{hcp} = [\bar{\eta}] \bar{M}_w \left(\frac{Q_{1w}}{Q_{2w}} \right) \exp - \{K_H [\bar{\eta}] Q_{1w} C\} \quad (14)$$

where \hat{V}_{hcp} is the effective hydrodynamic volume of

the peak at a given concentration. Taking the logarithm of Eqs. (13) and (14) yields:

$$\begin{aligned} \ln \hat{V}_{\text{hcp}} &= a - bv_{\text{ec}} \\ &= \ln[\bar{\eta}]\bar{M}_w + \ln\left(\frac{Q_{1w}}{Q_{2w}}\right) - K_H[\bar{\eta}]Q_{1w}C \\ &\quad - K'[\bar{\eta}]^2Q_{1w}^2C^2 \end{aligned} \quad (15)$$

and

$$\begin{aligned} \ln \hat{V}_{\text{hop}} &= a - bv_{\text{eo}} \\ &= \ln[\bar{\eta}]\bar{M}_w + \ln\left(\frac{Q_{1w}}{Q_{2w}}\right) - K_H[\bar{\eta}]Q_{1w}C \end{aligned} \quad (16)$$

At infinitive dilution, Eq. (16) reduces to:

$$\ln \hat{V}_{\text{hop}} = a - bv_{\text{eo}} = \ln[\bar{\eta}]\bar{M}_w + \ln\left(\frac{Q_{1w}}{Q_{2w}}\right) \quad (16.1)$$

Eqs. (15) and (16) can be rewritten in the following form [12]:

For monodisperse polymer:

$$v_{\text{ec}} = v_{\text{eo}} + \frac{K_H[\bar{\eta}]C}{b} + \frac{K'[\bar{\eta}]^2C^2}{b} \quad (17)$$

For polydisperse polymer:

$$v_{\text{ec}} = v_{\text{eo}} + \frac{K_H[\bar{\eta}]C}{b}Q_{1n} + \frac{K'[\bar{\eta}]^2C^2}{b}Q_{1n}^2 \quad (18)$$

At relatively lower concentration the above equations reduce to:

$$v_{\text{ec}} = v_{\text{eo}} + K_H[\bar{\eta}]C/b \quad (17.1)$$

and

$$v_{\text{ec}} = v_{\text{eo}} + (K_H[\bar{\eta}]C/b)Q_{1n} \quad (18.1)$$

Taking the logarithm on both sides of Eqs. (17) and (18) yields:

$$\ln\left(\frac{v_{\text{ec}} - v_{\text{eo}}}{C}\right) = \ln\left(\frac{K_H[\bar{\eta}]}{b}\right) + \frac{[\bar{\eta}]C}{K_H}K' \quad (17.2)$$

and

$$\ln\left(\frac{v_{\text{ec}} - v_{\text{eo}}}{C}\right) = \ln\left(\frac{K_H[\bar{\eta}]}{b}Q_{1n}\right) + \frac{[\bar{\eta}]C}{K_H}Q_{1n}K' \quad (18.2)$$

where v_{ec} is the retention volume of the peak at a given concentration; v_{eo} is the retention volume of the peak at infinitive dilution.

For monodisperse polymers:

$$v_{\text{eo}} = (a - \ln[\bar{\eta}]M)/b$$

For polydisperse polymers:

$$v_{\text{eo}} = \left\{ a - \ln[\bar{\eta}]M_w - \ln\left(\frac{Q_{1n}}{Q}\right) \right\} / b$$

Q_{1n} is the correct factor for the polydispersity index of the molecular mass distribution obtained by the method of number average of hydrodynamic volumes, but it differs from Q_{1w} , Q is the correct factor for the polydispersity index of effective hydrodynamic volumes at infinitive dilution; $[\bar{\eta}]$ is the intrinsic viscosity, C is the concentration by weight. When the polydispersity index of the molecular mass is equal to one ($Q_{1w} = 1$, $Q_{1n} = 1$, $Q = 1$ and $Q_{2w} = 1$), then, Eqs. (14) and (18.1), respectively, reduce to:

$$\hat{V}_{\text{hop}} = [\bar{\eta}]\bar{M}_w \exp - \{K_H[\bar{\eta}]C\}$$

and

$$v_{\text{ec}} = [a - \ln([\bar{\eta}]\bar{M}_w)]/b + (K_H/b)[\bar{\eta}]C$$

They are identical with the other results [7].

2.1.3. Correlation between $(dv_{\text{ec}}/dC) = K_s$ and $[\bar{\eta}]$ or A_2M

In the previous paper [12] the correlation between the concentration dependence of the retention volume and the intrinsic viscosity of injected polymers may be expressed by the following equation:

For monodisperse polymers:

$$K_s = (dv_{\text{ec}}/dC)_{c \rightarrow 0} = K_H[\bar{\eta}]/b \quad (19)$$

For polydisperse polymers:

$$K_s = (dv_{\text{ec}}/dC)_{c \rightarrow 0} = (K_H[\bar{\eta}]/b)Q_{1n} \quad (20)$$

For a good solvent the second virial coefficient A_2 is proportional to the molecular mass by the following relation [16,17]:

For monodisperse polymers:

$$A_2 = K_{A_2}M^{-\nu} \quad (21)$$

For polydisperse polymers:

$$A_2 = K_{A_2}\bar{M}_w^{-\nu}\left(\frac{\bar{M}_w}{\bar{M}_n}\right)^{-(\nu+3/2)} = K_{A_2}\bar{M}_w^{-\nu}Q_{A_2} \quad (22)$$

Where K_{A_2} and ν are empirical constants, the low value of ν indicates a weak intermolecular excluded-volume effect, the value of ν is approximately equal to the difference $(1 - \alpha)$ [3], α being the exponent of relation $[\eta] = KM^\alpha$. Substituting the above relation of Eqs. (21) and (22) into Eqs. (19) and (20) yields:

$$K_s = K''A_2M \quad (23)$$

and

$$K_s = K''A_2\bar{M}_w \left(\frac{Q_{1n}}{Q_{A_2}} \right) \quad (24)$$

Where K_s is the initial slope of the concentration dependence of retention volume; $K'' = K_H K / b K_{A_2}$; K_{A_2} is a constant for a given polymer solvent-temperature system, for monodisperse polymers it is equal to 1.0×10^{-2} ; \bar{M}_w is the weight average molecular mass of polymers; Q_{A_2} is correct factor for polydispersity index of molecular mass distribution, $Q_{A_2} = (\bar{M}_w / \bar{M}_n)^{-(\nu+3/2)}$. Combining Eq. (20) with (24), we finally get the expression of dv_{ec}/dC as a function of A_2M :

$$\left(\frac{dv_{ec}}{dC} \right) = K_s = K''A_2\bar{M}_w \frac{Q_{1n}}{Q_{A_2}} \quad (25)$$

for a given polymer-solvent column its value is determined by K_H , b , K , and K_{A_2} , they are all constants. Eq. (25) shows that (dv_{ec}/dC) increases with increasing $A_2\bar{M}_w Q_{1n}/Q_{A_2}$.

It is evident that Eq. (25) is distinguished from the following Eizner and Yamakawa relations [6] in characterizing the slope of the concentration dependence of retention volume ($K_c = dv_e/dC$).

For ($K_s = dv_e/dC$) of Eizner:

$$K_s^E = 1.303A_2MF_E/[b(1 - A_2MF_EC)] \quad (25.1)$$

For K_s of Yamakawa:

$$K_s^Y = 1.303A_2MF_Y/b \quad (25.2)$$

In Eq. (25) the term of (Q_{1n}/Q_{A_2}) can effectively reflect the dependence of excluded-volume effect for a segment on the molecular mass, the polydispersity index of the molecular mass distribution and the properties of the polymer-solvent-temperature system, but in Eqs. (25.1) and (25.2) the terms of F_E and F_Y are the complicated function of the param-

eters of excluded-volume and it cannot directly give the effects of excluded-volume on the molecular mass, the polydispersity index of the molecular mass distribution and the properties of the polymer-solvent systems. Therefore, Eq. (25) can be quantitatively in agreement with experimental data, but Eqs. (25.1) and (25.2) can only be qualitatively in agreement with experimental data [6].

2.1.4. Eluent composition and concentration dependences of GPC retention volumes at theta condition [17]

Experimental results show that at theta condition the concentration effect is non-existent. According to our model theory the hydrodynamic volume would have no volume contraction effects. So the volume contraction coefficient (β) is equal to one, therefore the effective hydrodynamic volume, V_{hc} , of the solvated macromolecules with mono- and polydisperse at a given concentration may be expressed as;

for monodisperse polymers:

$$\langle V_{hcw} \rangle = [\bar{\eta}]_\theta M \quad (26)$$

for polydisperse polymers:

$$\langle V_{hcw} \rangle = \left(\sum_i \bar{W}_i [\eta]_{i\theta} M_{iw} Q_{1w} \right) = [\bar{\eta}]_\theta \bar{M}_w Q_{1w} \quad (27)$$

where $[\bar{\eta}]_\theta$ is the intrinsic viscosity at theta condition, it is the function of eluent composition and concentration at a given temperature. Their corresponding retention volume of the peak in GPC for mono- and polydisperse polymers at a given concentration may be expressed by the following equation;

for monodisperse polymers:

$$v_{ec} = v_{eo} = \left[a + \ln\left(\frac{1}{M}\right) + \ln\left(\frac{1}{[\bar{\eta}]_\theta}\right) \right] \cdot \frac{1}{b} \quad (28)$$

for polydisperse polymers:

$$v_{ec} = v_{eo} = \left[a + \ln\left(\frac{1}{\bar{M}_w Q_{1w}}\right) + \ln\left(\frac{1}{[\bar{\eta}]_\theta}\right) \right] \cdot \frac{1}{b} \quad (29)$$

At theta condition the correlation between $(dv_{ec}/dC_x)_\theta$ and A_2M can be easily obtained by differen-

tiating Eqs. (28) and (29) on both sides with respect to concentration or composition C_x , then substituting the relations $A_2 = K_{A_2} M^{-\nu}$ and $A_2 = K_{A_2} \bar{M}_w^{-\nu} Q_{A_2}$ into Eqs. (28) and (29), we have;

for monodisperse polymers:

$$\left[\frac{dv_{ec}}{dC_x} \right]_{\theta} \cdot \left[\frac{dC_x}{d\left(\frac{1}{[\eta]_{\theta}}\right)} \right] = \left(\frac{K}{b}\right) \left(M \frac{A_2}{K_{A_2}}\right) = 0 \quad (30)$$

for polydisperse polymers:

$$\left[\frac{dv_{ec}}{dC_x} \right]_{\theta} \cdot \left[\frac{dC_x}{d\left(\frac{1}{[\eta]_{\theta}}\right)} \right] = \left(\frac{K}{b}\right) \left(\bar{M}_w \frac{A_2 Q_{A_2}}{K_{A_2}}\right) = 0 \quad (31)$$

Owing to $(dv_{ec}/dC_x)_{\theta}$ being always equal to zero, thus, Eqs. (30) and (31) also must be equal to zero, therefore we have:

$$(A_2) = 0. \quad (32)$$

2.2. Concentration dependence of the polydispersity index for hydrodynamic volume distribution [12]

2.2.1. The average hydrodynamic volume of polymers

According to the definition the weight and number-average hydrodynamic volume of the original polymers at a given concentration and infinite dilution which has been corrected for the axial dispersion are given by the following equation:

For infinite dilution:

$$\langle V_{how} \rangle = \int_0^{\infty} C(V_{ho}) V_{ho} dV_{ho} = V_{hop} \exp\{r^*/2\} \quad (33)$$

and

$$\langle V_{hon} \rangle = 1 / \left[\int_0^{\infty} \{C(V_{ho})/V_{ho}\} dV_{ho} \right] = V_{hop} \exp - \{r^*/2\} \quad (34)$$

for a given concentration:

$$\langle V_{hcw} \rangle = \int_0^{\infty} C(V_{hc}) V_{hc} dV_{hc} = V_{hop} \exp\{r^*/2\} \exp - \{K_H[\bar{\eta}]CQ_{1w}\} \quad (35)$$

$$\langle V_{hcn} \rangle = 1 / \left[\int_0^{\infty} \{C(V_{hc})/V_{hc}\} dV_{hc} \right] = V_{hop} \exp - \{r^*/2\} \exp - \{K_H[\bar{\eta}]CQ_{1n}\} \quad (36)$$

where $V_{hc} = V_{hop} \exp - \{K_H V_{hc} \cdot C_M\}$.

If the polymer has a Wesslau type distribution function [14] and it obeys the Mark-Houwink relation $[\eta] = KM^{\alpha}$, then the distribution function $C(V_h)$ has the following form:

$$C(V_h) = C'(\ln V_h) = \frac{1}{\sqrt{2\pi r^*}} \frac{1}{V_h} \exp - \left\{ \frac{1}{2r^*} \ln^2 \left(\frac{V_h}{\hat{V}_{hcp}} \right) \right\} \quad (37)$$

where $r^* = \sigma/A^2$ is the axial dispersion parameter, after substituting Eq. (37) into Eqs. (33)–(36) and integrating them, then, Eqs. (33)–(36) may be written in their simplest forms. Their simplest forms are given on the right sides of Eqs. (33)–(36) where \hat{V}_{hcp} is the effective hydrodynamic volume of the peak at a given concentration.

2.2.2. The polydispersity index of hydrodynamic volume distribution for polymers

The polydispersity index of hydrodynamic volume distribution which has been corrected for the dispersion resulting from the column at a given concentration and infinite dilution can be obtained from the definition and they are given as follows:

For infinite dilution:

$$D_o = \langle V_{how} \rangle / \langle V_{hon} \rangle = \exp(r^*) \quad (38)$$

For a given concentration:

$$D_c = \langle V_{hcw} \rangle / \langle V_{hcn} \rangle = D_o \exp\{K_H[\bar{\eta}]C(Q_{1n} - Q_{1w})\} \quad (39)$$

In Eq. (39) Q_{1n} is always smaller than Q_{1w} . Thus $\exp\{K_H[\bar{\eta}]C(Q_{1n} - Q_{1w})\}$ is always less than one. This result shows that the polydispersity index of hydrodynamic volume distribution at a given concentration is narrowed. The degree of narrowing is not only determined by the concentration, but also by

the polydispersity index of the molecular mass distribution. It decreases with increasing the concentration C , the polydispersity index of the molecular mass distribution, \bar{M}_w/\bar{M}_n , the polymer–solvent, (α), and the intrinsic viscosity, $[\eta]$.

In contrast to hydrodynamic volume, the width of the chromatogram for the retention volumes is broadened by the concentration effects through the relation $\Delta V_{hD} = a \exp(-b \Delta v_{eD})$. Where ΔV_{hD} represents the decrement of the width of the chromatogram for hydrodynamic volume due to the concentration effects; Δv_{eD} represents the increment of the width of the chromatogram for retention volume due to the concentration effects. The above relation demonstrates that the increment of the width of the chromatogram for retention volume increases with the decrement of the width of the chromatogram for hydrodynamic volume. It is easy to show that when the sample has a monodispersity index ($Q_{1w} = Q_{1n}$) then D_c is equal to D_o , so that the axial spreading due to the concentration effect is no longer existent.

3. Experimental results

3.1. Experimental method

Sample: Monodisperse polystyrenes were provided by the Ji Lin University and Nan Jing University. Their molecular masses are in the range 17×10^4 to 150×10^4 ; polydisperse polystyrenes were prepared by suspension polymerization in our

laboratory. Their molecular masses are in the range 7.4×10^4 to 40×10^4 . The preparative method for poly(methylmethacrylate) (PMMA), poly(dodecylmethacrylate) (PDCMA) and poly(tridecylmethacrylate) (PTDMA), are, respectively, given in Refs. [18] and [19]. The narrow distribution PDCMA and PTDMA were prepared by the method of crossly fractional precipitation fractionation [19]. The molecular characteristics of PS, PMMA, PDCMA and PTDMA are given in Tables 1–4.

Solvents: THF was obtained from Shanghai Chemical Co., and was purified by redistillation and drying.

3.1.1. Determination of $[\eta]$ and K_H

The dilute solution viscosities and K_H were measured by using the Cannon–Ubbelohde viscometer in THF solvent at 25 °C. The intrinsic viscosities and K_H were obtained by extrapolating the line of plotting the η_{sp}/C vs. C to zero concentration with the Huggins equation, then the intrinsic viscosities and K_H are, respectively, determined from the intercept and the slope of the resultant line.

3.1.2. Determination of \bar{M}_w and A_2

The weight–average molecular masses and A_2 were determined by using the JS-LA low angle photometer (China) and LS601 wide angle photometer (Japan) in THF solvent at 25 °C.

3.1.3. Determination of \bar{M}_n

The number–average molecular masses were de-

Table 1
The molecular parameters of polystyrene

Sample	$\bar{M}_w \times 10^{-4}$ (g/mol)	$\bar{M}_n \times 10^{-4}$ (g/mol)	\bar{M}_w/\bar{M}_n	Q_{1n}^a	$Q_{A_2}^b$	K_H
PS-P-3	8.90	3.99	2.33	0.3023	0.2390	0.310
PS-P-5	18.80	7.22	2.60	0.2405	0.1820	0.320
PS-P-6	22.70	8.74	2.60	0.2405	0.1820	0.310
PS-P-7	40.30	8.99	4.48	0.1068	0.0689	0.340
PS-M-2	17.00		1.07	1	1	0.339
PS-M-4	34.00		1.17	1	1	
PS-M-6	150.00		1.17	1	1	
PS- θ -1	5.10		1.10	1	1	
PS- θ -2	9.70		1.10	1	1	
PS- θ -3	16.00		1.10	1	1	
PS- θ -4	49.80		1.10	1	1	

^{a,b} These values were computed from experimental data.

P—polydisperse, M—narrow disperse, θ —theta condition.

Table 2
Molecular characteristics for narrow disperse and polydisperse PS

Sample	$\bar{M}_w \times 10^{-4}$	$[\eta]$ (ml/g)	\bar{M}_w/\bar{M}_n	K_H	Q_{1w}	Q_{2w}	Q'_{2w}	$C \times 10^3$ (g/ml)
Monodisperse PS								
PS-1	311.17		–	0.30	1	1	1	0.650
PS-2	47.36		1.13	0.30	1	1	1	0.905
PS-3	20.44		1.01	0.30	1	1	1	0.905
PS-4	10.97		1.07	0.30	1	1	1	0.850
PS-5	3.33		1.03	0.30	1	1	1	1.100
PS-6	0.86		1.01	0.30	1	1	1	1.020
Polydisperse PS								
PS-22	0.48	7.63	1.27	0.23	1.0554	1.2263	1.2278	2.282
PS-18	1.31	14.81	1.43	0.30	1.0841	1.3574	1.3574	0.950
PS-1	7.30	34.05	1.80	0.33	1.1419	1.6438	1.6438	0.936
PS-2	8.40	42.12	1.95	0.34	1.1627	1.7547	1.7547	0.924
PS-4	9.60	44.02	1.84	0.31	1.1475	1.6720	1.6720	0.838
PS-5		60.95	3.47	0.32	1.3242	2.8608	2.8608	0.755
PS-6		82.60	2.48	0.28	1.2275	2.1505	2.1505	0.644
PS-14		179.00	3.68	0.29	1.3419	2.9576	2.9576	0.550

Table 3
Molecular characteristics of poly(methyl methacrylate) [18]

Sample	$\bar{M}_w \times 10^{-4}$ (g/mol)	\bar{M}_w/\bar{M}_n	Q_{1n}	Q_{1w}	K_H
PMMA-1	24.60	1.15	0.8136	1.0304	0.33
PMMA-2	11.22	1.90	0.3878	1.1472	0.35
PMMA-3	5.96	1.09	0.8806	1.0186	0.35
PMMA-4	4.40	1.21	0.7547	1.0416	0.36
PMMA-5	3.25	1.95	0.3732	1.1536	0.36
PMMA-6	2.40	1.24	0.7280	1.0471	0.36

Table 4
Molecular characteristics for polydisperse PDCMA and PTDMA [19]

Sample	$[\eta]$ (dl/g)	$\bar{M}_n \times 10^{-4}$ (g/mol)	\bar{M}_w/\bar{M}_n	Q_{1w}	Q'_{2w}
DCMA					
III-6	0.118	5.68	1.45	1.0738	1.3562
III-4	0.203	14.70	1.32	1.0546	1.2556
III-1	0.468	53.10	1.31	1.0531	1.2478
II-3	0.573	70.80	1.23	1.0401	1.1849
II-2	0.770	114.00	1.37	1.0622	1.2945
II-1	0.856	135.00	1.41	1.0681	1.3254
TDMA					
I-4	0.170	10.00	1.34	1.0673	1.2843
II-3	0.352	28.30	1.29	1.0583	1.2432
II-2	0.546	53.00	1.42	1.0812	1.3495
II-1-2	0.776	84.80	1.44	1.0846	1.3657
II-1-1	1.103	138.00	1.45	1.0863	1.3738

PDCMA (polydicycymethacrylate); PTDMA (polytridecylmethacrylate).

terminated by using the Wescan osmometer equipped with membranes. THF was used as the solvent and the temperature of measurement was 25 °C.

3.1.4. Measurement of GPC chromatograms

The GPC chromatograms were measured by use of a Water 150 °C type chromatograph, it was produced by the Waters Company, Milford, MA, USA. The column set consists of three to seven styragel columns each being 30 cm long, the column set is also manufactured by the Waters Company, Milford, MA, USA. Their porosities ranged from 10^3 to 10^6 Å. Purified and dried THF was used as the eluent, its flow-rate was 1 ml/min, and the injected quantity was 200 µl, the temperature of measurement was 25 °C. The concentration ranged from 0.025 to 1.00 g/100 ml.

3.2. Experimental results

The molecular parameters \bar{M}_w , \bar{M}_n , \bar{M}_w/\bar{M}_n , K_H , Q_{1n} , Q_{1w} , Q_{2w} and Q_{A_2} for narrow disperse and polydisperse PS, PDCMA, PTDMA and PMMA are given in Tables 1–4.

4. Comparison of model theory with experimental results

4.1. Dependence of molecular mass and concentration on the chromatogram of GPC

The concentration effect is more pronounced for the polymer with higher molecular mass and at higher concentration. It is shown in Fig. 1 that the higher molecular mass and higher concentration in good solvents can cause a shift of the retention volumes, the axial spreading and skewing. The molecular mass is larger and the concentration effect is more pronounced. Therefore the concentration dependencies of the polydispersity index of the molecular mass distribution and the hydrodynamic volume distribution must be taken into account. At a given concentration each kind of macromolecule in the whole sample has a different effective hydrodynamic volume and a different volume contraction coefficient. The molecules with higher molecular

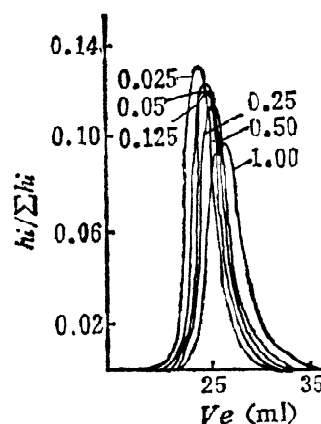


Fig. 1. The chromatogram for PS with different concentrations (0.025–1.00 g/100 ml).

mass have a larger effective hydrodynamic volume and a larger volume contraction coefficient. But the molecules with lower molecular mass have a smaller effective hydrodynamic volume and a smaller volume contraction coefficient. These differences in the effective hydrodynamic volumes and the volume contraction coefficients can lead to axial spreading and skewing.

4.2. Dependence of concentration effects on the GPC retention volumes

For a given polymer–solvent–temperature system the concentration effect is more pronounced at higher concentration. Retention volumes of the peak tend to increase with increasing concentration in the samples. It is given in Fig. 1. The experimental data of retention volumes and concentrations for PS and PMMA [18] were used to plot the v_{ec} vs. C with Eq. (18.1). These plots are given in Figs. 2–4. These results show that v_{ec} is a linear function of C with a slope K_H at relatively lower concentration. For the PS and PMMA with higher molecular mass and higher concentration the experimental data were used to plot the $\ln[(v_{ec} - v_{eo})/C]$ vs. C with Eq. (18.2). These plots are given in Figs. 5–7. It shows that at higher concentration the $\ln[(v_{ec} - v_{eo})/C]$ is an approximately linear function of C with an intercept of $\ln[K_H[\bar{\eta}]Q_{1n}/b]$. Where $([\eta]Q_{1n}) \times (K'/K_H)$ is the initial slope of the resultant line, (dv_{ec}/dC) . At theta conditions [3,20] (benzene/methyl alcohol and chlo-

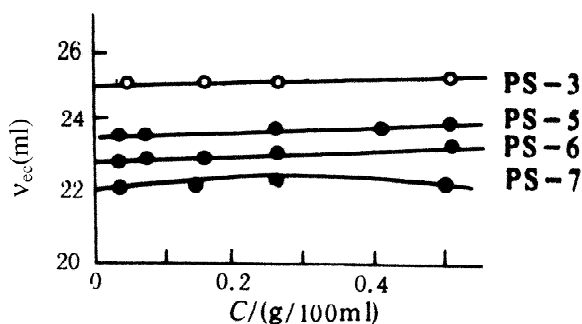


Fig. 2. Plot of v_{ec} vs. C for polydisperse PS; 1—PS3; 2—PS5; 3—PS6; 4—PS7.

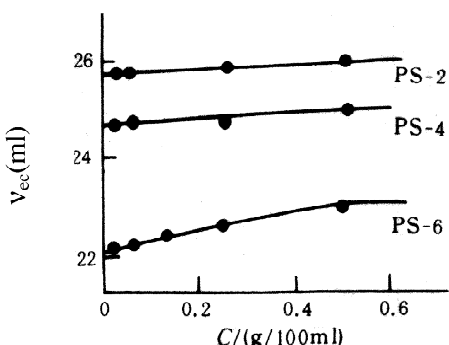


Fig. 3. Plot of v_{ec} vs. C for narrow disperse PS; PS-2; PS-4; PS-6.

reform/methyl alcohol) the retention volume of the peak are independent of the concentration. They are given in Figs. 8 and 9.

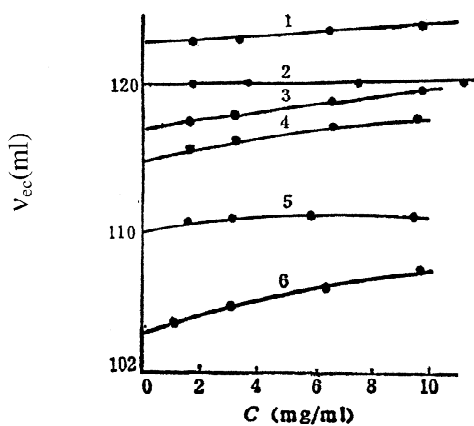


Fig. 4. Plot of v_{ec} vs. C for polydisperse PMMA [18]; 1—PMMA6; 2—PMMA5; 3—PMMA4; 4—PMMA3; 5—PMMA2; 6—PMMA1.

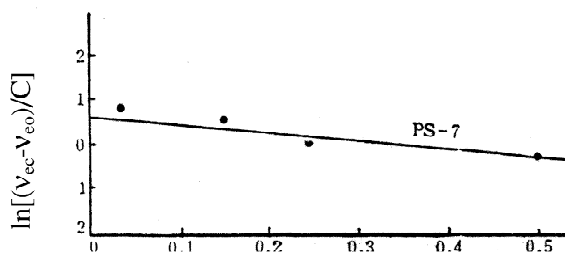


Fig. 5. Plot of $\ln[(v_{ec} - v_{eo})/C]$ vs. C for polydisperse PS-7.

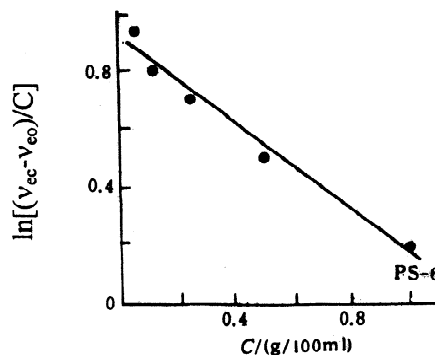


Fig. 6. Plot of $\ln[(v_{ec} - v_{eo})/C]$ vs. C for narrow disperse PS-6.

4.3. Calibration on universal calibration curve with polydisperse polymers [21]

4.3.1. Universal calibration curve equation for monodisperse standards

According to the model theory of concentration

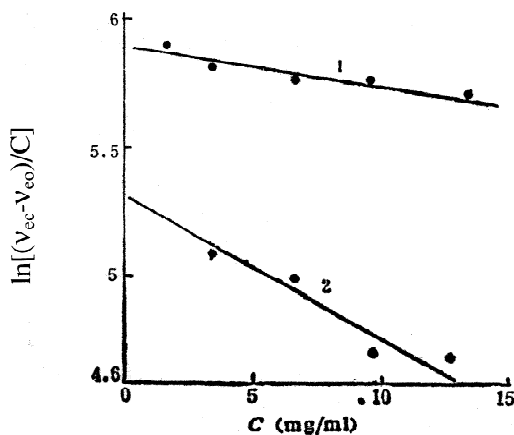


Fig. 7. Plot of $\ln[(v_{ec} - v_{eo})/C]$ vs. C for polydisperse PMMA; 1—PMMA3; 2—PMMA2.

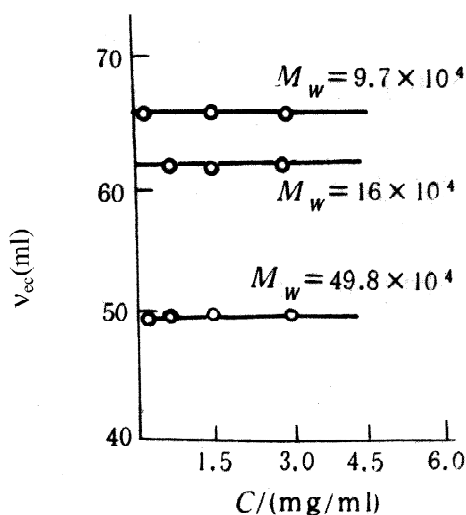


Fig. 8. Plot of v_{ec} vs. C at theta condition (benzene/methyl alcohol) for narrow disperse PS [3,20].

effect [7,12], for monodisperse polymers at lower concentration the concentration effects only show the shift of retention volumes. The axial spreading and the skewing resulting from monodisperse polymers are absent; therefore the shift of retention volumes only was taken into account. After the correction for the concentration effects of the shift of retention volumes, the universal calibration curve equation for monodisperse polymers can be directly obtained from Eq. (15), after introducing the conditions of $Q_{1w}=1$ and $Q_{2w}=1$, we have:

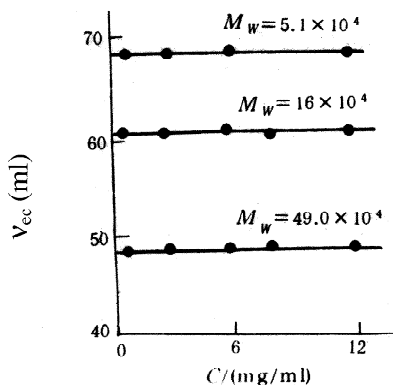


Fig. 9. Plot of v_{ec} vs. C at theta condition (benzene/methyl alcohol) for narrow disperse PS [3,20].

$$\begin{aligned} \ln \hat{V}_{hcp} &= a - bv_{ec} \\ &= \ln([\eta]M) - K_H[\eta]C - K'[\eta]^2C^2 \end{aligned} \quad (15.1)$$

At relatively low concentration and infinite dilution the above equation reduces to:

$$\ln \hat{V}_{hcp} = a - bv_{ec} = \ln([\eta]M) - K_H[\eta]C \quad (40)$$

$$\ln \hat{V}_{hop} = a - bv_{eo} = \ln([\eta]M) \quad (41)$$

The experimental data were used to calculate $\ln([\eta]M)$ with Eq. (41) then the universal calibration curves without correction for concentration effects for narrow disperse polymers were constructed by plotting $\ln([\eta]M)$ or $\ln \hat{V}_{hop}$ vs. v_{eo} . These plots are given in Figs. 10–12, by full line; the parameters a and b were obtained from the intercept and slope of these lines. These equations are given in Table 5.

4.3.2. Universal calibration curve equation for polydisperse polymers

At higher molecular mass and higher concentration the polydispersity index of the hydrodynamic volume distribution has a great influence on the axial dispersion. It can be seen from the following equation:

$$\begin{aligned} D_c &= \langle V_{hcw} \rangle / \langle V_{hcn} \rangle \\ &= D_o \exp\{K_H[\bar{\eta}]C(Q_{1n} - Q_{1w})\} \end{aligned} \quad (39)$$

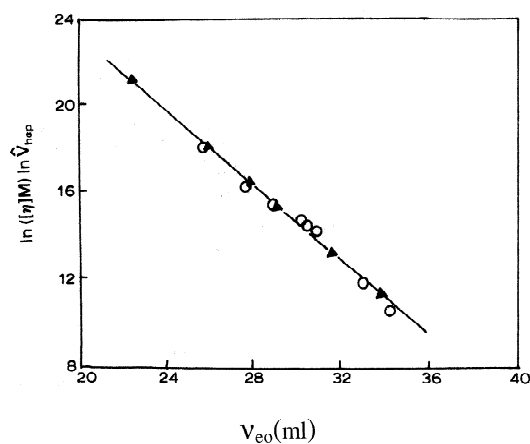


Fig. 10. Universal calibration curves for narrow disperse and polydisperse PS; \blacktriangle , narrow disperse values; \circ , polydisperse values.

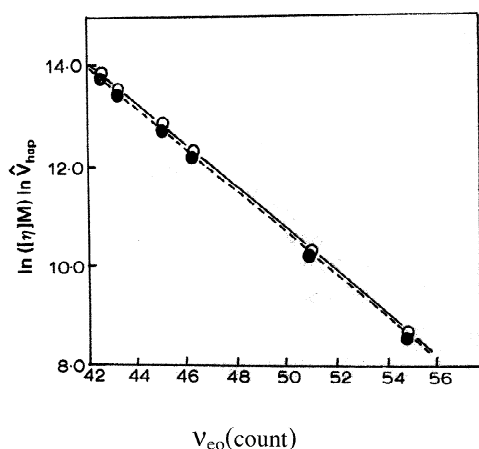


Fig. 11. Universal calibration curves for narrow disperse PDCMA and polydisperse PDCMA; ○, narrow disperse values; ●, polydisperse values.

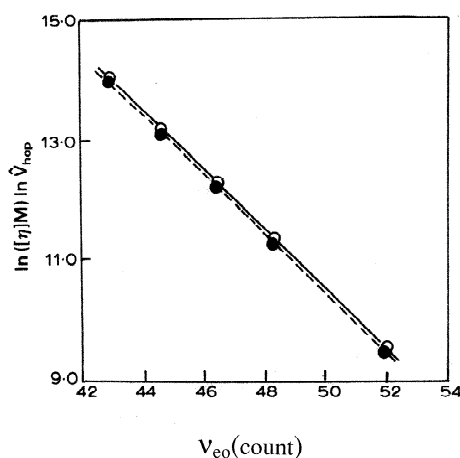


Fig. 12. Universal calibration curves for narrow disperse PTDMA and polydisperse PTDMA; ○, narrow disperse values, ●, polydisperse values.

where Q_{1n} is a correction factor for the polydispersity index of the molecular mass distribution obtained by the number-average method; Q_{1n} is always smaller than Q_{1w} . Thus, $\exp\{K_H[\bar{\eta}]C(Q_{1n} - Q_{1w})\}$ is always less than one. This result shows that the polydispersity index of the hydrodynamic volume at a given concentration is narrowed. The degree of narrowing is determined not only by the concentration, but also depends on the polydispersity index of the molecular mass distribution. It decreases with increasing concentration, polydispersity index, intrinsic viscosity and K_H . In comparison with the hydrodynamic volume, the chromatogram of the retention volumes is broader.

The experimental data for $[\bar{\eta}]$, \bar{M}_w , Q_{1w} , Q'_{2w} , Q_{2w} , C and K_H listed in Tables 2 and 4 were used to calculate $\ln(\hat{V}_{hop})$ with Eq. (16.1). Then the universal calibration curves without correction for concentration effects were constructed by plotting $\ln(\hat{V}_{hop})$ vs. v_{eo} . These plots are given in Figs. 10–12 by broken lines. The constants a and b were obtained from the intercept and slope of the lines by a least-squares method. These universal calibration curve equations without correction for concentration effects are given in Table 5.

4.3.3. Universal calibration curve equations for mono- and polydisperse polymers corrected for concentration effects

The experimental data listed in Table 2 were used to calculate $\ln \hat{V}_{hcp}$ for narrow and polydisperse PS by Eqs. (40) and (16), then the universal calibration curves being corrected for concentration effects for narrow disperse and polydisperse polymers were constructed by plotting $\ln \hat{V}_{hcp}$ vs. v_{ec} . These plots are given in Fig. 13. These equations and coefficients a and b are given in Table 5.

Table 5
Universal calibration curve equations for narrow disperse and polydisperse polymers

Sample	Polydisperse polymers $\text{Log } \hat{V}_{hcp} = a - bv_{ec}$	Narrow disperse polymers $\text{Log}[\eta]M = a - bv_{eo}$
PS	$\text{Log } \hat{V}_{hop} = 17.654 - 0.378v_{eo}$	$\text{Log}[\eta]M = 17.659 - 0.3777v_{eo}$
PS (after correction for concentration effect)	$\text{Log } \hat{V}_{hcp} = 17.651 - 0.3784v_{ec}$	$\text{Log } \hat{V}_{hcp} = 17.541 - 0.3740v_{eo}$
DCMA	$\text{Log } \hat{V}_{hop} = 13.850 - 0.1854v_{eo}$	$\text{Log}[\eta]M = 13.980 - 0.1867v_{eo}$
TDMA	$\text{Log } \hat{V}_{hop} = 13.850 - 0.2098v_{eo}$	$\text{Log}[\eta]M = 15.140 - 0.2111v_{eo}$

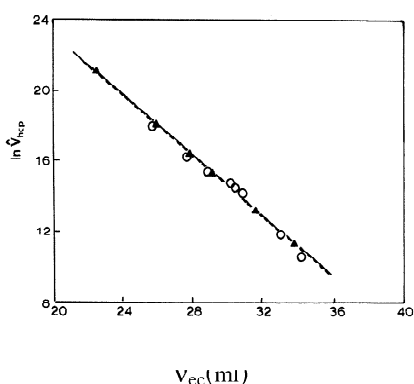


Fig. 13. Universal calibration curves corrected for concentration effects with narrow disperse and polydisperse PS; \blacktriangle , narrow disperse values, \circ , polydisperse values.

4.3.4. Comparison between the universal calibration curves of narrow disperse and polydisperse polymers

By comparing the coefficients a and b in the universal calibration curve equations for narrow disperse and polydisperse polymers listed in Table 5, it is found that the difference of the coefficients between the narrow disperse and polydisperse polymers is less than 1% in relative error. An excellent agreement between the narrow disperse PS and polydisperse PS was obtained. After correction for the concentration effects the universal calibration curves of narrow disperse PS and polydisperse PS are given in Fig. 13.

These results show that the new method for calibrating universal calibration curves with polydisperse polymers is acceptable.

4.4. Determination of A_2 from concentration effects and the correlation between K_s and A_2M [6,17]

4.4.1. Determination of K_s

For the narrow disperse and polydisperse PS with relatively lower molecular mass and at the relatively lower concentration the parameter K_s was determined by the least squares method from the slope of the line by plotting v_{ec} vs. C according to Eqs. (17.1) and (18.1). These plots are given in Figs. 2 and 3.

Table 6
Comparison of A_2 values obtained by two methods

Sample	$A_2 \times 10^4$ (GPC) (mol cm ³ /g ²)	$A_2 \times 10^4$ (LS) (mol cm ³ /g ²)
PS-P-3	8.46	8.15
PS-P-5	7.05	6.97
PS-P-6	7.35	5.70
PS-P-7	5.80	6.18
PS-M-2	5.90	5.41
PS-M-4	4.50	5.22
PS-M-6	3.40	3.50
PS- θ -1	0	/
PS- θ -2	0	/
PS- θ -3	0	/
PS- θ -4	0	/

These results show that the retention volumes are the linear function of the concentration. For the polystyrenes with higher molecular mass and at relatively higher concentration, the concentration effects are more pronounced. The parameter K_s was determined by the least squares method from the intercept of the line by plotting $\ln[(v_{ec} - v_{e0})/C]$ vs. C according to Eqs. (17.2) and (18.2). These plots are given in Figs. 6 and 7. The signs of the slope are determined by the value of K'' , for higher molecular mass polymers the value of K' is negative. At the theta conditions (benzene/methyl alcohol and chloroform/methyl alcohol) the parameters of K_s are equal to zero. Their plots are given in Figs. 8 and 9.

4.4.2. Determination of A_2

The second virial coefficients for all PS samples were calculated by Eqs. (21) and (22) with a given

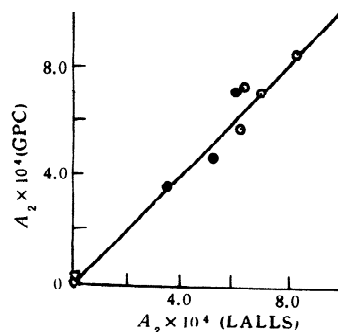


Fig. 14. Plot of A_2 (GPC) vs. A_2 (LALLS); (\bullet) narrow PS; (\circ) poly-PS; (θ) θ condition.

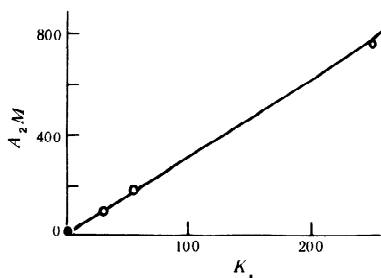


Fig. 15. Correlation between K_s and $A_2 M_w$ for narrow disperse PS; (○) narrow PS (●) θ condition.

set of parameters Q_{A_2} , $M^{-\nu}$ and K_{A_2} listed in Table 1. The results are given in Table 6 and Fig. 14. It is shown that the values of A_2 obtained by the proposed method are in agreement with those obtained by the LALLS method. Differences between the two methods are in the range of experimental error. At the theta condition the second virial coefficients are equal to zero, and they are given in Table 6.

4.4.3. Correlation between K_s and $A_2 M$

The plots of K_s vs. $A_2 M$ and $A_2 \bar{M}_w (Q_{1n}/Q_{A_2})$ for the narrow disperse and polydisperse polystyrenes are given in Figs. 15 and 16. They show that two straight lines pass through the origin. The following facts can be manifested by the result:

1. K_{A_2} obtained from the slope of the line by plotting K_s vs. $A_2 M$ is really equal to 1×10^{-2} ;
2. the straight line passed through the origin shows that $K_{s\theta} = A_{2\theta} = 0$ and it is in very good agreement with the experimental value [17,20];
3. Eqs. (23) and (24) can be used to quantitatively characterize the dependence of K_s on A_2 .

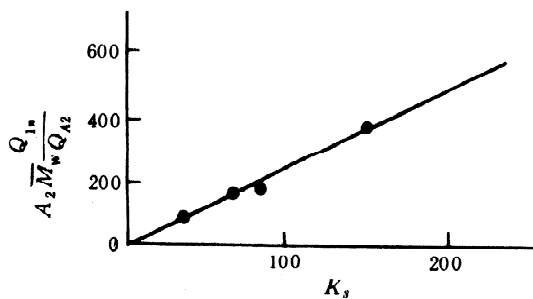


Fig. 16. Correlation between K_s and $A_2 \bar{M}_w (Q_{1n}/Q_{A_2})$ for polydisperse PS.

A refined method for determination of second virial coefficients was presented. It is based on the model theory of concentration effects for mono- and polydisperse polymers.

The second virial coefficients for narrow disperse and polydisperse polystyrene with a wide range of molecular masses (10^4 – 10^6) were determined by this method, and their values of A_2 are in agreement with those obtained by the LALLS method.

5. Conclusion

1. A model theory of concentration effects for polydisperse polymers was proposed. It is successful in relating the concentration to the effective hydrodynamic volume of the peak, the retention volumes, the polydispersity index of the hydrodynamic volume distribution and the molecular mass distribution at a given concentration.
2. The dependence of the concentration of polymer solutions on the effective hydrodynamic volumes, the retention volumes and the polydispersity index of the hydrodynamic volume distribution for narrow disperse and polydisperse PS, PDCMA, PTDMA and PMMA in THF solvents were studied, and the proposed theory was verified by these experimental data.
3. A new method for calibration on universal calibration curves with polydisperse polymers was developed from the theory of concentration effects. It is found that the two universal calibration curves with narrow disperse and polydisperse polymers are in excellent agreement.
4. A developed method for determination of the second virial coefficients A_2 was present. The determined values of A_2 for narrow disperse and polydisperse polystyrenes are in excellent agreement with those obtained by the LALLS method.
5. These results show that the proposed theory can predict the concentration effects for polydisperse polymers quantitatively and can provide a theoretical foundation for “the new method of calibrating the universal calibration curves with polydisperse polymers” and “the developed method for determining the second virial coefficients (A_2) of polymers.”

6. Nomenclature of parameters Q

Q	Correction factor for the polydispersity index of effective hydrodynamic volume distribution at infinitive dilution
Q_{1n}	Correction factor for the polydispersity index of the molecular mass distribution obtained by the method of number-average hydrodynamic volume, it is the function of the polydispersity index of the molecular mass distribution and the properties of the polymer-solvent system, their analytical expressions differ from Q_{1w}
Q_{1w}	Correction factor for the polydispersity index of the molecular mass distribution obtained by the method of weight-average hydrodynamic volume. It is the function of the polydispersity index of the molecular mass distribution and the properties of the polymer-solvent system.
Q_{2w}	Conversion (or correction) factor for the effective hydrodynamic volume of the peak at a given concentration. It is the function of the polydispersity index of the molecular mass distribution, the intrinsic viscosity, the concentration and the properties of the polymer-solvent system.
Q'_{2w}	Conversion (or correction) factor for the effective hydrodynamic volume of the peak at infinitive dilution. It is the function of the polydispersity index of the molecular mass distribution and the properties of the polymer-solvent system.

The above parameters had been theoretically defined in the text of the paper (2) [12] and paper (6) [15]. Their derivations and analytical expressions are given in the articles [22] of research reports of BUCT (Beijing University of Chemical Technology).

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