# Polymer diffusion in a dilute theta solution: 1. Polystyrene in cyclohexane

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Translational diffusion coefficients of two narrow molecular weight distributions of polystyrene in cyclohexane under theta conditions have been studied using Rayleigh linewidth spectroscopy. Experimental evaluation of the time correlation function profiles according to the histogram approximation shows that the diffusion coefficient at zero concentration ($D_0$) and the concentration dependence of the first-order friction coefficient ($k_f$) can be determined by making only one measurement of the time correlation function of a polymer solution of known molecular weight (such as $\overline{M}_z$, $\overline{M}_w$ or $\overline{M}_n$) at one concentration and one scattering angle. By making photon correlation measurements at two different concentrations, we are able to make a definitive comparison of our experiments with the theoretical descriptions of Yamakawa, Imai, and Pyun and Fixman. In contrast to earlier findings of King, Knox, Lee and McAdam (*Polymer* 1973, **14**, 151), our results are in excellent agreement with the theoretical prediction of Pyun and Fixman at the theta temperature.

## INTRODUCTION

In photon correlation spectroscopy the cumulants method[1] is a powerful technique because no *a priori* assumption on the form of the linewidth distribution function is required. However, only limited information is available in terms of an average linewidth $\overline{\Gamma}$ and its variance $\mu_2/\overline{\Gamma}^2$ where

$$\overline{\Gamma} = \int G(\Gamma)\Gamma d\Gamma \qquad (1)$$

$$\mu_i = \int(\Gamma - \overline{\Gamma})^i G(\Gamma) d\Gamma \qquad (2)$$

with $G(\Gamma)$ being the normalized distribution function of linewidths. Higher-order moments, e.g. beyond the third moment ($\mu_3$), are usually not accessible even under very favourable experimental conditions. Recently, we have established an experimental method which permits a direct estimate of the linewidth distribution function[2]. In this technique, the linewidth distribution function $G(\Gamma)$ is represented by an equally segmented histogram in $\Gamma$ space. The histogram parameters are varied in the upper ($\Gamma_{max}$) and lower ($\Gamma_{min}$) boundaries, the number of steps ($n$) and the strength of each step $[a_j \equiv G(\Gamma_j)]$ so as to yield a computed intensity autocorrelation function $G^{(2)}(\tau)$ which most closely approximates the measured $G^{(2)}(\tau)$ to within the experimental error limits. The non-linear least-squares method which minimizes a measure of the goodness of the fit $\chi^2$ with respect to each step strength ($a_j$) of the histogram simultaneously uses the Marquardt algorithm and has been applied successfully for determining the colloidal particle size distribution of aqueous suspensions of Dow latex spheres[2].

The purpose of this paper is to extend the histogram technique to dilute polymer solutions. In particular, we show that we need only one time correlation function measurement of a dilute polymer solution of known concentration and molecular weight in order to determine the concentration dependence of the first order friction coefficient ($k_f$) and the diffusion coefficient at infinite dilution ($D_0$) under theta conditions. By making time correlation function measurements at two different concentrations, we establish a definitive conclusion that, at the theta temperature, the theoretical prediction of Pyun and Fixman[3] is in excellent agreement with our experiments, while that of Yamakawa[4] and Imai[5] fails.

## THEORETICAL BACKGROUND

The translational diffusion coefficient for dilute polymer solutions can be expanded to first order in concentration as:

$$D = D_0(1 + k_D c + \ldots) \qquad (3)$$

where $D_0(= k_B T/f_0)$ is the diffusion coefficient at infinite dilution, with $f_0$ denoting the frictional coefficient at infinite dilution and $k_B$ the Boltzmann constant. The thermodynamic and hydrodynamic factors are combined in $k_D$ as:

$$k_D = 2A_2 M - k_f - \frac{N_a V_1}{M} \qquad (4)$$

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where $A_2$ is the second virial coefficient and $\bar{v} = (N_a V_1/M)$ is the specific volume of the polymer with $N_a$, $V_1$ and $M$ being the Avogadro number, the polymer molecular volume, and the molecular weight, respectively.

At the theta temperature, $A_2$ may be taken as zero and:

$$k_D^\theta = -(k_f + \bar{v}) \tag{5}$$

Furthermore, at the theta temperature ($\theta$), for the Yamakawa[4] and Imai[5] (Y, I) theories:

$$k_f = N_a V_h/M \tag{6}$$

and the Pyun and Fixman (PF) theory[3]:

$$k_f = 2.23 N_a V_h/M \tag{7}$$

where $V_h$ is the hydrodynamic volume of the polymer molecule. Thus, we have:

$$k_D^\theta = -\frac{N_a}{M}(V_1 + V_h) \qquad \text{(Y, I)} \tag{8}$$

$$k_D^\theta = -\frac{N_a}{M}(V_1 + 2.23\,V_h) \qquad \text{(PF)} \tag{9}$$

If we take $V_h = 4/3\pi r_h^3$ with $r_h$ being the hydrodynamic radius, we can express $V_h$ in terms of $M$ by invoking the relation[6,7]:

$$D_0^\theta = k_T M^{-1/2} \tag{10}$$

and the Stokes–Einstein relation $D_0^\theta = k_B T/6\pi\eta r_h$ where $\eta$ is the solvent viscosity. Then:

$$V_h = \frac{4}{3}\pi \left[\frac{k_B T}{6\pi\eta k_T}\right]^3 M^{3/2} \tag{11}$$

By using the relation $V_1 = M/N_a\rho$ and equation (11), we can express equation (8) in terms of molecular weight:

$$k_D^\theta = -\frac{1}{\rho} - \frac{4}{3}\pi N_a \left[\frac{k_B T}{6\pi\eta k_T}\right]^3 M^{1/2} \qquad \text{(Y, I)} \tag{12}$$

where $\rho$ is the density of the polymer. For polystyrene in cyclohexane, $\Theta = 308.15$ K, $\rho = 1.05$ g/cm$^3$. Then, equation (12) has the following numerical constants:

$$k_D^\theta = -0.94 - \frac{6.86 \times 10^{-14}}{k_T^3} M^{1/2}\ \text{cm}^3/\text{g} \qquad \text{(Y, I)} \tag{13}$$

where $[M]$ and $[k_T]$ are expressed in units of g/mol and cm$^2$ g$^{1/2}$/sec mol$^{1/2}$, respectively. By substituting equations (3) and (13) to the relation $\Gamma = DK^2$, we obtain an expression which relates $\Gamma$ to $M$ at finite concentrations:

$$D^\theta = \Gamma/K^2 = k_T M^{-1/2}$$

$$\left[1 - 0.94c - \frac{6.86 \times 10^{-14}}{k_T^3} M^{1/2} c + \ldots\right] \qquad \text{(Y, I)} \tag{14}$$

where $K\ [= (4\pi/\lambda)\sin(\theta/2)]$ is the magnitude of momentum transfer vector with $\lambda$ and $\theta$ being the wavelength of light in the medium and the scattering angle, respectively. Conversely, we can rewrite equation (14) to express $M$ as a function of $c$ and $\Gamma$:

$$M = \left[\frac{k_T(1 - 0.94c)}{\Gamma/K^2 + 6.86 \times 10^{-14} c/k_T^2}\right]^2 \qquad \text{(Y, I)} \tag{15}$$

if we truncate the $c^2$ and higher order concentration terms. Equations similar to equations (14) and (15) can be written for the PF theory with:

$$D^\theta = \Gamma/K^2 = k_T M^{-1/2}$$

$$\left[1 - 0.94c - 2.23 \times \frac{6.86 \times 10^{-14}}{k_T^3} M^{1/2} c + \ldots\right] \qquad \text{(PF)} \tag{16}$$

$$M = \left[\frac{k_T(1 - 0.94c)}{\Gamma/K^2 + 2.23 \times 6.86 \times 10^{-14} c/k_T^2}\right]^2 \qquad \text{(PF)} \tag{17}$$

One way to test Y, I and PF theories would be to use *very narrow* molecular weight distribution polymers and to measure the concentration dependence of the translational diffusion coefficient whereby contributions of the third term in equations (14) and (16) become appreciable. A more precise approach is to try to take into account the effects of polydispersity at finite concentrations. As synthetic polymers are almost always polydisperse, we want to utilize the information on the molecular weight distribution function, which is invariant, in order to test whether equation (14) or equation (16) agrees better with experiments. $k_T$ can be determined at a fixed concentration using either equation (14) or equation (16). Then, the Y, I and PF theories can be tested by comparing calculated and measured time correlation functions at a different concentration. The first approach has been used by King *et al.*[8], who observed experimental results to be intermediate between the theoretical descriptions of Yamakawa, Imai, and Pyun and Fixman. Unfortunately, the fitting of the time correlation function with only a single exponential curve was not sufficiently precise to distinguish the predictions of the two theories. The use of $\bar{\Gamma}$ from the cumulants method would have been appropriate. However, this method neglects information on the correlation function profile at large delay times. Thus, we want to use the histogram method of data analysis which accounts for the entire correlation function profile within a reasonable delay time range.

## HISTOGRAM METHOD OF DATA ANALYSIS

The measured single-clipped, photoelectron-count autocorrelation function has the form:

$$G_k^{(2)}(\tau) = A(1 + \beta|g^{(1)}(\tau)|^2) \tag{18}$$

where $g^{(1)}(\tau)$ is the normalized correlation function of the scattered electric field, $k$ is the clipping level, $\tau$ is the delay time, $A$ is the background which can be computed from the total number of samples, the mean clipped and unclipped counts per sample time, and $\beta$ is usually assumed to be an unknown parameter in the data fitting procedure because the conditions of complete coherence are difficult to achieve.

For a polydisperse sample with a continuous distribution of sizes and in the absence of internal motions, $g^{(1)}(\tau)$ has the form:

$$|g^{(1)}(\tau)| = \int_0^\infty G(\Gamma)\exp(-\Gamma\tau)\mathrm{d}\Gamma \tag{19}$$

We shall approximate $G(\Gamma)$ by means of a histogram such that:

$$|g^{(1)}(\tau)| = \sum_{j=0}^{n} G(\Gamma_j) \int_{\Gamma_j - \Delta\Gamma/2}^{\Gamma_j + \Delta\Gamma/2} \exp(-\Gamma I\Delta\tau)\mathrm{d}\Gamma \tag{20}$$

where $G(\Gamma_j)$ is the total integrated intensity scattered by all the molecules having linewidths from $\Gamma_j - \Delta\Gamma/2$ to $\Gamma_j + \Delta\Gamma/2$, $n$ is the number of steps in the histogram, $\Delta\Gamma[=(\Gamma_{\max} - \Gamma_{\min})/n]$ is the width of each step, $\Delta\tau$ is the delay time increment, and $I$ is the delay channel number with $\tau = I\Delta\tau$. The normalization condition for $G(\Gamma)$ has been approximated by the condition:

$$\sum_{j=1}^{n} G(\Gamma_j)\Delta\Gamma = 1 \tag{21}$$

From equation (20), we obtain a computed net signal autocorrelation function $Y(I\Delta\tau)$ $[= A\beta|g^{(1)}(I\Delta\tau)|^2]$ in the form:

$$Y(I\Delta\tau) = A\beta \left\{ \sum_{j=1}^{n} a_j \left( -\frac{1}{I\Delta\tau} \right) \{\exp[-(\Gamma_j + \Delta\Gamma/2)I\Delta\tau] - \exp[-(\Gamma_j - \Delta\Gamma/2)I\Delta\tau]\} \right\}^2 \tag{22}$$

The values of $a_j$ $(\equiv G(\Gamma_j))$ are obtained by the method of non-linear least squares where we minimize $\chi^2$ with respect to each $a_j$ simultaneously:

$$\frac{\partial}{\partial a_j}\chi^2 = \frac{\partial}{\partial a_j}\Sigma \left\{ \frac{1}{\sigma_I^2} [Y_m(I\Delta\tau) - Y(I\Delta\tau)]^2 \right\} = 0 \tag{23}$$

where $\sigma_I$ represents the uncertainty of data point $Y_m(I\Delta\tau)$ with the subscript $m$ denoting the measured value. Initial values for $\Gamma_{\min}$ and $\Gamma_{\max}$ signalling the start and stop of the range of the linewidth distribution function is immaterial. In the computations a step is set equal to zero when its contribution is less than 0.25% of an averaged step in $G(\Gamma)$ and we use a range of $n$ such that the computed net signal autocorrelation function agrees with the measured value to within statistical counting error limits.

## DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTION FUNCTION f(M) FROM G(Γ)

According to the Y, I or PF theory, the discrete limits in the Γ-histogram can be transformed to corresponding values of molecular weight in $M$-space using equations (15) or (17). Thus, for $\Gamma_{j1}(= \Gamma_j - \Delta\Gamma/2)$ and $\Gamma_{j2}$ $(= \Gamma_j + \Delta\Gamma/2)$, we have corresponding values for $M_{j1}$ and $M_{j2}$, respectively. If we take $\Delta\Gamma_j = \Gamma_{j2} - \Gamma_{jl}$ where all the $\Delta\Gamma_j$ values are of equal magnitude in Γ-space, the corresponding values in $M$ space are not of equal magnitude and we have:

$$\bar{M}_j = (M_{j2} + M_{j1})/2 \tag{24}$$

and

$$\Delta M_j = \mathrm{Abs}(M_{j2} - M_{j1}) \tag{25}$$

In $M$ space, we can express:

$$G(\Gamma)\mathrm{d}\Gamma = M^2 P(M) f^*(M) M^{-3/2}\mathrm{d}M \tag{26}$$

at the theta temperature. In equation (26), we have used the relation[9] that the polarizability of random coils is proportional to the square of the radius of gyration, $r_g^2$, which, in turn, is proportional to the molecular weight. $P(M)$ and $f^*(M)$ are, respectively, the particle scattering factor expressed in $M$ (instead of $r$) at constant $K$ and the *unnormalized* molecular weight distribution function. The normalized number distribution function of the polymer, $f(M)$, has the form:

$$f(M) = \frac{f^*(M)}{\Sigma f^*(M)\Delta M_j} \tag{27}$$

Furthermore, at the theta temperature, the relation $\mathrm{d}\Gamma \propto M^{-3/2}\mathrm{d}M$ remains valid at finite concentrations so long as the $c^2$ and higher order concentration terms in equations (14) or (16) can be neglected. For Gaussian coils, the particel scattering factor[10] has the form:

$$P(X) = \frac{2}{X^2}(\mathrm{e}^{-X} - 1 + X) \tag{28}$$

where $X = (Kr_g)^2$. In our case, we have used polystyrene polymers of moderate molecular weight. Thus, equation (28) can be approximated by:

$$P(X) = 1 - X/3 \tag{29}$$

and for the polystyrene–cyclohexane system at the theta temperature[11,12]:

$$r_g^2 = 9.18 \times 10^{-18} M \text{ cm}^2 \tag{30}$$

where $M$ is expressed in g/mol. We have assumed equation (30) to be valid for dilute solutions since the correlation term $(X/3)$ is quite small for both polymer molecular weights in the $K$-range which we have investigated. Then, we have:

$$P(M) \approx 1 - 3.06 \times 10^{-18} K^2 M \tag{31}$$

with $K$ and $M$ expressed in units of $\mathrm{cm}^{-1}$ and g/mol, respectively. By substituting equations (24), (25) and (31) into equation (26), we obtain for the histogram approximation:

$$G(\Gamma_j)\,\Delta\Gamma_j = \bar{M}_j^{1/2}(1 - 3.06 \times 10^{-18}\bar{M}_j) f^*(M)\Delta M_j \tag{32}$$

*Table 1*

| Sample | $c_1$ (g/cm$^3$) | $c_2$ (g/cm$^3$) | $c_m$(g/cm$^3$) | $c$*(g/cm$^3$) |
|---|---|---|---|---|
| NBS 705 ($\bar{M}_w$ = 1.79 x 10$^5$) | 0.00433 | 0.00244 | 0.014 | 0.141 |
| Pressure chemical ($M$ = 10 300) | 0.0260 | 0.0130 | 0.060 | 0.597 |

$c_m = 6.0\,\bar{M}_w^{-0.5}$ from ref 8
$c^* = M/N_A r_g^3$ from ref 15

or conversely,

$$f^*(M) = G(\Gamma_j)\Delta\Gamma_j/[\bar{M}_j^{1/2}(1 - 3.06 \times 10^{-18}\bar{M}_j)\Delta M_j] \tag{33}$$

The molecular weight distribution function $f(M)$ for the polystyrene–cyclohexane system at the theta temperature can be determined from photon correlation measurements as follows. First we compute $G(\Gamma_j)$ of a dilute solution of polystyrene in cyclohexane using the histogram approximation. Then we get $f(M)$ by means of equations (33) and (27). It should be noted that $f(M)$ is invariant, and in this procedure, we have assumed the validity of either Y, I or PF theory because we need equation (15) or equation (17) in order to make a proper transform from $\Gamma$-space to $M$-space. If we have a correct theory, we can then determine $k_T$ using a polystyrene sample of known molecular weight, or conversely, we can determine $f(M)$ for polystyrene polymers once we have determined $k_T$.

In this article, we first determine $k_T$ using polymer systems of known molecular weight. Either theory yields a value for $k_T$ at one finite concentration and we cannot distinguish which theory is correct. However, by invoking the invariance of the molecular weight distribution function, we can then predict the net signal time correlation function at a different concentration. The measured and computed time correlation function at the second concentration permits us to make a definitive test on the theoretical predictions of Y, I and PF theories. Again, we stress that our approach permits us to utilize the complete correlation function profile and to take into account the polydispersity effects. We need to make only two time correlation function measurements of known molecular weight at two separate concentrations in order to test the theoretical predictions definitively.

## EXPERIMENTAL

Two polystyrene samples were used for this investigation. One sample was a special standard (Mellon Institute) from the Pressure Chemical Company (Lot No. 8a) with $\bar{M}_n$ = 10 300 and $\bar{M}_w/\bar{M}_n < 1.06$. The other one was an NBS 705 standard with $\bar{M}_w$ = 179 300 ± 740 and $\bar{M}_z:\bar{M}_w:\bar{M}_n$ = 1.12:1.07:1.

Cyclohexane was passed through a silica gel column and dried with $CaCl_2$, and then distilled in a Perkin–Elmer Model 251 auto-annular still under argon gas. Dry polystyrene was dissolved in the purified cyclohexane and kept at 38°C overnight. The solution was then filtered through a millipore filter (type GS, nominal pore size = 0.22 $\mu$m).

Before each light scattering measurement, the samples were stirred frequently and conditioned at 38°C for several days.

In *Table 1*, for each sample the concentrations $c_1$ and $c_2$, at which the measurements were made, are listed together with $c_m$ and $c$* values, which are the limiting concentrations for the dilute solution range according to refs 9 and 16, respectively.

The detailed design of the light-scattering spectrometer has been described elsewhere[2,13,14]. In the present experiment, we used an argon ion laser (Spectra Physics Model 165) operating at 488.0 nm. The single-clipped photoelectron count autocorrelation function was measured using a Malvern correlator. Temperature at 35°C was controlled to ±0.01°C.

## RESULTS AND DISCUSSION

Two polystyrene samples of different molecular weights were studied. We discuss their results separately. As our data analysis is based mainly on the histogram method, we want to render the validity of this approach by making a comparison of the more established methods including those of cumulants and of Pearson[16,17].

In the cumulant expansion:

$$\ln|g^{(1)}(\tau)| = -\bar{\Gamma}\tau + \frac{1}{2!}\mu_2\tau^2 \ldots \tag{34}$$

where $\bar{\Gamma}$ and $\mu_2$ have been defined by equations (1) and (2). In the Pearson method, we used a Pearson Type I equation which can be represented by:

$$G(\Gamma) = C(\Gamma/A_1' - 1)^{m_1}(1 - \Gamma/A_2')^{m_2} \tag{35}$$

where $C$ is a normalization constant, and $A_1'$, $A_2'$, $m_1$, and $m_2$ can be determined by the method of nonlinear least squares.

### *NBS 705 polystyrene* ($\bar{M}_w$ = *1.79* x *10*$^5$)

*Figure 1* shows plots of $G(\Gamma)$ *versus* $\Gamma$ (sec$^{-1}$) for NBS polystyrene in cyclohexane measured at two different con-

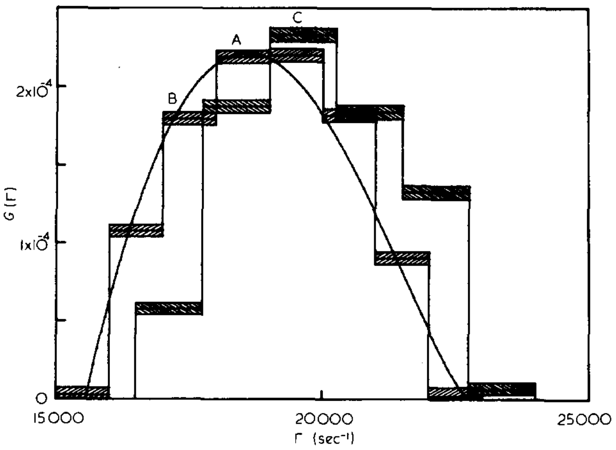

*Figure 1* Plots of $G(\Gamma)$ *versus* $\Gamma$ for NBS 705 polystyrene in cyclohexane measured at the theta temperature ($t$ ≈ 35.0°C) with $\theta$ = 90° and $\Delta\tau$ = 1.2 $\mu$sec. $c_1$ = 0.00433 g/cm$^3$: (A) Histogram method: (B) Pearson method with

$$G(\Gamma) = 0.012622(\Gamma/15555-1)^{1.008}\ (1-\Gamma/22791)^{1.416} \tag{36}$$

(C) Histogram method only, $c_2$ = 0.00244 g/cm$^3$. Shaded areas represent uncertainties in the parameters determined by the non-linear least squares method. A, Histogram, $c_1$; B, Pearson, $c_1$; C, Histogram, $c_2$

*Table 2* Comparison of average linewidth $\bar{\Gamma}$ by means of equation (34) and the histograms of *Figure 1*. NBS 705 polystyrene in cyclohexane, $\theta = 90°$; $t = 35.0°C$; $\Delta\tau = 1.2$ μsec. $c_1 = 0.00433$ g/cm$^3$; $c_2 = 0.00244$ g/cm$^3$

| | Histogram | | Cumulants | |
|---|---|---|---|---|
| | $c_1$ | $c_2$ | $c_1$[a] | $c_2$[b] |
| $\bar{\Gamma}$ (sec$^{-1}$) | 19 034 ± 60 | 19 917 ± 132 | 18 776 ± 50 | 19 762 ± 42 |
| $\mu_2/\bar{\Gamma}^2$ | 0.006 | 0.006 | – | – |
| $\mu_3 \times 10^{-9}$ (sec$^{-3}$) | −0.53 ± 0.36 | −0.14 ± 0.3 | – | – |
| $\mu_4 \times 10^{-13}$ (sec$^{-4}$) | 1.15 ± 0.04 | 1.27 ± 0.05 | – | – |
| $\bar{\Gamma}\tau_{max}$ | 2.2 | 2.3 | 2.2 | 2.3 |

[a] Single exponential fit; [b] quadratic fit

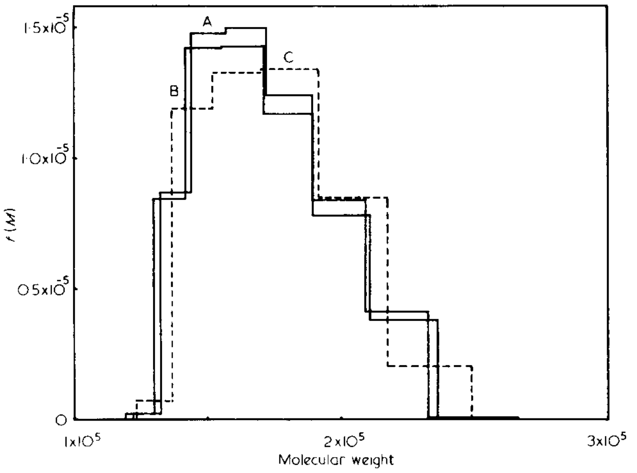

*Figure 2* Plots of $f(M)$ *versus* $M$ for the NBS 705 polystyrene. The histograms were transformed from Γ-space to $M$-space using equations (15) or (17), equation (33) and equation (27). $c_1 = 0.00433$ g/cm$^3$ solid histograms with $k_T = (1.338 \pm 0.005) \times 10^{-4}$ and $(1.259 \pm 0.005) \times 10^{-4}$ (cm$^2$/sec) (g/mol)$^{1/2}$ according to PF and Y, I theories, respectively. $c_2 = 0.00244$ g/cm$^3$ broken histogram with $k_T = (1.338 \pm 0.005) \times 10^{-4}$ (cm$^2$/sec) (g/mol)$^{1/2}$ according to the PF theory. The agreement between the histograms using the same $k_T$ value shows that the PF theory predicts the correct concentration dependence. A, PF theory, $c_1$; B, YI theory, $c_1$; C, PF theory, $c_2$

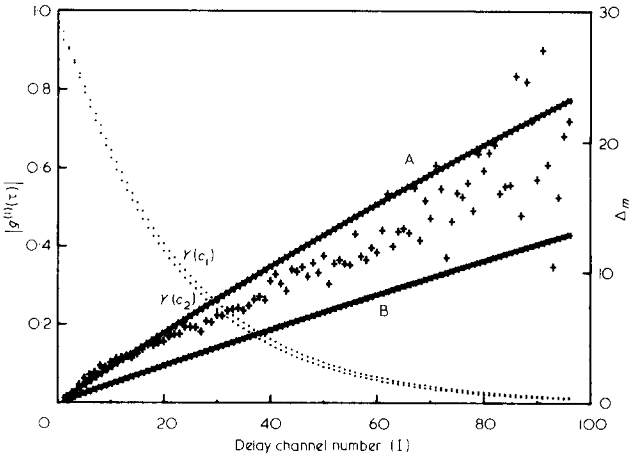

*Figure 3* Plots of $g^{(1)}(I\Delta\tau)|^2$ *versus* $I$ and $\Delta\{= 100\ [Y(c_1) - Y(c_2)]/Y(c_1)\}$ *versus* $I$ for NBS 705 polystyrene in cyclohexane, measured at the theta temperature ($t = 35.0°C$) with $\theta = 90°$ and $\Delta\tau = 1.2$ μsec. $c_1 = 0.00433$ g/cm$^3$; $c_2 = 0.00244$ g/cm$^3$. $|g^{(1)}(\tau)|^2$ and $I$ are the normalized net signal correlation function and the delay channel number, respectively. The dots denote measured $|g^{(1)}(\tau)|^2$ with the upper and lower curves being $c_1$ and $c_2$, respectively. The crosses denote the measured $\Delta_m[=(100\ (Y(c_1) - Y(c_2))/Y(c_1)]_{meas.}$ The stars represent the computed $\Delta\{= 100[Y(c_1) - Y(c_2)]/Y(c_1)\}$ $f(M)$ based on the solid histogram (curve A) of *Figure 2* computed at $c_1 = 0.00433$ g/cm$^3$. Upper stars, (A) PF theory; lower stars, (B) YI theory.

centrations with $c_1$ and $c_2$ being 0.00433 g/cm$^3$ and 0.00244 g/cm$^3$, respectively. The $G(\Gamma_j)$ values for the histogram were determined by the method outlined above using $G_k^{(2)}(\tau)$ measured at $t = 35°C$, $\Delta\tau = 1.2$ μsec and $\theta = 90°$. The essential feature of this result is revealed by the concentration dependence of $G(\Gamma_j)$. As our histogram method[2] of data analysis represents a new approach to polymer polydispersity effects, we confirm that $G(\Gamma)$ denotes a correct determination of the line-width distribution function by comparing its values with those determined by the Pearson method and by the method of cumulants. *Figure 1* shows a Pearson distribution function for $c_1 = 0.00433$ g/cm$^3$:

$$G(\Gamma) = 0.012622(\Gamma/15555 - 1)^{1.008}(1 - \Gamma/22791)^{1.416} \tag{36}$$

which is in excellent agreement with the histogram result. A comparison of $\bar{\Gamma}$ computed from the histograms of *Figure 1* is in excellent agreement with values determined directly from the measured $G_k^{(2)}(\tau)$ and equation (34). The results are listed in *Table 2*. The histogram method also permits us to obtain estimates of $\mu_3$ and $\mu_4$, not accessible by the usual cumulants expansion technique.

*Figure 2* shows plots of $f(M)$ *versus* $M$ using the histograms of *Figure 1* and equations (15) or (17), equation (33), and equation (27). The solid histograms represent results obtained by matching $f(M)$ such that the weight-average molecular weight $\bar{M}_w = 179\,300$. Then, at $c_1 = 0.00433$ g/cm$^3$, we obtain:

$$k_T = (1.338 \pm 0.005) \times 10^{-4} \quad \text{(PF)} \tag{37}$$

$$k_T = (1.259 \pm 0.005) \times 10^{-4} \quad \text{(Y, I)} \tag{38}$$

where $k_T$ is expressed in (cm$^2$/sec)(g/mol)$^{1/2}$. Once we have determined $k_T$, the measured time correlation function of the same polymer system at other concentrations can be predicted.

Also in *Figure 2*, $f(M)$ obtained from the measured $G(\Gamma)$ at $c_2 = 0.00244$ g/cm$^3$ using PF theory and $k_T = 1.338 \times 10^{-4}$ is shown by the broken-line histogram. The agreement between the histograms using the same $k_T$ value (curves A and C) shows that the PF theory predicts the correct concentration dependence.

*Figure 3* shows plots of $|g^{(1)}(I\Delta\tau)|^2$ *versus* $I$ and 100 $[Y(c_1) - Y(c_2)]/Y(c_1)$ *versus* $I$ for the NBS 705 polystyrene in cyclohexane measured at the theta temperature ($t = 35.0°C$) with $\theta = 90°$ and $\Delta\tau = 1.2$ μsec. In order to

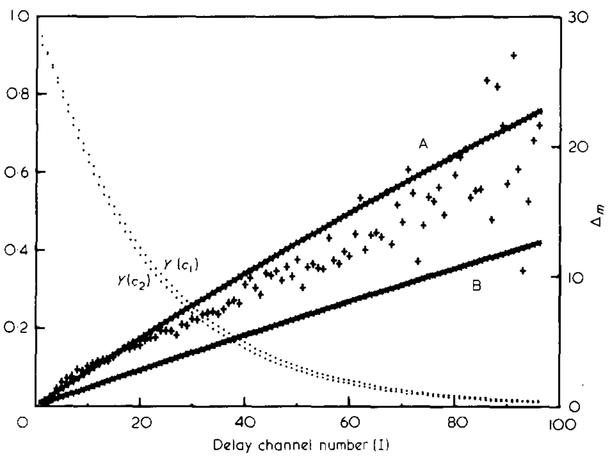

*Figure 4* Plots of $|g^{(1)}(\tau)|^2$ *versus I* and $\Delta$ (or $\Delta_m$) *versus I* for NBS 705 polystyrene in cyclohexane. See *Figure 3* captions for definition and experimental conditions. The stars denote $\Delta$ values using $f(M)$ based on the Pearson curve of *Figure 1*. A, PF theory; B, YI theory

make a proper comparison of the time correlation function at two different concentrations, we have normalized $A\beta|g^{(1)}(I\Delta\tau)|^2$ such that $|g^{(1)}(I\Delta\tau = 0)|^2 = 1$. The dots in *Figure 3* show the two measured net signal time correlation functions with the upper and lower curves corresponding to concentrations $c_1 = 0.00433$ and $c_2 = 0.00244$ g/cm$^3$, respectively. The difference curve in terms of $\Delta_m [= \{100[Y(c_1) - Y(c_2)]/Y(c_1)\}_{\text{meas}}]$ is represented by the crosses. If we use $Y(c_1)$ to compute $k_T$, then the PF and Y, I theories can predict the net signal time correlation function at $c_2$. The stars in *Figure 3* represent the expected $\Delta[= [Y(c_1) - Y(c_2)]/Y(c_1)]$ based on either the PF theory (upper curve with equation 37 or the Y, I theory, lower curve with equation 38). The results clearly show agreement of experiments with the PF theory. In particular, the initial slope represents evaluation of linewidths based on the average linewidth $\bar{\Gamma}$ (equation 1). Thus, equation (16) holds for polydisperse polymers with $\Gamma$ replaced by $\bar{\Gamma}$. As a further test of the validity of the histogram method and the PF theory, we have plotted in *Figure 4* the computed $\Delta[= 100[Y(c_1) - Y(c_2)]/Y(c_1)]$ based on the $f(M)$ from the Pearson curve of *Figure 1*. Again, the upper stars in *Figure 4* denote the PF theory with $k_T = 1.32 \times 10^{-4}$ (cm$^2$/sec)(g/mol)$^{1/2}$ while the lower stars denote the Y, I theory with $k_T = 1.240 \times 10^{-4}$ (cm$^2$/sec)(g/mol)$^{1/2}$. The agreement between the two star curves in *Figures 3* and *4* (upper to upper and lower to lower) shows that we can take into account the concentration dependence of a polydisperse polymer independent of the techniques used in the data analysis. Thus, we have shown that our histogram method of data analysis is consistent with other established but more restrictive methods. In addition, our results show that the PF theory is in excellent agreement with experiments of dilute polymer solutions at the theta temperature.

In our analysis, we have based our computations on measurements at $\theta = 90°$, which automatically compensates for the back reflection problem. *Figure 5* shows a scaled plot of $\ln|g^{(1)}(\tau)|^2$ *versus* $K^2I\Delta\tau$ for the NBS 705 polystyrene in cyclohexane measured at $t = 35.0°$C, $\theta = 90°$ and 130° using, respectively, $\Delta\tau = 1.2$ and 0.8 $\mu$sec. The dots show that correlation functions measured at different scattering angles can essentially be superimposed whenever $P(M,K) \approx 1$. Furthermore, according to equation (34), the difference term ($\ln|g^{(1)}(\tau)|^2$ at $c_1 = 0.00433$ g/cm$^3$ − $\ln|g^{(1)}(\tau)|^2$ at $c_2 = 0.00244$ g/cm$^3$) can be represented by:

$$\ln|g_1^{(1)}(\tau)|^2 - \ln|g_2^{(1)}(\tau)|^2 =$$

$$-2(\bar{\Gamma}_1 - \bar{\Gamma}_2)\tau + 2(\mu_{2,1} - \mu_{2,2})\tau^2 - \ldots$$

$$= -2(\bar{D}_1 - \bar{D}_2)K^2I\Delta\tau + 2(\mu_{2,1} - \mu_{2,2})\tau^2 - \ldots \quad (39)$$

A plot of $\ln|g_1^{(1)}(\tau)|^2 - \ln|g_2^{(1)}(\tau)|^2$ *versus* $K^2I\Delta\tau$ using the time correlation function measured at two different concentrations shows that the dominant factor is the change in $\bar{D}$ due to the concentration change. In fact, the measured difference, $\bar{D}_2^\theta - \bar{D}_1^\theta = 0.13 \times 10^{-7}$ cm$^2$/sec. is in close agreement with the value of slope/2, $0.14 \times 10^{-7}$ cm$^2$/sec, as shown in *Figure 5*. Consequently, the essential feature of equation (16) remains valid for polydisperse systems when we replace $D^\theta$ by $\bar{D}^\theta$, and such a conclusion is independent of the model. Here, we present a very precise determination of $k_T$ for polystyrene in cyclohexane at the theta temperatue because we use $\bar{D}^\theta$ together with the polydispersity effects. It would have been difficult to determine $k_T$ accurately using $\bar{D}^\theta$ only.

Finally, we should point out that there is a slight dependence of $k_T$ on the models used. *Figure 6* shows a plot of $A\beta|g^{(1)}(\tau)|^2$ *versus I* for the NBS 705 polystyrene in cyclohexane with $t = 35.0°$C, $\theta = 90°$, $\Delta\tau = 1.2$ $\mu$sec and $c_1 = 0.00433$ g/cm$^3$. The measured curve can be fitted to within limits of experimental error using the histogram (+) and the Pearson (x) methods where

$$\%\text{Dev} = 100(Y_m - Y)/Y_m$$

In addition, we have used a Schultz distribution function where:

$$f(M) \sim \left(\frac{M}{\bar{M}}\right)^Z / \bar{M}\exp[(Z+1)M/\bar{M}] \quad (40)$$

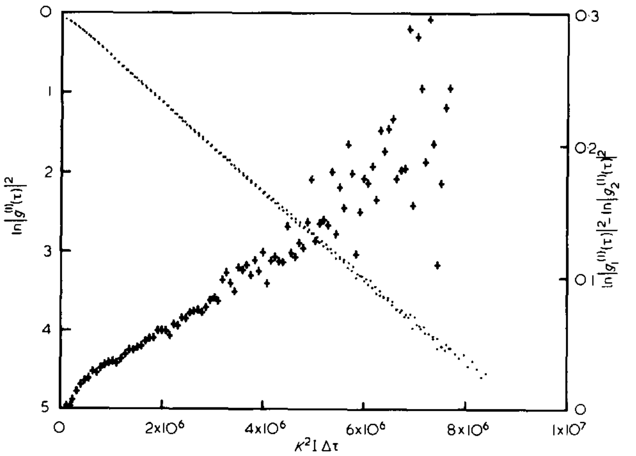

*Figure 5* Plots of $\ln|g^{(1)}(K,\tau)|^2$ and $\ln|g_1^{(1)}(\tau,\theta = 90°, c_1)|^2 - \ln|g_2^{(1)}(\tau,\theta = 90°, c_2)|^2$ *versus* $K^2I\Delta\tau$ for NBS 705 polystyrene in cyclohexane at the theta temperature. The dots represent $\ln|g^{(1)}(K,\tau)|^2$ at $\theta = 90°$ and 130° with $\Delta\tau = 1.2$ and 0.8 $\mu$sec, respectively. $\bar{D}_1(\theta = 90°, c_1 = 0.00433$ g/cm$^3$, $\Delta\tau = 1.2$ $\mu$sec) $= 2.86 \times 10^{-7}$ cm$^2$/sec; $\bar{D}_1(\theta = 130, c_1 = 0.00433$ g/cm$^3$, $\Delta\tau = 0.8$ $\mu$sec) $= 2.80 \times 10^{-7}$ cm$^2$/sec; $\bar{D}_2(\theta = 90°, c_2 = 0.00244$ g/cm$^3$, $\Delta\tau = 1.2$ $\mu$sec) $= 2.99 \times 10^{-7}$ cm$^2$/sec; $(\bar{D}_2 - \bar{D}_1) = 0.13 \times 10^{-7}$ cm$^2$/sec; slope/2 $= 0.14 \times 10^{-7}$ cm$^2$/sec

and obtained, according to equation (26):

$$A\beta|g^{(1)}(\tau)|^2 = \left\{P1 \int_{M_{\min}}^{M_{\max}} M^{1/2}(1 - 3.06 \times 10^{-18}K^2M)e^{-\Gamma\tau}\left(\frac{M}{P3}\right)^{P2} / P3 \cdot \exp[(P2+1)M/P3]\,dM\right\}^2 \tag{41}$$

where the constants to be determined are $P1$, a proportionality constant, $P2 \equiv Z$, and $P3 \equiv \bar{M}$. With $\Gamma$ represented by equation (16) which includes a fourth constant $P4 \equiv k_T$, we can also determine $f(M)$ using the form of the Schultz distribution function. % Dev based on the Schultz distribution (as denoted by □) shows similar precision to those of the histogram and the Pearson methods. *Figure 7* shows plots of $f(M)$ *versus* $M$ for the NBS 705 polystyrene standard using the three different methods. The results for $k_T$ are listed in *Table 3* and a value of $1.34 \times 10^{-4}$ cm$^2$ g$^{1/2}$/sec mol$^{1/2}$ is a good representation of our experiments.

### *Pressure Chemical polystyrene standard (*M = 10 300)

In our study of the Pressure Chemical (PC) sample, we have essentially repeated the experiment using a polymer of lower molecular weight. *Figure 8* shows plots of $G(\Gamma)$ *versus* $\Gamma$ at two different concentrations. Again, as listed in *Table 4*,

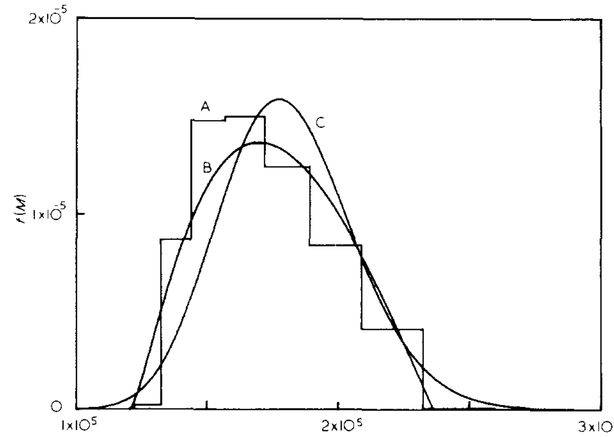

*Figure 7* Plots of $f(M)$ *versus* $M$ for the NBS 705 polystyrene sample for $\theta = 90°$, $t = 35.0°$C, $c_1 = 0.00433$ g/cm$^3$. A, Histogram; B, Pearson; C, Shultz

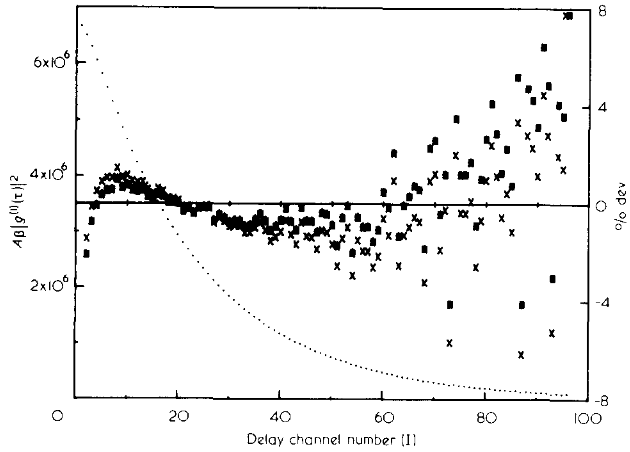

*Figure 6* Plots of $A\beta|g^{(1)}(\tau)|^2$ and % Dev *versus* delay channel number I. % Dev = 100 $(Y_m - Y)/Y_m$. +, Histogram method; □, Schultz distribution; x, Pearson method. NBS Polystyrene in cyclo hexane, $\theta = 90°$, $t = 35.0°$C, $c_1 = 0.00433$ g/cm$^3$

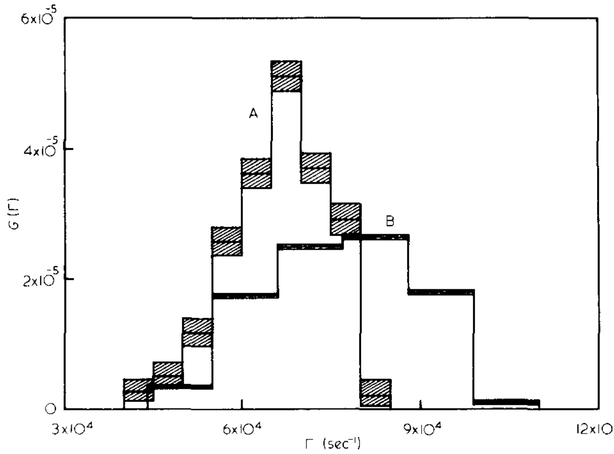

*Figure 8* Plots of $G(\Gamma)$ *versus* $\Gamma$ for PC polystyrene in cyclohexane measured at $t = 35.0°$C, $\theta = 90°$, $\Delta\tau = 0.35$ μsec. $c_1 = 0.0260$ g/cm$^3$ $c_2 = 0.0130$ g/cm$^3$. Shaded areas represent uncertainties in the parameters determined by the non-linear least squares method. A, Histogram, $c_1$; B, Histogram, $c_2$

*Table 3* Values of $k_T$ determined according to the PF theory using different methods. $t = 35°$C; $[k_T]$ expressed in (cm$^2$/sec)(g/mol)$^{1/2}$. NBS 750 polystyrene in cyclohexane

| Method | Histogram | Pearson | Schultz | NBS Data |
|---|---|---|---|---|
| $k_T$ | $1.338 \times 10^{-4}$ | $1.321 \times 10^4$ | $1.367 \times 10^4$ | – |
| $\bar{M}_z/\bar{M}_n$ | 1.04 | 1.04 | 1.04 | 1.12 |
| $\bar{M}_w/\bar{M}_n$ | 1.02 | 1.02 | 1.02 | 1.07 |
| Set $\bar{M}_w$ | 179 300 | 179 300 | 179 300 | 179 300 |

PC polystyrene in cyclohexane ($\bar{M}_n$ = 10 300)

| Method | Histogram | Data from Supplier |
|---|---|---|
| $k_T$[a] | $1.275 \times 10^{-4}$ | – |
| $\bar{M}_w/\bar{M}_n$ | 1.05 | ⩽ 1.06 |

[a] The value of $k_T$ depends upon the precision of known *M*. In the case of PC polystyrene, *M* was not quoted by the supplier as precisely as that of the NBS standard

*Table 4* Comparison of average linewidth $\overline{\Gamma}$ by means of equation (34) and the histograms of *Figure 8*. PC polystyrene in cyclohexane $\theta$ = 90°, $t$ = 35.0°C, $\Delta\tau$ = 0.35 $\mu$sec. $c_1$ = 0.0260 g/cm$^3$; $c_2$ = 0.0130 g/cm$^3$

| | Histogram | | Cumulants (2nd order fit) | |
|---|---|---|---|---|
| | $c_1$ | $c_2$ | $c_1$ | $c_2$ |
| $\overline{\Gamma}$ (sec$^{-1}$) | 66 247 ± 292 | 76 594 ± 200 | 65 861 ± 100 | 76 083 ± 128 |
| $\mu_2/\overline{\Gamma}^2$ | 0.016 | 0.029 | 0.011 | 0.022 |
| $\mu_3 \times 10^{-11}$ (sec$^{-3}$) | −2.90 ± 2.24 | −3.19 ± 0.64 | – | – |
| $\mu_4 \times 10^{-16}$ (sec$^{-4}$) | 1.43 ± 0.35 | 6.62 ± 0.20 | – | – |
| $\overline{\Gamma}\tau_{max}$ | 2.2 | 2.6 | 2.2 | 2.6 |

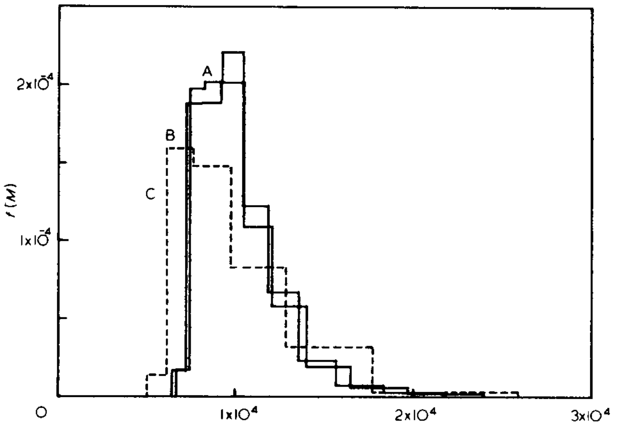

*Figure 9* Plots of $f(M)$ *versus* $M$ for the PC polystyrene in cyclohexane. Equations (15) or (17), equation (33) and equation (27) were used to transform the histogram data of *Figure 8*. A, PF theory, $c_1$; B, YI theory, $c_1$; C, PF theory, $c_2$

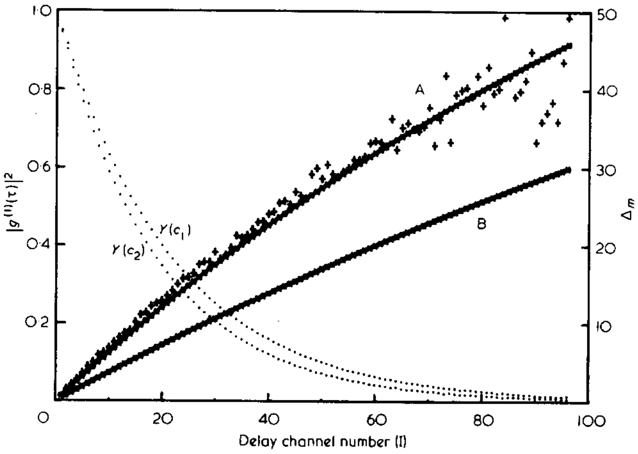

*Figure 10* Plots of $|g^{(1)}(\tau)|^2$ *versus* $I$ and $\Delta$ *versus* $I$. See *Figure 3* for definitions and notation. PC polystyrene in cyclohexane with $\theta$ = 90°, $t$ = 35.0°C, $\Delta\tau$ = 0.35 $\mu$sec, $c_1$ = 0.0260 g/cm$^3$, $c_2$ = 0.0130 g/cm$^3$. A, PF theory; B, YI theory

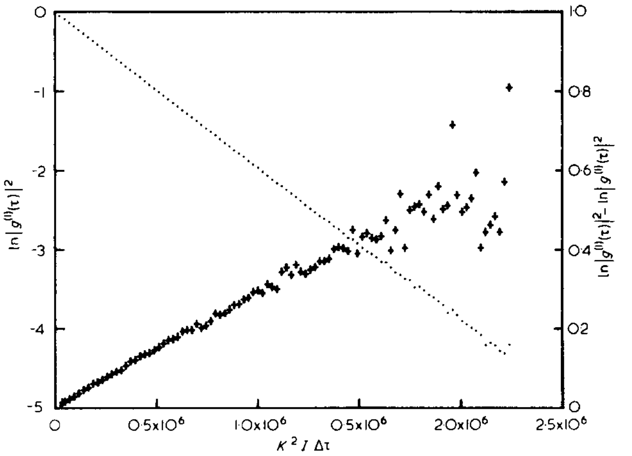

*Figure 11* Plots of $\ln|g^{(1)}(\tau)|^2$ and $\ln Y(c_1) - \ln Y(c_2)$ *versus* $K^2/\Delta\tau$. PC polystyrene in cylcohexane at $t$ = 35.0°C. Dots denote $c_1$ = 0.0260 g/cm$^3$, $\theta$ = 90°, $\Delta\tau$ = 0.35 $\mu$sec. Crosses denote $\ln Y(c_1) - \ln Y(c_2)$ with $c_2$ = 0.0130 g/cm$^3$. $\overline{D}_1(\theta = 90°, c_1 = 0.026$ g/cm$^3$, $\Delta\tau$ = 0.35 $\mu$sec) = 9.94 × 10$^{-7}$ cm$^2$/sec; $\overline{D}_2(\theta = 90°, c_2 = 0.013$ g/cm$^3$, $\Delta\tau$ = 0.35 $\mu$sec) = 11.49 × 10$^{-7}$ cm$^2$/sec; $(\overline{D}_2 - \overline{D}_1)$ = 1.55 cm$^2$/sec; slope/2 = 1.44 × 10$^{-7}$ cm$^2$/sec

the histogram parameters can be shown to be consistent with parameters determined by the method of cumulants. *Figure 9* shows plots of $f(M)$ *versus* $M$ for the PC polystyrene in cyclohexane. The solid histograms represent results at $c_1$ = 0.0260 g/cm$^3$ using PF theory with $k_T$ = 1.275 × 10$^{-4}$ and Y, I theory with $k_T$ = 1.16 × 10$^{-4}$ where $[k_T] \equiv$ (cm$^2$/sec)(g/mol)$^{1/2}$. The broken-line histogram represents results at $c_2$ = 0.0130 g/cm$^3$ using PF theory with $k_T$ = 1.275 × 10$^{-4}$. We believe that the lower value of $k_T$ for the PC polystyrene sample could be due to a slight imprecision in the molecular weight value provided by the supplier. *Figure 10* (equivalent to *Figure 3*) shows plots of $|g^{(1)}(\tau)|^2$ and $\Delta$ *versus* $I$ for the PC polystyrene in cyclohexane. The agreement between experiments and the PF theory is indeed excellent. *Figure 11* (equivalent to *Figure 5*) shows a plot of $\ln|g^{(1)}(\tau)|^2$ *versus* $K^2I\Delta\tau$. The straight line behaviour suggests that $\mu_2/\overline{\Gamma}^2$ must be very small as listed in *Table 4*. The difference $\ln Y(c_1) - \ln Y(c_2)$ also reveals a straight line behaviour indicating negligible contributions due to $(\mu_{2,1} - \mu_{2,2})\tau^2$ in equation (39). The measured $\overline{D}_2^\theta - \overline{D}_1^\theta$ = 1.55 cm$^2$/sec agrees well with slope/2 = 1.44 cm$^2$/sec of *Figure 11*.

## CONCLUSIONS

We have established a histogram method of data analysis which takes into account the effects of polydispersity in photon correlation spectroscopy. The method yields parameters which agree with established but more restrictive techniques such as those of cumulants and of Pearson. By utilizing the information from the entire time correlation function profile, we have made a precise determination of $k_T$[= 1.34 × 10$^{-4}$ (cm$^2$/sec)(g/mol)$^{1/2}$] for polystyrene in cyclohexane at the theta temperature. Furthermore, in contrast to earlier findings of King *et al.*[8], our experimental results are in excellent agreement with the Pyun and Fixman theory.

Our technique permits a fairly precise determination of $f(M)$ by combining classical light scattering intensity measurements with the Rayleigh linewidth study at the theta temperature. It should be noted that only small quantities of the polymer are required to carry out such an investigation.

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