High-Temperature Dynamic Laser Light-Scattering Characterization of Polyethylene in Trichlorobenzene

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SYNOPSIS

Polyethylene samples were characterized in trichlorobenzene at 135°C by high-temperature dynamic laser light scattering (LLS). Precise measurements of the intensity–intensity time correlation function permit us to make a Laplace inversion to obtain an estimate of the normalized translational diffusion coefficient distribution [$G(D)$]. After establishing a calibration between the translational diffusion coefficient (D) and molar mass, by using six moderately dispersed polyethylene samples, we were able to transform $G(D)$ to molecular weight distribution (MWD), and to calculate the weight average molecular weight (M_w), which weights were comparable with the ones obtained by using static LLS and size exclusion chromatograph (SEC). The advantages and limitations of using dynamic LLS as a routine method to characterize of polyethylene are discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Light scattering (LS), especially static light scattering (SLS), has been extensively used to characterize polyethylene in various solvents, including trichlorobenzene (TCB), to obtain the weight average molecular weight (M_w), the z-average radius of gyration ($\langle R_g \rangle_z^{1/2}$), and the second virial coefficient (A_2).[1,2] According to the light scattering principle, the angular dependence of the excess absolute time-averaged scattered intensity {known as the excess Rayleigh ratio [$R_{vv}(\theta)$]} of a dilute polymer solution at concentration C (g/mL), and scattering angle θ, can be approximately expressed as[3]

$$\frac{KC}{R_{vv}(\theta)} \cong \frac{1}{M_w P(\theta)} + 2A_2C \tag{1}$$

where $K = 4\pi^2 n^2 \left(\frac{dn}{dC}\right)^2 \Big/ (N_A \lambda_o^4)$ with N_A, n, and λ_o being Avogadro's number, the solvent refractive index, and the wavelength of light *in vacuo*, respectively. $P(\theta) \cong 1 + \frac{1}{3}\langle R_g^2 \rangle_z q^2$ and $q = \frac{4\pi n}{\lambda_o} \sin\left(\frac{\theta}{2}\right)$. The accuracy of the measured $R_{vv}(\theta)$ is strongly dependent on the experimental conditions. For example, we have noticed one intrinsic problem with using TCB as solvent in the LLS characterization of polyethylene. On the one hand, due to the low contrast ($dn/dC \sim 0.1$), we must use a more concentrated solution in order to obtain enough excess scattering intensity. On the other hand, due to the high second virial coefficient ($A_2 \sim 10^{-3}$ mL $\times$ mol/g^2), we must use a dilute solution, because eq. (1) is only valid when $2A_2M_wC \ll 1$. Therefore, the applicable concentration range is narrow. This problem has been overlooked in the past.

Only few results of using dynamic light scattering to characterize polyethylene in TCB have heretofore been reported, primarily because the high-temperature dynamic light scattering (HTDLS) instrument is not commercially available.[4,5] We have recently developed a high-temperature laser light scattering spectrometer, whose operating temperature can be as high as 200°C. The purposes of the present work are (1) to establish a calibration between the translational diffusion coefficient and

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molar mass and (2) to investigate the possibility, the advantages, and the limitations of using HTDLS, instead of a conventional SLS or SEC, as a routine method to characterize polyethylene.

EXPERIMENTAL

Samples

Six moderately dispersed polyethylene samples (A162, A175, A168, A194, A134, and A164) were obtained by using metalloceue catalysis. Trichlorobenzene (TCB, synthesis-grade), with the addition of 0.05 wt % 2,6-di-tert-butyl-4-methylphenol (antioxidant), was used as solvent without further purification.

Solution Preparation

The polyethylene concentrations were 2×10^{-4} to 2×10^{-3} g/mL, depending on the molar mass. All solutions were made and were clarified at 145°C in order to ensure a complete dissolution of polyethylene. In comparison with the LLS experiment at room temperature, it is more difficult to clarify polymer solutions at high temperatures. After many failures in testing various types of filters, we found a workable glass fiber filter, which was 25 mm in diameter and had a pore size of 0.5–1.49 μm (No. 6, 370018, Schleicher & Schuell, Dassel, Germany). The operation temperature of the filter can be as high as 500°C. The retention volume of the filter is small, which is crucial in our sample preparations. At high temperatures, all sample preparations (dissolution and clarification) have to be performed remotely. Therefore, we designed and constructed one suitable dissolution/clarification device, which consisted of a temperature-maintaining brass block, a cuvette for dissolving polymer (preparative cuvette), a light-scattering cuvette, a filter-holder, and a stainless steel tube which connected the two cuvettes through the filter-holder. After the polymer was dissolved, the filtered N_2 is used to push the solution from the preparative cuvette through the filter into a dust-free light scattering cuvette. After many unsuccessful attempts, we finally developed the following procedure: (1) clean the whole filtration device (i.e., the filter, the needle, the tube, and the scattering cell) at room temperature, (ii) filter the solvent (TCB) into both the preparative with the abovementioned glass fiber filter and the light scattering cuvettes, (iii) use laser light to check the solvent in both cuvettes to assure that there is no dust inside, (iv) introduce a certain amount of polyethylene into the preparative cuvette and seal both cuvettes, which contain the dust-free solvent, (v) raise the temperature and dissolve the polymer, (vi) use controlled N_2 pressure to push the solution from the preparative cuvette into the scattering cuvette through the dust-free filter, and (vi) calculate the final polymer concentration, based on the known weights of the two cuvettes, the polymer, and the solvent in each cuvette before and after the filtration.

After adopting this precautionary procedure, the successful rate for producing a dust-free solution for laser light scattering at high temperature is significantly improved and the final solution is usually clean.

Dynamic Light Scattering (DLS)

The details of DLS can be found elsewhere.[6] In DLS, an intensity–intensity time correlation function $G^2(n\Delta\tau, \theta)$ in the self-beating mode is normally measured, which has the following form[3,6]

$$\begin{aligned} G^{(2)}(n\Delta\tau, \theta) &= \langle I(n\Delta\tau, \theta) I(0, \theta)\rangle \\ &= A[1 + \beta |g^{(1)}(n\Delta\tau, \theta)|^2] \end{aligned} \tag{2}$$

where A is a measured baseline, β is a parameter, depending on the coherence of the detection, n is the channel number, $\Delta\tau$ is the sample time, and $g^{(1)}(n\Delta\tau, \theta)$ is the normalized, first-order electric field–time correlation function. In our correlation function measurements, instead of using A as an adjustable parameter, we insisted that A and $\lim_{n\to\infty} G^{(2)}(n\Delta\tau, \theta)$ (the calculated baseline) should agree to within 0.1%. For a polydisperse sample, $g^{(1)}(n\Delta\tau, \theta)$ is related to the line–width distribution $G(\Gamma)$ by

$$\begin{aligned} g^{(1)}(n\Delta\tau, \theta) &= \langle E(n\Delta\tau, \theta) E^*(0, \theta)\rangle \\ &= \int_o^\infty G(\Gamma) e^{-\Gamma n\Delta\tau}\, d\Gamma \end{aligned} \tag{3}$$

where the line–width, Γ, usually depends on both concentration and scattering vector, q. The increasing interaction between polymer molecules, with concentration, will affect the diffusion process. This effect, in a dilute polymer solution, is proportional to concentration. In addition, at a higher scattering angle, Γ usually contains some contributions from the internal molecular motions. Those effects can be expressed in the following equation[7]

$$\frac{\Gamma}{q^2} = D(1 + k_d C)(1 + f\langle R_g^2\rangle q^2) \qquad (4)$$

where D is the translational diffusion coefficient, f is a number without dimension, and k_d is the diffusion second virial coefficient. The typical value of f for a polymer, with flexible chain in a good solvent, is between 0.1 and 0.2, which depends on chain structure, polydispersity, and solvent quality.[7] k_d contains a thermodynamic and a hydrodynamic contribution, which can be expressed as[8]

$$k_d = 2A_2M_w - C_D N_A R_h^3/M_w \qquad (5)$$

where C_D is a semiempirical positive constant and R_h is the hydrodynamic radius. Various theories have been presented to evaluate C_D. However, there is no general agreement between the measured values and the calculated values. The values still remain within an experimental parameter. When $A_2 > 0$, the thermodynamic term is partially cancelled by the hydrodynamic part, so that the term $(1 + k_d C)$ is smaller than $(1 + 2A_2M_wC)$ in eq. (1). Therefore, Γ/q^2 is normally less dependent on C and θ than $R_{vv}(\theta)$, which means that DLS experiments can be performed at higher C and higher θ, or the corrections of Γ/q^2 to both $C = 0$ and $\theta = 0$ are not so serious, if one is using a dilute solution and is measuring at a relatively small angle. This is one of the advantages of using DLS in a routine characterization of polyethylene.

All laser light-scattering measurements were done at 135°C. The detail of the HTLLS measurement can be found elsewhere[7] and the size exclusion chromatograph (SEC) was performed according to a standard procedure. In the present work, all experiments were performed at 135°C. TCB was used not only as a solvent, but also as a secondary standard in the calculation of the absolute scattered intensities, that is, $R_{vv}(\theta)$.

RESULTS AND DISCUSSION

The weight average molecular weights of samples A162 and A168 were carefully characterized by static light scattering (SLS), in order to confirm the weight average molecular weight (M_w), obtained by using SEC. The SLS results, together with the SEC results, are summarized in Table I. They are comparable, if we consider the uncertainties in both experiments. Therefore, instead of using a time-consuming SLS to characterize the rest of the samples to obtain M_w, we have simply used the SEC results in the following data analysis.

Figure 1 shows a typical, measured intensity–intensity time correlation function of polyethylene in TCB at 135°C, where $C = 1.45 \times 10^{-4}$ g/mL and $\theta = 20°$. The widely accepted Laplace transform program, CONTIN,[9] kindly furnished by S. W. Provencher, was used in the present work to calculate $G(\Gamma)$ from $G^{(2)}(n\Delta\tau, \theta)$. By using eq. (4), $G(\Gamma)$ can be reduced to $G(D)$, if k_d and f are known.

Figure 2 shows the translational diffusion coefficient distribution ($G(D)$) of polyethylene in TCB at 135°C, where $C \to 0$ and $\theta \to 0$, by using eq. (4). It should be stated that in the extrapolation, we have used an approximation that both k_d and f are independent in molecular weight and are equal to the average values $\bar{k}_d$ and $\bar{f}$, which approximation breaks

Table I SEC, Static, and Dynamic Light Scattering Results of Polyethylene in Trichlorobenzene at 135°C

	A162	A175	A168	A194	A134	A164
SEC Results:						
$M_w/(10^5$ g/mol)	1.09	3.74	4.10	4.35	6.85	8.40
Static LLS Results:						
$M_w/(10^5$ g/mol)	0.89	—	4.15	—	—	—
A_2 (10^{-3} mL × mol/g^2)	1.14	—	0.91	—	—	
$\langle R_g^2\rangle_z^{1/2}$/nm	20	—	46	—	—	—
Dynamic LLS Results:						
$M_w/(10^5$ g/mol)[a]	1.10	3.61	4.08	4.57	6.47	8.65

[a] Calculated from $G(D)$, using $D = 5.25 \times 10^{-4} M^{-0.577}$ and eqs. (9) and (10).

down if the molecular weight is broadly distributed. As mentioned previously, for a sufficient dilute solution and low scattering angle, both corrections for C and θ are no more than a few percent, which are much smaller than the corresponding corrections in static light scattering for the same C and θ. By using this approximation, the transformation from $G(\Gamma)$ to $G(D)$ merely represents a uniform shift in Γ-axis and a normalization after it.

In order to calculate the molecular weight distribution (MWD) from $G(D)$, we need a calibration between D and M, that is, we need to find the calibration constants k_D and α_D in

$$D = k_D M^{-\alpha_D} \tag{6}$$

where both k_D and α_D are independent on M for a given solvent and a fixed experimental temperature, as long as the polymer conformation does not change as M. By using eq. (6), $G(D)$ can be transferred to MWD according to the following principles: based on eqs. (1) and (3), as $C \rightarrow 0$ and $\theta \rightarrow 0$, we have

$$\int_o^\infty G(D)\,dD = \gamma \times \int_o^\infty F_n(M)M^2\,dM \tag{7}$$

where γ is a normalization constant and $F_n(M)$ is a number distribution. Equation (7) can be rewritten as

$$\int_o^\infty G(D)\frac{dD}{dM}\,dM = \gamma \times \int_o^\infty F_n(M)M^2\,dM \tag{8}$$

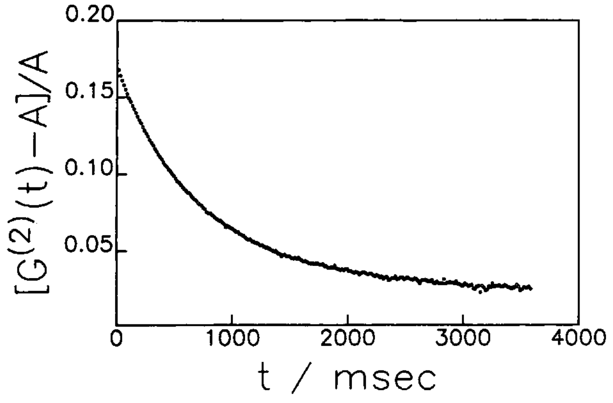

Figure 1 Typical, measured intensity–intensity time correlation function of polyethylene (A168) in trichlorobenzene at 135°C, where $C = 1.45 \times 10^{-4}$ g/mL and $\theta = 20°$.

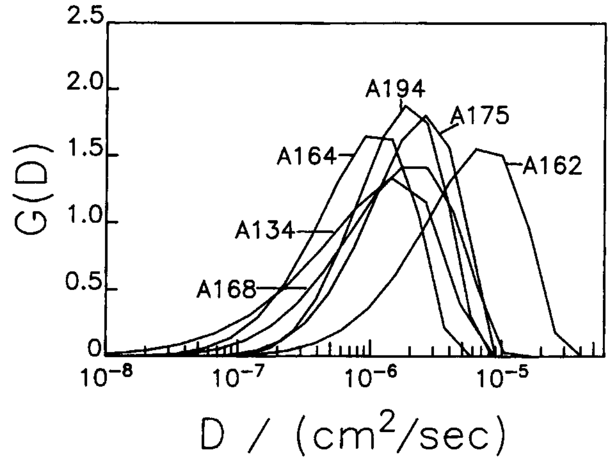

Figure 2 Translational diffusion coefficient distribution of polyethylene in trichlorobenzene at 135°C, where $C \rightarrow 0$ and $\theta \rightarrow 0$.

By comparing both sides of eq. (8), we have

$$F_w(M) = F_n(M)M \propto \frac{G(D)}{M} \times \frac{dD}{dM}$$

$$\text{or} \quad F_n(M) \propto \frac{G(D)}{M^2}\cdot\frac{dD}{dM} \tag{9}$$

where $F_w(M)$ is a weight distribution and all proportional constants have been omitted, since they are irrelevant to both distributions. For a given calibration, between D and M, we can first calculate both M and $\frac{dD}{dM}$, according to eq. (6), and then $F_w(M)$ or $F_n(M)$, according to eq. (9).

Figure 3 shows a log–log plot of $\bar{D}$ vs. M_w (the circles). They can be represented by a least-square fit of eq. (6), with $\bar{k}_D$, $= 7.08 \times 10^{-4}$ and $\bar{\alpha}_D = 0.612$ (the dotted line) where the dashed line emphasizes that they are obtained by using $\bar{D}$ and M_w instead of D and M. The first attempt was to use $\bar{k}_D$ and $\bar{\alpha}_D$ to transform $G(D)$ to MWD and to calculate M_w and M_n according to their definitions:

$$(M_w)_{\text{calcd}} = \frac{\int_o^\infty F_w(M)M\,dM}{\int_o^\infty F_w(M)\,dM}$$

$$= \frac{\int_o^\infty G(D)\,dD}{\int_o^\infty \frac{G(D)}{M}\,dD} \tag{10}$$

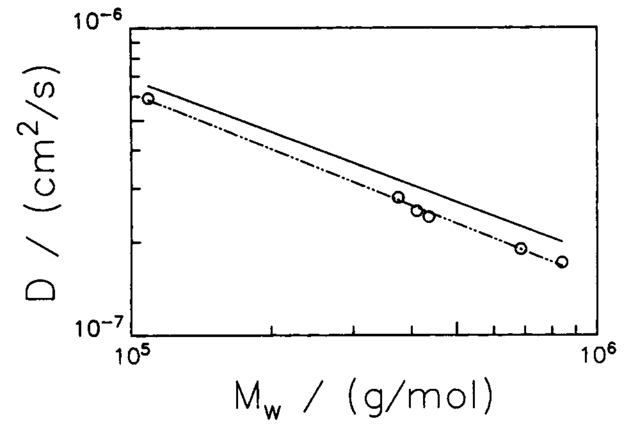

Figure 3 Log–log plot of the z-average translational diffusion coefficient ($\bar{D}$) vs. the weight average molecular weight (M_w). The dashed line represents a least-square fit of the measured data ($\bar{D} = 7.08 \times 10^{-4}\ M_w^{-0.612}$) and the continuous line represents a calibration of $D = 5.25 \times 10^{-4}\ M^{-0.577}$.

and

$$(M_n)_{\text{calcd}} = \frac{\int_o^\infty F_n(M) M\, dM}{\int_o^\infty F_n(M)\, dM} = \frac{\int_o^\infty \frac{G(D)}{M}\, dD}{\int_o^\infty \frac{G(D)}{M^2}\, dD} \tag{11}$$

The weight and number average molecular weights, calculated with $\bar{k}_D$ and $\bar{\alpha}_D$, are much smaller than those obtained by using SLS and SEC. This disagreement is understandable, because we have used $\bar{k}_D$ and $\bar{\alpha}_D$ instead of k_D and α_D, respectively. In the past, various methods have been used to find k_D and α_D, such as (i) measuring D and M of many narrowly distributed standards,[10] (ii) using $G(D)$ and M_w of at least two broadly distributed samples,[11] (iii) estimating the calibration constants from other experimental results (for example, from polymer conformation, solvent quality, and viscosity data),[12] and (iv) combining the elution volume distribution $[C(V)]$ of a broadly distributed sample from SEC with both $G(D)$ and M_w from laser light scattering.[13] In the present work, method (ii) was used, which is briefly described as follows:

For N-number samples, we have N-number measured M_w and $G(D)$, denoted as $M_{w,i}$ and $G_i(D)$, where $i = 1$ to N. By assuming a pair of k_D and α_D in eq. (6), and by using eq. (10), we are able to calculate the N-number, $(M_w)_{\text{calcd}}$, denoted as $(M_{w,i})_{\text{calcd}}$, where $i = 1$ to N. In principle, $(M_{w,i})_{\text{calcd}}$ should equal $M_{w,i}$, if k_D and α_D are chosen correctly. Therefore, our goal is to find a pair of k_D and α_D, which can minimize the ERROR, defined as

$$\text{ERROR} = \frac{1}{N}\sum_{i=1}^{N}\left[\frac{M_{w,i} - (M_{w,i})_{\text{calcd}}}{M_{w,i}}\right]^2 \tag{12}$$

It is clear that this procedure is an M_w-constrained analysis. In this way, by using k_D and α_D instead of $\bar{k}_D$ and $\bar{\alpha}_D$, we avoided the polydisperse problem.

Figure 4 shows a plot of ERROR vs. k_D, with different α_D. It is clear that there is a minimum for each chosen α_D and that there is an overall minimum. This overall minimum corresponds to a pair of optimized $k_D = 5.25 \times 10^{-4}$ and $\alpha_D = 0.577$, which defines a calibration between D and M. The continuous line in Figure 3 represents such a calibration. The obvious deviation from our measured $\bar{D}$ and M_w clearly shows how serious error could be introduced in practice if we used $\bar{D}$ and M_w measured from a set of broadly distributed samples, instead of D and M. It is of interest to note that $3\alpha_D - 1 = 0.731$ and $\alpha_{[\eta]} = 0.72$–0.75, that is, $3\alpha_D - 1 = \alpha_{[\eta]}$, where $\alpha_{[\eta]}$ is a scaling constant in the Mark–Houwink equation, $[\eta] = k_{[\eta]}M^{-\alpha_{[\eta]}}$, which is close to Flory's prediction.[14]

However, from the experimental point of view, this overall minimum (i.e., k_D and α_D) is not well defined, because of the experimental noise in both M_w and $G(D)$. The important question is how much

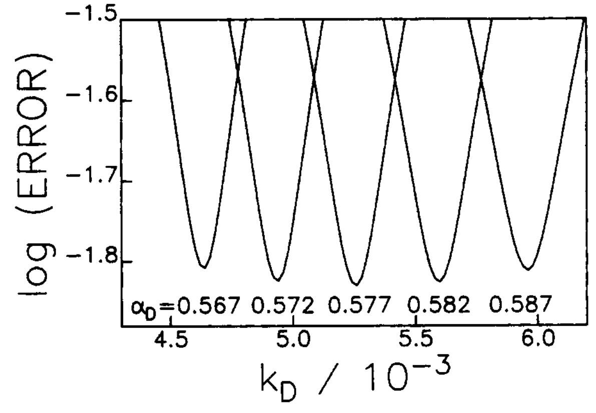

Figure 4 Typical plot of ERROR vs. k_D with different α_D, where ERROR $= \frac{1}{N}\sum_{i=l}^{N}\left[\frac{M_{w,i} - (M_{w,i})_{\text{calcd}}}{M_{w,i}}\right]^2$, and N = 6 in this case.

error this uncertainty will introduce into the final molecular weight distributions.

Figure 5 shows three cumulative weight distributions of A168, calculated with three different sets of k_D and α_D, where we have intentionally shifted the minimums to both sides of the overall minimum. Figure 5 shows that there is no significant difference among those three distributions, that is, a small uncertainty in this overall minimum will not introduce serious errors in our calculated molecular weight distribution.

Figure 6 shows a comparison between $(F_w(M))_{\mathrm{DLS}}$ [the circles, calculated from $G(D)$] and $(F_w(M))_{\mathrm{SEC}}$ (the squares, obtained by using SEC) of polyethylene A168. It can be seen in Figure 6 that $[F_w(M)_{\mathrm{DLS}}]$ is narrower than $[F_w(M)_{\mathrm{SEC}}]$, even though they have similar M_w. This difference is understandable, because the scattered light intensity is proportional to $f_n(M)M^2$, so that small molecules in a broad distribution cannot be "seen" by the light scattering detector. Therefore, for a broadly distributed sample, the MWD obtained by using LLS is normally narrower than the real MWD. This is certainly a shortcoming of using dynamic light scattering to estimate the molecular weight distribution of a broadly distributed polymer sample.

Based on the above discussion, we are confident in using this pair of calculated k_D and α_D, located at the overall minimum, to transform $G(D)$s in Figure 3 into $F_w(M)$s. The calculated $F_w(M)$ and $\int_o^M F_w(M)\,dM$, of six polyethylene samples, are shown in Figures 7(A) and (B), respectively. The calculated values of M_w are listed in Table I, which essentially agrees with those values obtained from SEC, if one takes into account all experimental noises in both DLS and SEC. However, the calculated number average molecular weights are higher than the ones obtained by using SEC. This difference could be partially due to the reasons we have previously discussed and partially due to some baseline fluctuations in SEC.

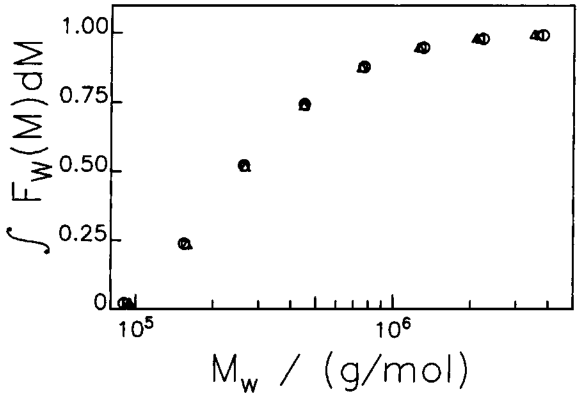

Figure 5 Comparison of three cumulative weight distributions, calculated using eqs. (6) and (9), with three different pairs of k_D and α_D.

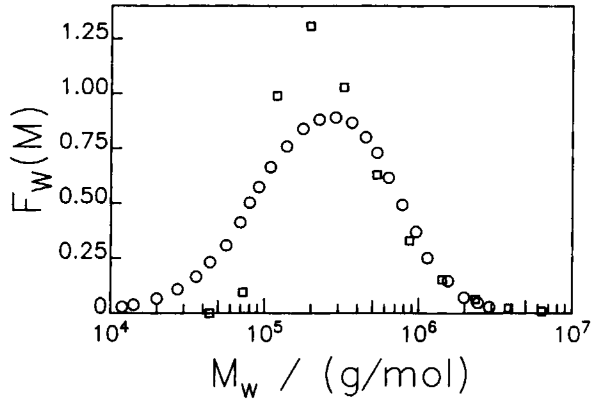

Figure 6 Comparison of two weight distributions $[F_w(M)]$ of polyethylene (A168). The squares were calculated from $G(D)$ by using eqs. (6) and (9), with $k_D = 5.25 \times 10^{-4}$ and $\alpha_D = 0.577$; the circles were obtained using SEC.

CONCLUSION

By accomplishing a calibration between molecular weight and the translational diffusion coefficient of polyethylene in trichlorobenzene at 135°C, and by using it successfully to transform the measured translational diffusion coefficient distribution to the molecular weight distribution, we have demonstrated that dynamic light scattering can be used, not only to characterize the weight average molecular weight of polyethylene in trichlorobenzene at 135°, but also to yield an estimate of molecular weight distribution, even though it is normally narrower than the distribution obtained by using size exclusion chromatography. It should be emphasized that the calibration is independent on our particular light scattering spectrometer, which means that the obtained k_D and α_D can be used in any other laser light scattering spectrometer, as long as the same solvent and temperature are used. As for a routine characterization of polyethylene, dynamic light scattering has an advantage over static light scattering because the measured translational diffusion coefficient depends much less on the polymer concentration, the scattering angle, and the instrument calibration. Therefore, it is possible to characterize polyethylene by using only one concentration at only

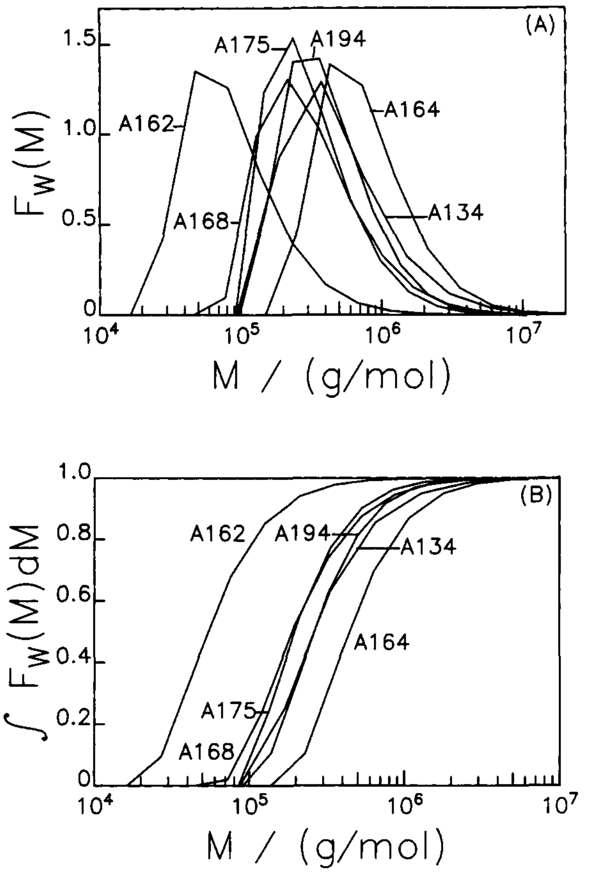

Figure 7 (A) Weight distributions of six polyethylene samples, calculated from $G(D)$s in Figure 3, using eqs. (6) and (9) with $k_D = 5.25 \times 10^{-4}$ and $\alpha_D = 0.575$, and (B) cumulative weight distributions of six polyethylene samples, calculated from $F_w(M)$s in Figure 7(A).

one scattering angle, for example, by using 5×10^{-4} g/mol at 20°, and then to extrapolate the measured translational diffusion coefficient to $C = 0$ and $\theta = 0$, by estimating the correction constants from the existing experimental results. The extrapolation error will be no more than a few percent.

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