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Light-scattering Characterization of the Molecular Weight Distributions of Some Intractable Polymers

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ABSTRACT

Recent developments of using laser light scattering (LLS) to characterize the molecular weight distribution f(M) of special polymers such as Kevlar, Tefzel, Teflon, branched epoxy clusters, gelatin, dextran, segment copolymers and polymer mixtures, are reviewed. The basic principle of combining static (classic) and dynamic LLS results is outlined. In dynamic LLS, the line-width (or the translational diffusion coefficient) distribution G(Γ) can be obtained from the precisely measured intensity–intensity time correlation function. The key problem is transforming G(Γ) to a corresponding molecular weight distribution f(M) is to establish a calibration between D (the translational diffusion coefficient) and M. Typical examples were used to illustrate different calibration methods, including the methods of using a series of narrowly distributed polymer standards with different molecular weights, using two or more broadly distributed polymer samples, and one broadly distributed polymer samples plus an additional experimental method (e.g. viscometry or size exclusion chromatography). The advantages and disadvantages of the LLS method are discussed by comparison with size exclusion chromatography. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

In contrast with small molecules, a typical polymer has a higher molecular weight of ~10^4 g/mol or larger and a wide distribution in its chain length. For a given type of polymer, its properties and even its appearance can be greatly influenced not only by its average molecular weight, but also by its molecular weight distribution, e.g. from a flexible rubber to a hard plastic. Therefore, the development and application of a polymer often require a precise characterization of its molecular weight distribution.

A number of methods including laser light scattering (LLS) are routinely used to characterize the average molecular weight and molecular weight distribution of a polymer. Among these methods, the end-group chemical analysis, vapor pressure osmometry, membrane osmometry, ultracentrifuge, static (classic) LLS and very recently developed matrix-assisted time-fly mass spectroscopy are absolute methods: they do not require calibration with a set of polymer samples with known molecular weights. The relative methods include viscometry, size exclusion (or gel permeation) chromatography (SEC or GPC), field flow fractionation (FFF) and dynamic LLS, which will be discussed in detail in this article.

For a polydisperse sample, its average molecular weight $\langle M\rangle$ can be generally defined as

$$\langle M\rangle=\frac{\int_0^\infty f_n(M)M^\beta\,dM}{\int_0^\infty f_n(M)M^{\beta-1}\,dM} \qquad (1)$$

where β can be an integer number, such as $\beta=1$ for the number-average molecular weight (M_n), $\beta=2$ for the weight-average molecular weight (M_w) and $\beta=3$ for intensity-average (or z-average) molecular weight (M_z) or even a non-integer number such as in viscometry, much depending on the method used to characterize the average molecular weight or molecular weight distribution of a given polymer sample. For example, M_n is measured in the end-group analysis and osmometry methods, M_w, ultracen-

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trifuge (concentration measurement) and static LLS; and M_z, in ultracentrifuge (concentration gradient measurement) and dynamic LLS. In practice, the ratio of M_w/M_n is normally introduced as the polydispersity index to characterize the distribution width of a given polymer sample.

Static light scattering as a classic and absolute method has been long and widely used to characterize both synthetic and natural macromolecules. In the last decade, owing to the advance of laser, fast electronics and personal computers, laser light scattering (LLS), especially dynamic LLS, has gradually changed from a very special tool in LLS laboratories to a routine analytical method in polymer laboratories or even to a daily quality-control device in production lines [1–3]. Nowadays, an LLS instrument is normally capable of doing both static and dynamic measurements simultaneously.

Laser Light Scattering (LLS)

When a monochromatic and coherent light is focused into a dilute macromolecule solution, if solvent molecules and macromolecules have different refractive indices, the incident light will be scattered by each illuminated macromolecule to all directions [4, 5]. The scattered light waves from different macromolecules mutually interfere, or combine, at a distant and fast photomultiplier tube detector to product a net scattering intensity $I(t)$ or photon counts $n(t)$. If all macromolecules are stationary, the scattered light intensity at each given direction would be a constant, i.e. independent of time. However, in reality, all macromolecules in solution are undergoing constant Brownian motion, which leads to fluctuation in $I(t)$. The fluctuation rate is directly related to the translational diffusion. The faster the diffusion, the faster the fluctuation will be.

In static LLS, the angular dependence of the excess absolute time-averaged scattered intenisty, known as the excess Rayleigh ratio, $R_{vv}(\theta)$, is normally measured:

$$R_{vv}(\theta)=(\langle I\rangle_{\text{solution}}-\langle I\rangle_{\text{solvent}})R_{vv,\,\text{standard}}(\theta)\ (n/n_{\text{standard}})^a$$

where $\langle I\rangle$ and n are the time-averaged scattering intensity and refractive index, respectively, and $1 \leqslant a \leqslant 2$ depending on the detection geometry. For a dilute polymer solution at a relatively low scattering angle θ, $R_{vv}(\theta)$ can be related to the weight-average molecular weight M_w, the second virial coefficient A_2 and the root mean square z-average radius of gyration $\langle R_g^2\rangle^{1/2}$ (or written as R_g) as [5, 6]

$$\frac{KC}{R_{vv}(\theta)} \approx \frac{1}{M_w}\left(1+\tfrac{1}{3}\langle R_g^2\rangle g^2\right)+2A_2C \qquad (2)$$

where $K=4\pi^2n^2(\mathrm{d}n/\mathrm{d}C)^2/(N_A\lambda_0^4)$ and $q=(4\pi n/\lambda_0)\sin(\theta/2)$ with N_A, $\mathrm{d}n/\mathrm{d}C$ and λ_0 being the Avogadro number, the specific refractive index increment, the solvent refractive index and the wavelength of the laser light in vacuum, respectively. After measuring $R_{vv}(\theta)$ at a set of C and θ we can determine Mw, Rg, and A_2 on the basis of eq. 1 from a Zimm plot which incorporates θ and C extrapolation on a single grid [6]. Figure 1 shows a typical Zimm plot for chitosan ($M_w=1.06\times10^5$ g/mol, $R_g=34.4$ nm and $A_2=6.0\times10^{-3}$ mol ml/g^2) in 0.2 M CH_2COOH/0.1 M CH_3COONa aqueous solution at 25°C [7].

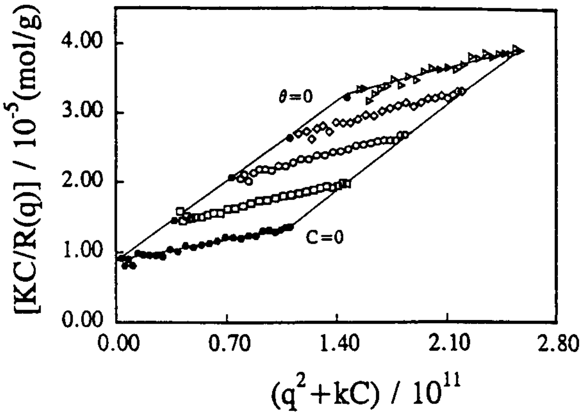

FIGURE 1. Typical Zimm plot for a chitosan sample ($M_w=1.06\times10^5$ g/mol, $R_g=34.4$ nm and $A_2=6.0\times10^{-3}$ mol ml/g^2) in 0.2 M CH_3COOH/0.1 M CH_3COONa aqueous solution at 25°C. (From [7] with permission.)

In dynamic light scattering the intensity fluctuation is measured. Dynamic light scattering can also be illustrated as follows. When the incident light is scattered by a moving macromolecule, the detected frequency of the scattered light will be slightly higher or lower than the original incident light frequency depending on whether the scatterer moves toward or away from the detector due to the Doppler effect, or in other words, the frequency of the scattered light is slightly broader than that of the incident light. This is exactly why dynamic light scattering is sometimes called quasi-elastic light scattering (QELS). It is very difficult, if not impossible, nowadays to detect this extremely small frequency broadening (~10^5–10^7 Hz in comparison with the incident light frequency ~10^{15} Hz) in the frequency domain, but it can be effectively recorded in the time domain through an intensity–intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode, so that dynamic light scattering is also known as photon correlation spectroscopy (PCS).

$G^{(2)}(t,q)$ can be related to the normalized first-order electric field time correlation function $|g^{(1)}(t,q)|$ as [4, 5]:

$$G^{(2)}(t,q)=\langle I(t,q)I(0,q)\rangle=A[1+\beta\,|g^{(1)}(t,q)|^2] \qquad (3)$$

where A is a measured base line; β, a parameter depending on the coherence of the detection optics; and t, the delay time. For a polydisperse sample, $|g^{(1)}(t,q)|$ is related to the line-width distribution $G(\Gamma)$ by [4]:

$$|g^{(1)}(t,q)|=\langle E(t,q)E^*(0,q)\rangle=\int_0^\infty G(\Gamma)\,e^{-\Gamma t}\,d\Gamma \qquad (4)$$

Figure 2 shows a typical normalized intensity–intensity time correlation function for chitosan ($M_w=1.06\times10^5$ g/mol and $\langle\Gamma\rangle=2.19$ ms) in 0.2 M CH_3COOH/0.1 M CH_3COONa aqueous solution at $T=25$°C and $\theta=45$°, where $C=4.96\times10^{-4}$ g/mol.

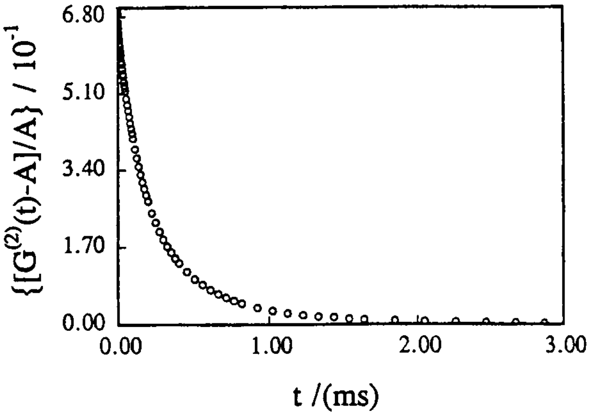

FIGURE 2. Typical normalized intensity–intensity time correlation function for chitosan (M_w=1.06×10^5 g/mol and $\langle\Gamma\rangle$=2.19 ms) in 0.2 M CH_3COOH/0.1 M CH_3COONa aqueous solution at T=25°C, θ=45° and C=4.96×10^{-4} g/mol.

Various Laplace inversion methods or programs were developed to calculate $G(\Gamma)$ or $\langle\Gamma\rangle$ ($=\int_0^\infty G(\Gamma)\Gamma\, d\Gamma$) from $G^{(2)}(t,q)$ or $|g^{(1)}(t,q)|$ [7–13]. However, owing to the bandwidth limitation for a photon correlation instrument, and unavoidable noises as well as a limited number of data points, the measured $|g^{(1)}(t)|$ is always less than that needed to describe $G(\Gamma)$ uniquely. The above Laplace inversion is a well-known ill-posed problem. Therefore, it is very important to reduce experimental noises in practice. Among all inversion methods, CONTIN [13] is one of the mostly used and accepted programs. For a diffusive relaxation, Γ usually depends on both C and q as [14]

$$\frac{\Gamma}{q^2}=D(1+k_dC)(1+f\langle R_g^2\rangle_z q^2) \qquad (5)$$

where D is the translational diffusion coefficient at $C\to0$, and $q\to0$; k_d, a diffusion second virial coefficient; and f, a dimensionless parameter whose value depends on polymer chain structure, polydispersity and solvent quality. The values of D, f and k_d can be calculated from $(\Gamma/q^2)_{C\to0,\,\theta\to0}$, $(\Gamma/q^2)_{C\to0}$ $v.$ q^2 and $(\Gamma/q^2)_{\theta\to0}$ $v.$ C, respectively. On the basis of eq. (5), $G(\Gamma)$ can be converted into a transitional diffusion coefficient distribution $G(D)$. Figure 3 shows a typical $G(D)$ for chitosan (M_w=1.06×10^5 g/mol and $\langle D\rangle$=5.92×10^{-8} cm^2/sec) in 0.2 M CH_3COOH/0.1 M CH_3COONa aqueous solution at T=25°C, $\theta\to0$ and $C\to0$.

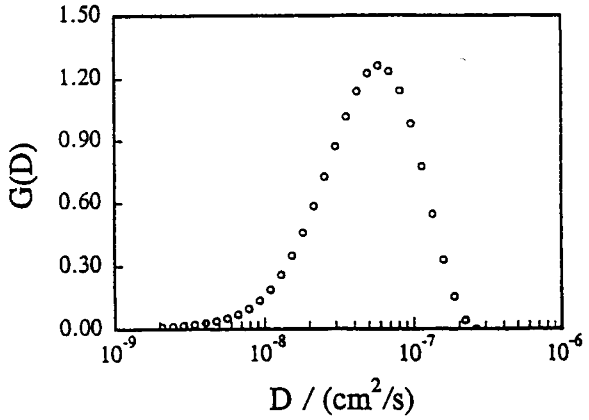

FIGURE 3. Typical translational diffusion coefficient $G(D)$ for chitosan (M_w=1.06×10^5 g/mol and $\langle D\rangle$=5.92×10^{-8} cm^2/sec) in 0.2 M CH_3COOH/0.1 M CH_3COONa aqueous solution at T=25°C°C, $\theta\to0$ and $C\to0$. (From [7] with permission.).

Transform $G(D)$ to a Molecular Weight Distribution

It is well known in polymer science that for the first-order approximation the translational diffusion coefficient D can be related to molecular weight M by [15]

$$D=k_DM^{-\alpha_D} \qquad (6)$$

where k_D and α_D are two scaling constants whose values depend mainly on polymer chain conformation and solvent quality. For a flexible polymer chain, $0.5<\alpha_D<0.6$ in a good solvent and $\alpha_D=0.5$ in a Flory Θ solvent; for a rigid rod-like chain, $\alpha_D=1$; and for a semi-rigid worm-like chain, $0.6<\alpha_D<1$. According to the definition, in dynamic LLS,

$$[g^{(1)}(t)]_{t\to0}=\langle E(t)E^*(0)\rangle_{t\to0}=\int_0^\infty G(\Gamma)\,d\Gamma\propto\langle I\rangle \qquad (7)$$

where $\langle I\rangle(=\langle I\rangle_{\text{solution}}-\langle I\rangle_{\text{solvent}})$ is the net average scattering intensity. On the other hand, in static LLS, when $C\to0$, and $q\to0$,

$$R_{vv}(q\to0)\propto\langle I\rangle\propto M_w\propto\int_0^\infty f_w(M)M\,dM \qquad (8)$$

where $f_w(M)$ is a differential weight distribution. A comparison of eqs (7) and (8) leads to

$$\int_0^\infty G(\Gamma)\,d\Gamma\propto\int_0^\infty f_w(M)M\,dM \qquad (9)$$

where $G(\Gamma)\propto G(D)$ and $d\Gamma\propto dD$ because $\Gamma=Dq^2$. Therefore, eq. (9) can be rewritten as

$$\int_0^\infty G(D)\frac{dD}{dM}\,dM\propto\int_0^\infty f_w(M)M\,dM \qquad (10)$$

On the basis of eq. (6), eq. (10) leads to

$$f_w(M)\propto\frac{G(D)}{M}\frac{dD}{dM}\propto G(D)D^{1+(2/\alpha_D)} \qquad (11)$$

where all proportional constants have been omitted because they are irrelevant to a given distribution. According to eqs (6) and (11), the values of k_D and α_D are needed to transform D to M and $G(D)$ to $f_w(M)$.

Calibration between D and M

Using a Set of Narrowly Distributed Standards. The most straightforward calibration method would be to measure both D and M of a set of monodisperse samples with different molecular weights. In a real experiment, the monodisperse samples have to be replaced by a set of narrowly

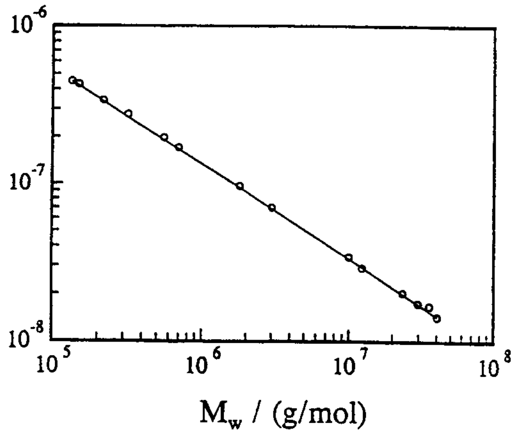

FIGURE 4. Typical plot of log(D) versus log(M) for polystyrene in toluene at 20°C [16]. The line represents a least-square fitting of $D\,(\mathrm{cm/sec}) = 3.64 \times 10^{-4}\,M^{-0.577}$. (From [16] with permission.)

distributed standards made either directly from special polymerization methods or indirectly from the fractionation of a broadly distributed sample. However, it should be noted that only a few kinds of polymers, e.g. polystyrene and poly(methyl methylacrylate), can be directly made with a narrow molecular weight distribution ($M_w/M_n \sim 1.1$). On the other hand, the fractionation is very time consuming, if not impossible. Thus, the application of this straightforward method is very limited in practice. Figure 4 shows a typical plot of log(D) versus log(M) for polystyrene in toluene at 20°C [16]. The line represents a least-square fitting of $D(\mathrm{cm^2/sec}) = 3.64 \times 10^{-4}\,M^{-0.577}$ which enables the molecular weight distribution of polystyrene to be obtained by using only dynamic LLS [17].

Using Two or More Broadly Distributed Samples

In reality, there are often two or more broadly distributed samples with different molecular weights. It has been shown that a combination of static and dynamic LLS can establish a calibration between D and M from two or more broadly distributed samples. The principle is outlined as follows. According to the definition of M_w and on the basis of eqs (6) and (11):

$$M^{\mathrm{DLS}}_{\mathrm{w,\,calcd}} = \frac{\int_0^\infty F_w(M) M\,\mathrm{d}M}{\int_0^\infty F_w(M)\,\mathrm{d}M} = \frac{k_D^{1/\alpha_D} \int_0^\infty G(D)\,\mathrm{d}D}{\int_0^\infty G(D) D^{1/\alpha_D}\,\mathrm{d}D} = \frac{k_D^{1/\alpha_D}}{\int_0^\infty G(D) D^{1/\alpha_D}\,\mathrm{d}D} \qquad (12)$$

where the normalization condition $\int_0^\infty G(D)\,\mathrm{d}D = 1$ has been used. On the basis of eq. (12), for two samples 1 and 2:

$$\frac{(M^{\mathrm{DLS}}_{\mathrm{w,\,calcd}})_1}{(M^{\mathrm{DLS}}_{\mathrm{w,\,calcd}})_2} = \left[\int_0^\infty G_2(D) D^{1/\alpha_D}\,\mathrm{d}D\right] \Bigg/ \left[\int_0^\infty G_1(D) D^{1/\alpha_D}\,\mathrm{d}D\right] \qquad (13)$$

For a given polymer sample, $M^{\mathrm{DLS}}_{\mathrm{w,\,calcd}}$ calculated on the basis of $G(D)$ from dynamic LLS should equal to $M_{\mathrm{w,\,measd}}$ measured directly from static LLS. It is expected that a proper choice of α_D should lead to a minimum difference between $[(M_{w,1})/(M_{w,2})]_{\mathrm{calcd}}$ and $(M_{w,1})/(M_{w,2})]_{\mathrm{measd}}$, which is actually done by iterating α_D in a computer program. In general, for N samples, an error function can be defined as

$$\mathrm{ERROR}(\alpha_D) = \sum_{i=1,\,j=1}^{N} \left[\frac{M_{\mathrm{w,\,measd},\,i}}{M_{\mathrm{w,\,measd},\,j}} - \frac{M_{\mathrm{w,\,calcd},\,i}}{M_{\mathrm{w,\,calcd},\,j}}\right]^2 \qquad (14)$$

After finding a proper value of α_D, k_D can be calculated on the basis of eq. (11) with another error function defined as

$$\mathrm{ERROR}(k_D) = \sum_{i=1}^{N} \left[\frac{M_{\mathrm{w,\,calcd},\,i} - M_{\mathrm{w,\,measd},\,i}}{M_{\mathrm{w,\,measd},\,i}}\right]^2 \qquad (15)$$

Figure 5 shows a typical plot of ERROR(k_D) obtained from a calculation where five chitosan samples with different weight-average molecular weights were used. It shows that for each α_D, there exists a well-defined minimum in ERROR(k_D), while for different α_D, there also exists an overall minimum which corresponds to $\alpha_D = 0.665 \pm 0.015$ and $k_D = (3.14 \pm 0.20) \times 10^{-4}$. With this pair of α_D and k_D, the characterization of the molecular weight distributions of a set of chitosan samples has been accomplished [7].

Combining Viscometry with Dynamic LLS

If only one broadly distributed sample is available, the calibration between D and M has to be determined in different ways. One of them is to estimate

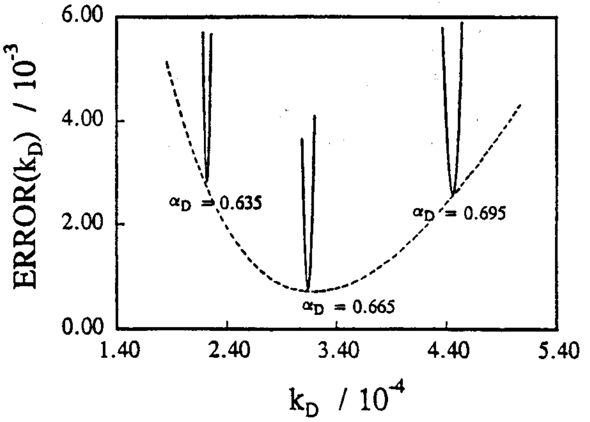

FIGURE 5. Typical plot of ERROR(k_D) obtained from a calculation using five chitosan samples with different weight-average molecular weights, where the overall minimum of ERROR(k_D) corresponds to $\alpha_D = 0.665 \pm 0.015$ and $k_D = (3.14 \pm 0.20) \times 10^{-4}$.

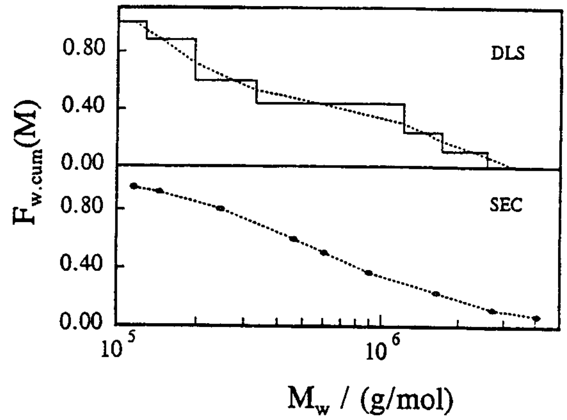

FIGURE 6. Typical cumulative weight distributions $F_{w,\,cum}(M)$ $[=\int_M^\infty f_w(M)\,dM]$ for a linear polyethylene measured in 1,2,4-trichlorobenzene at 135°C. The distribution from SEC is plotted for comparison. (From [20] with permission.)

α_D from the Mark–Houwink equation. It is known that the intrinsic viscosity $[\eta]$ can be scaled with M by the Mark–Houwink equation, i.e. $[\eta]=k_\eta M^{\alpha_\eta}$. As predicted by both Flory and de Gennes [15, 18], $\alpha_D=(\alpha_\eta+1)/3$. With an estimated α_D value, a combination of M_w from static LLS and $G(D)$ from dynamic LLS can lead to k_D on the basis of eq. (12). Chu and coworkers [19, 20] successfully applied this method to characterize the molecular weight distribution of linear polyethylene in 1,2,4-trichlorobenzene at 135°C from M_w and $G(D)$ respectively measured in static and dynamic LLS by estimating α_D from α_η $(=0.72)$ obtained in a previous intrinsic viscosity measurements [21]. Figure 6 shows a typical cumlative weight distribution $F_{w,cum}(M)$ $[=\int_M^\infty f_w(M)\,dM]$ of a linear polyethylene, which is obtained in 1,2,4-trichlorobenzene at 135°C, where the distribution from the high-temperature size exclusion chromatography (SEC) is plotted for comparison. The agreement between two cumulative weight distibutions are reasonable.

Combining SEC with Dynamic LLS

There is a similarity between dynamic light scattering and size exclusion chromatography (SEC or gel permeation chromatography, GPC), namely both the translational diffusion coefficient D obtained in dynamic LLS and the elution volume V measured in SEC are related to the hydrodynamic size, or the molecular weight, of a given macromolecular sample. For the first-order approximation,

$$V=A+B\log(M) \tag{16}$$

where A and B are two calibration constants similar to k_D and α_D It should be noted that the first-order approximation will simplify, but not affect, the following discussion: a combination of eqs (6) and (16) leads to

$$V=A+B\log(D) \tag{17}$$

where $A=A+B\log(k_D)/\alpha_D$ and $B=-B/\alpha_D$. Further, by taking the square of both sides of eq. (17):

$$V^2=A^2+2AB\log(D)+B^2\log^2(D) \tag{18}$$

After integrating both sides of eqs (17) and (18):

$$\langle V\rangle=A+B\langle\log(D)\rangle \tag{19}$$

and

$$\langle V^2\rangle=A^2+2AB\langle\log(D)\rangle+B^2\langle\log^2(D)\rangle \tag{20}$$

where

$$\left.\begin{aligned}\langle V\rangle&=\int_0^\infty VC(V)\,dV\\ \langle V^2\rangle&=\int_0^\infty V^2C(V)\,dV\end{aligned}\right\} \tag{21}$$

which can be calculated directly from $C(V)$, and

$$\left.\begin{aligned}\langle\log(D)\rangle&=\frac{\int_0^\infty \log(D)C(V)\,dV}{\int_0^\infty C(V)\,dV}\\ \langle\log^2(D)\rangle&=\frac{\int_0^\infty \log^2(D)C(V)\,dV}{\int_0^\infty C(V)\,dV}\end{aligned}\right\} \tag{22}$$

On the other hand, since $C(V)$ is a weight (or concentration) distribution:

$$\int_0^\infty C(V)\,dV\propto\int_0^\infty f_w(M)\,dM\propto\int_0^\infty f_w(M)M\,d[\log(M)] \tag{23}$$

Using $dV\propto d[\log(M)]\propto d[\log(D)]$ and eq. (11):

$$C(V)\propto f_w(M)M\propto G(D)D^{1+(1/\alpha_D)} \tag{24}$$

so that eq. (22) can be rewritten as

$$\left.\begin{aligned}\langle\log(D)\rangle&=\frac{\int_0^\infty \log(D)G(D)D^{1/\alpha_D}\,dV}{\int_0^\infty G(D)D^{1/\alpha_D}\,dV}\\ \langle\log^2(D)\rangle&=\frac{\int_0^\infty \log^2(D)G(D)D^{1/\alpha_D}\,dV}{\int_0^\infty G(D)D^{1/\alpha_D}\,dV}\end{aligned}\right\} \tag{25}$$

Using eq. (24), we can calculate M_w from $C(V)$ by

$$\begin{aligned}M_{w,\,calcd}^{SEC}&=\frac{\int_0^\infty F_w(M)M\,dM}{\int_0^\infty F_w(M)\,dM}\\ &=k_d^{1/\alpha_D}\int_0^\infty 10^{(A-V)/(\alpha_D B)}C(V)\,dV\end{aligned} \tag{26}$$

where $\int_0^\infty C(V)\,dV=1$ has been used. For a given polymer sample, $M_{w,\,calcd}^{SEC}$ should be equal to $M_{w,\,calcd}^{DLS}$, i.e. on the basis of eqs (12) and (26):

$$\left[\int_0^\infty 10^{(A-V)/(\alpha_D B)} C(V)\,\mathrm{d}V\right]\left[\int_0^\infty G(D) D^{1/\alpha_D}\,\mathrm{d}D\right]=1 \qquad (27)$$

This is only one unknown parameter, α_D, in eq. (25). For a chosen α_D, $\langle \log(D)\rangle$ and $\langle \log^2(D)\rangle$ can first be calculated using eq. (25); then A and B can be solved on the basis of eqs (19) and (20), and finally the left side of eq. (27) can be calculated. By iterating α_D, a proper value of α_D can be found which minimizes the difference between the left and right sides of eq. (27). With this α_D, k_D can be calculated from either eq. (12) or (26) by using M_w determined directly from static LLS and $C(V)$ from SEC or $G(D)$ from dynamic LLS. With A, B, k_D and α_D, A and B can be calculated. In this way, not only M with V, but also M with D can be calibrated in one single process with only one broadly distributed sample. This method has been tested and applied in the characterization of gelatin in water [22, 23].

APPLICATIONS

After establishing the calibration between D and M, $G(D)$ obtained in dynamic LLS can easily be transferred into a differential molecular weight distribution, such as $f_w(M)$, with the constraint of M_w measured in static LLS on the basis of eqs (6) and (12). The author has successfully applied the above methods for various kinds of polymeric and colloidal systems, such as for Kelvar [12, 24], fluoropolymers (Tefzel and Teflon) [25–32], polyethylene [36–37], Water-soluble polymers [7, 22, 38–41], copolymers [42–44], thermoplastics [45–48] and colloids [49–54]. Here, only two of those applications are described.

Segmented Copolymers

For a polydisperse copolymer sample with different molecular weight and chain compositon distribution, M_w determined in static LLS will be an apparent weight-average molecular weight, $M_{w,\mathrm{app}}$, which is defined as

$$M_{w,\mathrm{app}}=\int_0^\infty f_w(M)\,[\nu(M)/\nu]^2 M\,\mathrm{d}M \qquad (28)$$

where ν and $\nu(M)$ is the refractive index increment for the whole sample and for molecules with molecular weight M and weight distribution $f_w(M)$, respectively. Based on the assumption of the additivity of ν for a segmented copolymer of A and B,

$$\left.\begin{aligned}\nu(M)&=w_A(M)\nu_A+w_B(M)\nu_B\\ \nu&=w_A\nu_A+w_B\nu_B\end{aligned}\right\} \qquad (29)$$

where $w_A(M)$ and $w_B(M)$ $[=1-w_A(M)]$ are the weight fraction (chain composition) of A and B for a given polymer chain with fixed M and $f_w(M)$, respectively, and w_A and w_B are usually known parameters from polymerization. For a chosen solvent, ν, ν_A and ν_B are constants for a given copolymer at fixed experimental conditions. It should be noted that eq. (29) is not unique since different chain compositions can generate a polymer chain with identical M and $f_w(M)$. On the basis of eq. (11), we have

$$f_{w,\mathrm{app}}(M)=f_w(M)\,[\nu(M)/\nu]^2 \propto \frac{G(D)}{\mathrm{M}}\frac{\mathrm{d}D}{\mathrm{d}M} \propto G(D)D^{1+(2/\alpha_D)} \qquad (30)$$

For a given set of k_D and α_D, $G(D)$ can be converted into $f_{w,\mathrm{app}}(M)$ on the basis of eqs (6) and (30). If repeating the above procedure by using two different solvents (denoted as s1 and s2) with different $\nu(M)$ and ν, even for a given copolymer sample, there will be two different apparent weight distributions, $f_{w,\mathrm{app,s1}}(M)$ and $f_{w,\mathrm{app,s2}}(M)$. Therefore,

$$\frac{f_{w,\mathrm{app,s1}}(M)}{f_{w,\mathrm{app,s2}}(M)}=\left[\frac{\nu_{s2}}{\nu_{s1}}\frac{w_A(M)\nu_{A,s1}+[1-w_A(M)]\nu_{B,s1}}{w_A(M)\nu_{A,s2}+[1-w_A(M)]\nu_{B,s2}}\right]^2 \qquad (31)$$

where ν_{s1}, ν_{s2}, $\nu_{A,s1}$, $\nu_{A,s2}$, $\nu_{B,s1}$ and $\nu_{B,s2}$ can be determined by using a differential refractometer. Equation (31) shows that $w_A(M)$, the chain composition distribution, can be calculated from two apparent weight distributions if the values of ν_{s1}, ν_{s2}, $\nu_{A,s1}$, $\nu_{A,s2}$, $\nu_{B,s1}$ and $\nu_{B,s2}$ are known. After obtaining $w_A(M)$, first $\nu(M)$, then $f_w(M)$, and finally M_w can be calculated [43].

Polymer Mixtures

If a polymer mixture is made of individual linear chains and clusters, the measurement of static LLS will lead to an apparent weight-average molecular weight $M_{w,\mathrm{app}}$ and

$$M_{w,\mathrm{app}}=M_{w,L}x_L+M_{w,H}x_H \qquad (32)$$

where the subscripts "L" and "H" denote low molecular weight linear polymer chains and high molecular weight clusters, respectively; x_L and x_H are the weight fractions; and $x_L+x_H=1$. On the other hand, if linear chains and clusters are significanly different in the hydrodynamic size, dynamic LLS will detect two distinct distribution peaks in the measured line-width distribution $G(\Gamma)$. One peak corresponds to individual linear chain; and the other, clusters. The area ratio of these two peaks is

$$A_r=\frac{A_L}{A_H}=\frac{\int_0^\gamma G_L(\Gamma)\,\mathrm{d}\Gamma}{\int_\gamma^\infty G_H(\Gamma)\,\mathrm{d}\Gamma}=\frac{M_{w,L}\,x_L}{M_{w,H}\,x_H} \qquad (33)$$

where γ is the cutoff line width between $G_L(\Gamma)$ and $G_H(\Gamma)$. On the basis of eqs (32) and (33), a combination of $M_{w,\mathrm{app}}$ from static LLS and A_r from dynamic LLS will lead to $M_{w,L}x_L$ and $M_{w,H}x_H$. In principle, by knowing any one of the four parameters ($M_{w,L}$, $M_{w,H}$, x_L and x_H), the remaining three parameters can be determined. This method has been thoroughly tested by using the mixtures of polystyrene standards [48]. As for a particular polymer mixture, there should be a way to determine one of the four parameters independently. For example, in the study of polymer association, the $M_{w,L}$ of starting individual polymer chains can be determined; and in the study of gelation process, a filtration method can be used to remove large microgels, so that the weight fractions of x_L and x_H can be subsequently determined.

CONCLUSION

It has been shown that a combination of static and dynamic laser light scattering (LLS) can become a very powerful method for polymer characterization if it is properly used. LLS enjoys a number of intrinsic advantages over other polymer characterization methods, such as those based on sedimentation and chromatography, including speed, non-perturbation and extreme dissolution conditions (high temperature or strong acid). The most important is that the calibration is independent of the LLS instrument used. However, the LLS method described here has an intrinsic disadvantage, namely, its resoluton is not as good as other methods based on fractination principle, especially for samples with several closely packed distribution peaks. Therefore, we have to be very careful when LLS is applied to these samples. The LLS method should be used as a complementary method for those intractable polymers where conventional methods fail. In principle, dynamic LLS can be combined with other polymer characterization methods as long as they are based on the difference in the hydrodynamic volume.

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