Spectral Distribution of Light Scattered from Polydisperse Gaussian Coils

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ABSTRACT: Calculations of the Rayleigh spectra from translational motions of flexible-coil polymers in dilute solution assuming each of four distribution functions to describe the polydispersity effects are reported. The Schulz, Tung, and two-exponent functions predict values of $\bar{M}_c$, the average molecular weight from line broadening, essentially equal to $\bar{M}_z$ for values of $\bar{M}_w/\bar{M}_n$ up to 15 and values of the scattering parameter $x \leq 0.2$. The log-normal function produces the same results for low degrees of polydispersity but is totally unsatisfactory at high values of $\bar{M}_w/\bar{M}_n$. The $\bar{M}_c$ for NBS-706 polystyrene ($\bar{M}_w/\bar{M}_n = 2.1$) in butanone solution calculated from all four distribution functions agrees very well with the reported $\bar{M}_z$. Values of $\bar{M}_c$ for three broad polystyrenes prepared by physically blending existing samples qualitatively agreed with the values of $\bar{M}_z$ measured by GPC. Calculation of $\bar{M}_w$ from line-broadening measurements was found to be dependent on the shape of the distribution function, particularly at higher degrees of polydispersity.

The measurement of the spectral distribution of light which is quasielastically scattered from macromolecules in dilute solution is well established as a useful technique for obtaining polymeric diffusion coefficients. Pecora[1] has shown that the Rayleigh spectrum resulting from a dilute solution of monodisperse, optically isotropic, flexible-coil macromolecules is Lorentzian shaped with a half-width at half maximum height given by

$$\Delta\omega_{1/2} = \kappa^2 D \tag{1}$$

where $\kappa = (4\pi n/\lambda_0) \sin(\theta/2)$, n is the refractive index of the solution, λ_0 is the wavelength of the incident light, θ is the scattering angle, and D is the polymeric diffusion coefficient.

Although most work in this field has been with polymers whose molecular weight distributions are relatively narrow and whose results can be analyzed directly with eq 1, a few investigators have explored the effects of polydispersity in molecular weight on the resulting Rayleigh spectra.[2-5] Pecora and Tagami[2] calculated the effects of polydispersity in molecular weight on the spectral distribution arising solely from translational motions of flexible-coil and rigid-rod macromolecules. Frederick and coworkers,[3,4] using dilute solutions of NBS-706 polystyrene ($\bar{M}_w/\bar{M}_n = 2.1$) in cyclohexane and in butanone, have provided experimental evidence supporting the theoretical predictions of Pecora and Tagami.

In the present work, the effect of polydispersity on the Rayleigh spectra is calculated for flexible-coil polymers whose molecular weight distributions are broader than those considered previously. Besides the Schulz distribution function[6] used by Pecora and Tagami, the Tung,[7] log-normal,[8] and two-exponent[9] distributions are also included. The last three functions have been shown to successfully describe polydispersity effects of polymers with very broad molecular weight distributions. In Figure 1 is shown a comparison of the four distribution functions normalized to $\bar{M}_w$ for the cases $\bar{M}_w/\bar{M}_n = 2$ and 10. In all calculations, the polymers are considered to be optically isotropic and in dilute solution, and only the effects arising from translational motions are examined.

Theory

The Schulz distribution function given in eq 2 has been widely used to describe the polydispersity effects observed in fractionation and polymerization data for many vinyl and condensation polymers.

$$f(M) = (1/z!)[(z+1)/\bar{M}_w]^{z+1}M^z \exp[-(z+1)M/\bar{M}_w] \tag{2}$$

Here, $\bar{M}_w$ is the weight-average molecular weight, and z is an adjustable parameter whose value governs the breadth of the distribution; varying z from ∞ to 0 changes the distribution from monodisperse to infinitely broad. Some characteristics of this function are compared in Table I with those from the other three distributions used to describe the polydispersity.

The Rayleigh spectrum calculated for a polymer with a Schulz distribution of molecular weights has been shown to be[2]

$$S_{0z} = (z+1)^{z+1}(x_w z!\zeta^{z+1})^{-1} \int_0^\infty [\mathrm{erf}(1/2)\sqrt{x_w s/\zeta}]^2 s^z \times \{(\kappa^2 D_w s^{-\alpha}\zeta^\alpha)/[\omega^2 + (\kappa^2 D_w s^{-\alpha}\zeta^\alpha)^2]\} e^{-s}\mathrm{d}s \tag{3}$$

where ω is the angular frequency, and the other parameters are given by the equations below (the subscript w in eq 3 refers to a monodisperse polymer with molecular weight equal to $\bar{M}_w$ of the polydisperse sample)

$$x = \kappa^2 nl^2/6 \tag{4}$$

$$\zeta = z + 1 + x/6 \tag{5}$$

$$D = CM^{-\alpha} \tag{6}$$

The quantity $nl^2/6$ in eq 4 in many cases can be replaced by the mean-square radius of gyration, $\langle S^2 \rangle$. Equation 6 is an empirical relation between D and M in which the constants, C and α, apply to a particular polymer–solvent combination at the temperature of measurement; α for flexible-coil macromolecules varies between 0.5 in a theta solvent to approximately 0.7.

Values for S_{0z} as a function of the variables (x, α, z) were calculated numerically using a 24-point Gaussian-Laguerre quadrature formula[10] and a Honeywell 635 computer. Typ-

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(1) R. Pecora, *J. Chem. Phys.*, **40**, 1604 (1964).
(2) R. Pecora and Y. Tagami, *ibid.*, **51**, 3298 (1969).
(3) J. E. Frederick, T. F. Reed, and O. Kramer, *Macromolecules*, **4**, 242 (1971).
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(5) W. Lee, Ph.D. Thesis, University of Massachusetts, 1970.
(6) G. V. Schulz, *Z. Phys. Chem.*, **43**, 25 (1935).
(7) L. H. Tung, *J. Polym. Sci.*, **20**, 495 (1956).
(8) W. D. Lansing and E. O. Kraemer, *J. Amer. Chem. Soc.*, **57**, 1369 (1935).
(9) F. W. Billmeyer, Jr., and W. H. Stockmayer, *J. Polym. Sci.*, **5**, 121 (1950).
(10) A. H. Stroud and D. Secrest, "Gaussian Quadrature Formulas," Prentice-Hall, Englewood Cliffs, N. J., 1966.

Table I
Characteristics of Distribution Functions

	Schulz	Tung	Log normal	Two exponent
$\bar{M}_w/\bar{M}_n$	$(z+1)/z$	$(\pi/t)/\sin(\pi/t)$	$\mathrm{Exp}(\beta^2/2)$	$(2\gamma)/(\gamma+1)^2$
$\bar{M}_z/\bar{M}_w$	$(z+2)/(z+1)$	$\dfrac{\Gamma[1+(2/t)]}{\{\Gamma[1+(1/t)]\}^2}$	$\mathrm{Exp}(\beta^2/2)$	$3(\gamma^2+1)/(\gamma+1)^2$
$\bar{M}_w/\bar{M}_n$ Value	$\bar{M}_z/\bar{M}_w$ Value			
1.1	1.09	1.07	1.1	
1.3	1.25	1.19	1.3	
2	1.50	1.38	2	1.50
3	1.67	1.54	3	2.00
5	1.80	1.69	5	2.40
10	1.90	1.83	10	2.70
15	1.93	1.88	15	2.80

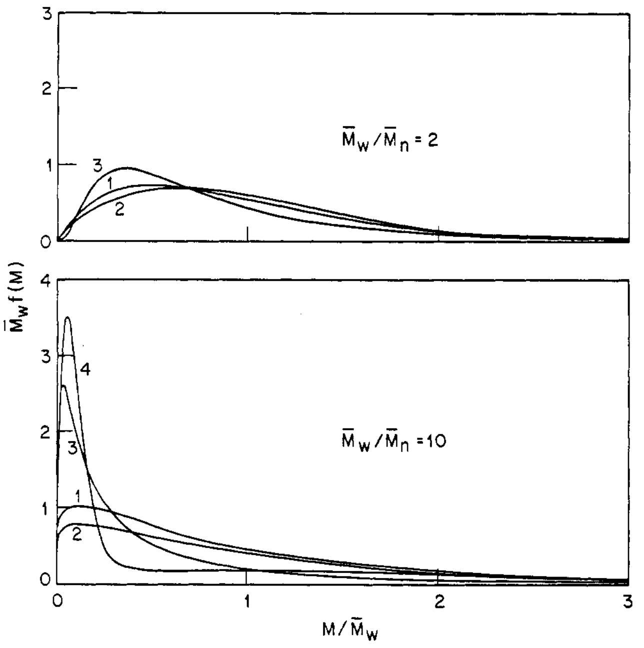

Figure 1. Analytical distribution function normalized to $\bar{M}_w$ of each distribution. Schulz = 1, Tung = 2, log normal = 3, two exponent = 4.

ical values were assumed for the other parameters, and the half-widths of the resulting (S_{0z}, ω) curves were obtained by numerical interpolation. Calculations of S_{0z} for selected values of (x, α, z) using a 32-point Gaussian–Laguerre quadrature formula yielded the same results to at least three significant figures. Several (S_{0z}, ω) spectra representing the entire range of (x, α, z) were found not to deviate appreciably from Lorentzian distributions of the same half-width. This same observation has been reported previously[3] for calculations using the Schulz distribution with $z \leq 0.5$, *i.e.*, for the narrower distributions considered here.

The half-width of each (S_{0z}, ω) spectrum was used to calculate a single diffusion coefficient, D_c, from eq 1 for all values of (x, α, z). The use of eq 1 assumes that the spectra are lorentzian, which is a reasonable approximation for the present calculations. The value of D_c is a weighted average of all of the diffusion coefficients of the individual molecules present in the polydisperse system. Each molecular weight species contributes to the composite spectrum a lorentzian line shape whose half-width is proportional to $M^{-\alpha}$; this can be shown for a monodisperse polymer by combining eq 1 and 6. In addition, the individual lorentzians are weighted by an intensity factor which depends on the scattering power of the corresponding molecular species. The result, eq 3, is a spectrum whose half-width is characteristic of a molecular weight greater than the $\bar{M}_w$ of the distribution. The ratios D_c/D_w were calculated for all of the (S_{0z}, ω) spectra and are given in Table II. Each of these ratios represents the predicted apparent reduction in spectral half-width due to polydispersity from that calculated on the basis of $\bar{M}_w$ of the polymer sample.

Another quantity that was calculated from the (S_{0z}, ω) spectra was the ratio $\bar{M}_z/\bar{M}_c$. Here, $\bar{M}_z$ is the third moment of the distribution function and is the average normally measured by sedimentation equilibrium, and $\bar{M}_c$ is the average molecular weight calculated from D_c using eq 6. The values for $\bar{M}_z/\bar{M}_c$ for the Schulz distribution are shown in Table III. It is worth noting that for Θ conditions in a polymer solution ($\alpha = 0.5$), the value of $\bar{M}_c$ is calculated to be within 3% of $\bar{M}_z$ for all values of z and for values of $x \leq 0.2$ which includes many polymers of practical interest. The effect of increasing solvent power (increasing values of α) is to increase the value of $\bar{M}_c$ above that calculated for Θ conditions.

The second distribution function used to describe the polydispersity of molecular weight is that due to Tung.[7] This is an empirical function that has been used to analyze polymer fractionation data and is given below

$$f(M) = (GtM^{t-1}/\bar{M}_w{}^t)\exp[-G(M/\bar{M}_w)^t] \tag{7}$$

where $G = [\Gamma(1 + 1/t)],^t$ Γ denotes the gamma function, and t is the parameter used to vary the width of the distribution. As t varies from ∞ to 0, the distribution changes from monodisperse to infinitely broad. The Rayleigh spectrum predicted for a Tung distribution of molecular weights is given by eq 8.

$$S_{0t} = (tG/x_w)\int_0^\infty u^{t-1}\exp(-Gu^t - x_w u/6) \times [\mathrm{erf}(\sqrt{x_w u}/2)]^2\{\kappa^2 D_w u^{-\alpha}/[\omega^2 + (\kappa^2 D_w u^{-\alpha})^2]\}\,\mathrm{d}u \tag{8}$$

Values of S_{0t} as functions of (x, α, t) and the half-widths of the resulting (S_{0t}, ω) spectra were calculated numerically using the 24-point Gaussian–Laguerre quadrature formula described previously for the Schulz distribution. In checking the results with a 32-point formula, however, it was found that the desired agreement could only be obtained for calculations where $\bar{M}_w/\bar{M}_n > 1.1$. To calculate values of S_{0t} for $\bar{M}_w/\bar{M}_n = 1.1$, it was necessary to change the integration variable in eq 8 and solve the result using a 32-point Gaussian–Hermite quadrature formula;[10] the half-widths obtained from

TABLE II
D_c/D_w FOR SCHULZ AND TUNG[a] DISTRIBUTIONS

		D_c/D_w for distributions whose $\bar{M}_w/\bar{M}_n$ =						
x	α	15	10	5	3	2	1.33	1.1
0.01	0.5	0.71	0.73	0.74	0.78	0.81	0.89	0.95
	0.6	0.65	0.65	0.67	0.71	0.76	0.86	0.95
	0.75	0.55	0.56	0.59	0.62	0.69	0.81	0.92
0.1	0.5	0.72	0.72	0.75	0.77	0.83	0.89	0.95
	0.6	0.65	0.66	0.69	0.73	0.78	0.88	0.95
	0.75	0.56	0.58	0.59	0.64	0.69	0.83	0.93
0.2	0.5	0.72	0.74	0.75	0.79	0.83	0.89	0.96
	0.6	0.68	0.68	0.69	0.72	0.77	0.88	0.95
	0.75	0.58	0.57	0.61	0.65	0.71	0.83	0.93
0.3	0.5	0.75	0.75	0.76	0.79	0.83	0.91	0.96
	0.6	0.67	0.69	0.71	0.74	0.79	0.88	0.95
	0.75	0.59	0.59	0.63	0.65	0.71	0.82	0.92
0.5	0.5	0.76	0.77	0.79	0.81	0.85	0.91	0.96
	0.6	0.71	0.71	0.72	0.75	0.79	0.87	0.95
	0.75	0.61	0.61	0.64	0.68	0.72	0.84	0.92
0.7	0.5	0.78	0.79	0.81	0.82	0.85	0.92	0.97
	0.6	0.73	0.73	0.75	0.78	0.81	0.89	0.95
	0.75	0.62	0.64	0.66	0.69	0.75	0.85	0.94
1.0	0.5	0.81	0.81	0.82	0.85	0.87	0.92	0.98
	0.6	0.75	0.75	0.78	0.79	0.82	0.91	0.96
	0.75	0.66	0.68	0.69	0.73	0.78	0.86	0.95

[a] See text.

TABLE III
$\bar{M}_z/\bar{M}_c$ FOR SCHULZ, TUNG,[a] AND TWO-EXPONENT[a] DISTRIBUTIONS

		$\bar{M}_z/\bar{M}_c$ for distributions whose $\bar{M}_w/\bar{M}_n$ =						
x	α	15	10	5	3	2	1.33	1.1
0.01	0.5	0.98	1.00	0.98	1.00	0.99	0.98	0.98
	0.6	0.94	0.93	0.93	0.95	0.95	0.98	1.00
	0.75	0.87	0.88	0.89	0.89	0.91	0.94	0.98
0.1	0.5	1.02	1.00	1.01	1.00	1.02	0.98	0.98
	0.6	0.94	0.96	0.96	0.98	0.98	1.00	1.00
	0.75	0.90	0.91	0.90	0.91	0.92	0.97	0.98
0.2	0.5	1.02	1.03	1.01	1.03	1.02	1.01	1.01
	0.6	1.00	0.99	0.98	0.98	0.98	1.00	1.00
	0.75	0.92	0.91	0.94	0.94	0.94	0.97	0.98
0.3	0.5	1.09	1.07	1.05	1.03	1.02	1.04	1.01
	0.6	1.00	1.02	1.02	1.00	1.01	1.00	1.00
	0.75	0.95	0.93	0.96	0.94	0.95	0.97	0.98
0.5	0.5	1.12	1.14	1.12	1.10	1.08	1.04	1.01
	0.6	1.08	1.08	1.05	1.03	1.02	1.00	1.00
	0.75	1.01	0.99	0.99	0.99	0.98	0.99	0.98
0.7	0.5	1.16	1.18	1.17	1.13	1.08	1.07	1.04
	0.6	1.13	1.11	1.11	1.09	1.06	1.02	1.00
	0.75	1.03	1.04	1.04	1.01	1.02	1.01	1.00
1.0	0.5	1.28	1.25	1.23	1.20	1.15	1.07	1.04
	0.6	1.20	1.18	1.18	1.13	1.09	1.06	1.02
	0.75	1.12	1.13	1.09	1.09	1.07	1.03	1.02

[a] See text.

numerical interpolation of these (S_{0t}, ω) spectra agreed to at least three significant figures with those calculated from a 40-point Gaussian–Hermite formula.

The values of D_c/D_w and $\bar{M}_z/\bar{M}_c$ for the Tung distribution of molecular weights were calculated from the half-widths of the (S_{0t}, ω) spectra as previously described. Both of these ratios were found to be typically within 0.02 of the corresponding values derived from the Schulz distribution; *e.g.*, a maximum difference between the results from the two distributions of 0.06 was observed for only three calculations of D_c/D_w and only twice for $\bar{M}_z/\bar{M}_c$. It was therefore concluded that the data given in Tables II and III also apply to values of D_c/D_w and $\bar{M}_z/\bar{M}_c$, respectively, for a Tung distribution of molecular weights. This result was anticipated; since, as shown in Figure 1, the two functions are similar over a wide range of molecular weight distribution. The interchangeability of these two functions is also reported by Green,[11] who showed that, within experimental error, the two distributions give comparable results when used to evaluate fractionation data.

The third function used to describe the molecular weight polydispersity was the log-normal distribution given by eq 9.

$$f(M) = (\sqrt{\pi}\beta M)^{-1} \exp[-\beta^{-2}\{\ln (M/\bar{M}_w) + \beta^2/4\}^2] \quad (9)$$

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(11) J. H. S. Green, *Chem. Ind.* (*London*), 924 (1959).

TABLE IV
D_c/D_w FOR LOG-NORMAL DISTRIBUTION

		D_c/D_w for distributions whose $\bar{M}_w/\bar{M}_n$ =						
x	α	15	10	5	3	2	1.33	1.1
0.01	0.5	0.29	0.34	0.46	0.59	0.71	0.88	0.95
	0.6	0.20	0.24	0.36	0.49	0.64	0.82	0.94
	0.75	0.10	0.14	0.23	0.36	0.53	0.76	0.91
0.1	0.5	0.41	0.44	0.53	0.63	0.72	0.88	0.95
	0.6	0.31	0.34	0.42	0.52	0.65	0.84	0.95
	0.75	0.19	0.22	0.30	0.41	0.55	0.78	0.92
0.2	0.5	0.47	0.51	0.58	0.65	0.75	0.87	0.95
	0.6	0.37	0.41	0.47	0.56	0.67	0.85	0.95
	0.75	0.26	0.28	0.35	0.45	0.58	0.77	0.93
0.3	0.5	0.52	0.55	0.61	0.67	0.76	0.87	0.95
	0.6	0.42	0.45	0.51	0.59	0.69	0.85	0.95
	0.75	0.31	0.33	0.39	0.47	0.59	0.79	0.93
0.5	0.5	0.61	0.63	0.68	0.72	0.79	0.89	0.96
	0.6	0.51	0.52	0.59	0.65	0.72	0.86	0.95
	0.75	0.38	0.41	0.46	0.52	0.62	0.81	0.92
0.7	0.5	0.67	0.67	0.73	0.76	0.83	0.91	0.96
	0.6	0.57	0.59	0.64	0.69	0.76	0.88	0.95
	0.75	0.45	0.46	0.51	0.57	0.66	0.83	0.92
1.0	0.5	0.75	0.75	0.77	0.81	0.85	0.93	0.98
	0.6	0.66	0.67	0.71	0.75	0.79	0.89	0.95
	0.75	0.52	0.55	0.59	0.64	0.71	0.85	0.94

TABLE V
$\bar{M}_z/\bar{M}_c$ FOR LOG-NORMAL DISTRIBUTION

		$\bar{M}_z/\bar{M}_c$ for distributions whose $\bar{M}_w/\bar{M}_n$ =						
x	α	15	10	5	3	2	1.33	1.1
0.01	0.5	1.29	1.14	1.07	1.04	1.02	1.02	0.99
	0.6	1.00	0.95	0.92	0.91	0.94	0.97	0.99
	0.75	0.73	0.69	0.70	0.78	0.85	0.93	0.97
0.1	0.5	2.55	1.91	1.38	1.17	1.05	1.02	0.99
	0.6	2.16	1.64	1.20	1.02	0.98	0.99	1.01
	0.75	1.68	1.32	0.99	0.90	0.90	0.95	0.99
0.2	0.5	3.38	2.56	1.65	1.27	1.13	1.02	0.99
	0.6	2.93	2.23	1.45	1.15	1.04	1.02	1.01
	0.75	2.44	1.84	1.23	1.03	0.96	0.95	0.99
0.3	0.5	4.13	3.03	1.88	1.37	1.16	1.02	0.99
	0.6	3.60	2.64	1.64	1.26	1.09	1.02	1.01
	0.75	3.10	2.23	1.41	1.11	0.98	0.97	0.99
0.5	0.5	5.63	3.91	2.28	1.58	1.24	1.05	1.02
	0.6	4.92	3.42	2.06	1.46	1.17	1.04	1.01
	0.75	4.15	3.01	1.79	1.27	1.07	1.01	0.99
0.7	0.5	6.83	4.56	2.63	1.74	1.36	1.11	1.02
	0.6	5.96	4.12	2.36	1.61	1.27	1.07	1.01
	0.75	5.17	3.58	2.05	1.43	1.16	1.03	0.99
1.0	0.5	8.44	5.62	3.00	1.98	1.45	1.14	1.05
	0.6	7.55	5.19	2.84	1.86	1.36	1.09	1.01
	0.75	6.35	4.51	2.46	1.65	1.27	1.07	1.01

Lansing and Kraemer[8] first proposed its use as an analytical expression for polydispersity effects; Wesslau[12] showed that fractionation data of very broad polyethylenes were well represented by this distribution function. As the polydispersity parameter, β, changes from 0 to ∞, the distribution is transformed from monodisperse to infinitely broad.

The Rayleigh spectrum predicted for a polydisperse polymer with a log-normal distribution of molecular weights is given by

$$S_{0\beta} = (\sqrt{\pi}\beta x_w)^{-1} \int_0^{+\infty} u^{-1} \exp[-\beta^{-2}(\ln u + \beta^2/4)^2 - x_w u/6][\operatorname{erf}\sqrt{x_w u/2})]^2 \times \{\kappa^2 D_w u^{-\alpha}/[\omega^2 + (\kappa^2 D_w u^{-\alpha})^2]\}\, \mathrm{d}u \quad (10)$$

In order to evaluate $S_{0\beta}$ as a function of (x, α, β), it was necessary to change integration variables in eq 10 and use a 24-point Gaussian–Hermite quadrature formula. The numerically interpolated half-widths of the ($S_{0\beta}$, ω) spectra calculated on a Honeywell 635 computer agreed to at least three significant figures with values for comparable spectra calculated with a 32-point Gaussian–Hermite formula.

Values of D_c/D_w and $\bar{M}_z/\bar{M}_c$ obtained from the ($S_{0\beta}$, ω) spectra by methods described previously for the other distributions are given in Tables IV and V, respectively. Contrasting these results with those obtained from the Schulz distribution in Tables II and III, we see that increasing polydispersity (*i.e.*, higher $\bar{M}_w/\bar{M}_n$), increasing molecular weight (higher x), and increasing solvent power (higher α) have more pronounced effects on the values of D_c/D_w and $\bar{M}_z/\bar{M}_c$ for

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(12) H. Wesslau, *Makromol. Chem.*, **20**, 111 (1956).

the log-normal distribution of molecular weights. It should also be noted, however, that for $\bar{M}_w/\bar{M}_n \leq 2$ and $x \leq 0.1$ which includes many polymers of practical interest, the log-normal (like the Schulz) distribution predicts that the molecular weight obtained from line-broadening measurements is approximately $\bar{M}_z$ of the distribution.

The last distribution function used to describe the polydispersity is an empirical one containing a weighted sum of two exponentials that was employed by Billmeyer and Stockmayer[9] to evaluate broad poly(methyl methacrylate) samples. This function, given in eq 11, is defined only for distributions having $\bar{M}_w/\bar{M}_n \geq 2$, at which point it and the Schulz distribution are identical.

$$f(M) = [(\gamma + 1)/\gamma]^2[M/2\bar{M}_w^2]\{\exp[-M(\gamma + 1)/(\bar{M}_w\gamma)] + \gamma^2 \exp[-M(\gamma + 1)/\bar{M}_w]\} \quad (11)$$

The distribution changes from most probable ($\bar{M}_w/\bar{M}_n = 2$) to infinitely broad as the polydispersity parameter, γ, changes from 1.0 to ∞.

The predicted spectral distribution of a polymer with a two-exponent distribution of molecular weights is given by

$$S_{0\gamma} = (2x_w)^{-1}[(\gamma + 1)/\gamma]^2 \int_0^\infty u[\exp(-u/\gamma) + \gamma^2 \exp(-u\gamma)] \exp(-x_w u/6)[\mathrm{erf}(\sqrt{x_w u}/2)]^2 \times [\kappa^2 D_w u^{-\alpha}/[\omega^2 + (\kappa^2 D_w u^{-\alpha})^2]\} e^{-u} \mathrm{d}u \quad (12)$$

Values for $S_{0\gamma}(x, \alpha, \gamma)$ were calculated numerically with a 24-point Gaussian–Laguerre quadrature formula. No problems were experienced in these calculations as judged by the ability to duplicate the numerically interpolated half-widths to at least three significant figures using a 32-point formula.

Values of D_c/D_w derived from the $S_{0\gamma}$ half-widths are presented in Table VI. These are seen to lie between results from the Schulz and log-normal distributions. The $\bar{M}_z/\bar{M}_c$ ratios, however, were found to be very close to those calculated from the Schulz distribution function. Corresponding values calculated from the two distribution functions are typically within 0.02; the maximum difference between them is 0.05 for $x \leq 0.5$ and 0.10 for $0.5 < x \leq 1.0$. The results from calculations of $\bar{M}_z/\bar{M}_c$ using the Schulz distribution function were therefore considered equivalent to those from the two-exponent distribution calculations, particularly for $x \leq 0.5$.

The calculated values of D_c/D_w and $\bar{M}_z/\bar{M}_c$ given in Tables II–VI represent predictions from distributions of light spectra and apply exactly to experimental spectra measured by a heterodyning spectrometer. If a homodyning spectrometer is used to measure the experimental spectra, the half-widths from which D_c and $\bar{M}_c$ are calculated are those of the self-convolutions of the light spectra S_{0z}, S_{0t}, $S_{0\beta}$, and $S_{0\gamma}$. It has been shown, however, using the Schulz distribution function that this convolution correction is small for the polymers evaluated in the present work;[13] therefore, in the discussion that follows the values of D_c/D_w and $\bar{M}_z/\bar{M}_c$ are taken directly from the appropriate tables.

TABLE VI
D_c/D_w FOR TWO-EXPONENT DISTRIBUTION

		D_c/D_w for distribution whose $\bar{M}_w/\bar{M}_n$ =				
x	α	15	10	5	3	2
0.01	0.5	0.59	0.59	0.64	0.69	0.81
	0.6	0.51	0.53	0.56	0.62	0.76
	0.75	0.43	0.43	0.46	0.52	0.69
0.1	0.5	0.59	0.61	0.65	0.71	0.83
	0.6	0.52	0.54	0.58	0.64	0.78
	0.75	0.43	0.44	0.48	0.54	0.69
0.2	0.5	0.61	0.61	0.65	0.73	0.83
	0.6	0.54	0.55	0.59	0.65	0.77
	0.75	0.44	0.45	0.48	0.55	0.71
0.3	0.5	0.61	0.63	0.66	0.72	0.82
	0.6	0.55	0.55	0.59	0.66	0.79
	0.75	0.45	0.46	0.49	0.56	0.71
0.5	0.5	0.64	0.64	0.69	0.75	0.85
	0.6	0.56	0.58	0.61	0.69	0.79
	0.75	0.47	0.47	0.51	0.59	0.72
0.7	0.5	0.65	0.66	0.71	0.78	0.85
	0.6	0.59	0.59	0.64	0.71	0.81
	0.75	0.49	0.49	0.54	0.61	0.75
1.0	0.5	0.68	0.69	0.74	0.81	0.88
	0.6	0.61	0.61	0.66	0.75	0.82
	0.75	0.51	0.53	0.56	0.65	0.78

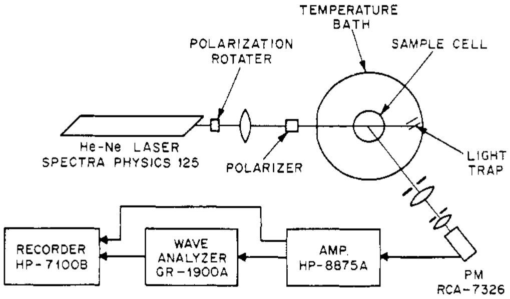

Figure 2. Block diagram of homodyning spectrometer.

Experimental Section

The homodyning spectrometer used to evaluate the polystyrene solutions is similar to one described previously;[14] the details of the instrument are shown in Figure 2. The incident beam from the laser is reduced in size by a long focal length converging lens, and its intensity is adjusted by rotating its plane of polarization relative to a stationary polarizer oriented perpendicular to the scattering plane. The scattered light is focused on the photocathode of an RCA 7326 photomultiplier tube. The scattering angle can be varied from 25 to 155°, and the collecting optics select approximately 1 mm of the incident beam in the sample cell with an angular variation of approximately ±0.15° when viewed perpendicular to the incident beam. The laser, photometer, and all optics are mounted on a vibration isolation system manufactured by Lansing Research Corp. The resonant frequency of the isolation system is approximately 1.1 Hz, and no problems from any vibrations have been experienced. Temperature control is provided by circulating water from a 20-gal. thermostated tank through channels surrounding and underneath the temperature bath; temperature within the bath can be controlled to a few hundredths of a degree as measured by an iron–constantan thermocouple.

The signal from the photomultiplier is amplified a factor of 100 by a Hewlett-Packard 8875A data amplifier. One of the two outputs from this amplifier is recorded directly and serves as a continuous monitor of the dc level of the photomultiplier; during an experimental run the anode current is maintained below 10 μA where the response of the photomultiplier is linear. The other output from the amplifier is used for analysis of the fluctuating components in the anode current by a General Radio 1900A wave analyzer whose output level is recorded on the second channel of the Hewlett-Packard 7100B recorder. The entire electronic system was calibrated in the range of 10–54,000 Hz for significant nonlinearities observed in the frequency and amplitude responses. The frequency calibration was made by injecting a white noise signal of constant amplitude at the anode pin in the photomultiplier

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(13) W.-N. Huang, E. Vrancken, and J. E. Frederick, *Macromolecules*, submitted for publication.

(14) T. F. Reed and J. E. Frederick, *ibid.*, **4**, 72 (1971).

Table VII

Polystyrene Molecular Weights and Spectral Results in Butanone at 25°

Polymer	$\bar{M}_w/\bar{M}_n{}^a$	$\bar{M}_w{}^a \times 10^{-5}$	$\bar{M}_z{}^a \times 10^{-5}$	Concn, wt %	$\Gamma_{1/2}/\sin^2(\theta/2)$	D/D_w
NBS-706	*2.1*	*2.58*	*3.6*	0.20	8596 (0.03)	0.86
NBS-706	2.7	2.67	4.9	0.20	8596 (0.03)	0.86
I-42	6.4	2.46	7.5	0.13	5743 (0.01)	0.61
I-43	7.0	5.19	13.8	0.13	3719 (0.02)	0.65
I-45	6.4	3.80	11.8	0.12	3999 (0.06)	0.57

[a] Italic values are from NBS.

socket and observing the response of the wave analyzer on the recorder for different frequency settings of the wave analyzer; essentially the same calibration was obtained by illuminating the phototube with a clear light bulb powered by a stable dc supply. The amplitude calibration was measured at several frequencies by injecting an oscillator signal of varying amplitudes at the anode pin and measuring the wave analyzer response on the recorder.

Spectral measurements of samples are made by selecting approximately 20 frequencies that define the spectrum and scanning each frequency for 1–1.5 min using a 10-Hz bandwidth on the wave analyzer. This procedure was found to give a standard deviation approximately 1.5% of the amplitude. Normally, a maximum of 30 min is required to measure a single spectrum, during which time no change in the dc level is observed. All of the spectral data points contain a flat shot noise contribution which is measured as the amplitude of the ac component that results from illuminating the photocathode with a white light to give the same dc output from the phototube. The data amplitudes, including the shot noise, are corrected by the amplitude and frequency calibrations and squared to give the amplitudes of the power measurements. The squared shot noise is subtracted from each of the other squared amplitudes, and the resulting values are least-squares fit to a single lorentzian, weighting each data point by its variance. The variance of each point was calculated from the square of its standard deviation, σ_L, given by

$$\sigma_L = R(A_T{}^2 + A_S{}^2)^{1/2} \tag{13}$$

R is assumed to be 0.03, A_T is the total squared amplitude of the signal at each frequency, and A_S is the total squared amplitude of the shot noise. The details of the origin and use of this equation are given elsewhere.[4,14] The vertical error bars on experimental spectral points represent $\pm\sigma_L$.

The final check on the instrument was made by measuring the spectral distribution of 109-nm polystyrene latex particles supplied by Diagnostic Products (a division of Dow Chemical Co.). The latex was diluted with filtered, distilled water to a solids concentration of 11 ppm, and the dilute suspension was transfered to a hypodermic syringe and then filtered into a previously cleaned glass sample cell through a 450-nm Millipore filter. The data obtained from the spectrometer were fit with single lorentzians as described above, and the diffusion coefficient was calculated from

$$D = (1/16\pi)(\lambda_0/n)^2[\Gamma_{1/2}/\sin^2(\theta/2)] \tag{14}$$

where $\Gamma_{1/2}$ is the half-width (in hertz) at half maximum height of the experimental photomultiplier power spectral density. Equation 14 assumes that the spectrum of the scattered light is lorentzian, which, when convoluted by a homodyning spectrometer, produces another lorentzian with twice the original half-width; the use of this equation for analyzing spectra from latex particles has been reported many times.[14-17] Spectra were measured at nine angles (30–150° in 15° increments) and the mean value of D was found to be $(4.33 \pm 0.23) \times 10^{-8}$ cm² sec⁻¹, which agrees very well with the value of 4.48×10^{-8} cm² sec⁻¹ calculated from the Stokes–Einstein diffusion equation for 109-nm spheres. The tolerance of D represents its standard deviation.

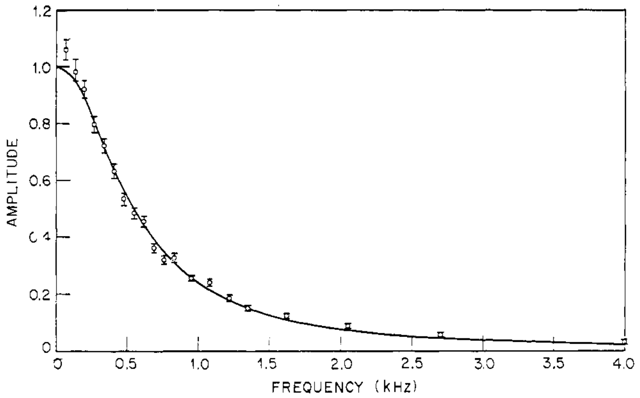

Figure 3. Homodyning spectrum for NBS-706 polystyrene, 0.2 wt % in butanone at 25°. Points, experiment; line, least-squares fit Lorentzian with $\Gamma_{1/2}$ = 559 Hz. Data taken at θ = 30°.

With completion of all tests on the instrument, solutions of four polystyrene samples in freshly distilled butanone were evaluated at 25°. The molecular weight averages and results from the line-broadening experiments are given in Table VII. NBS-706 polystyrene, originally prepared by thermal polymerization, has been thoroughly characterized by the National Bureau of Standards. These are the italic molecular weight results given in Table VII; the other results for this polymer are from GPC measurements. The other three polystyrenes are blends made from available narrow-distribution polymers and characterized by GPC. Solutions of the polystyrenes in freshly distilled butanone were prepared in glass weighing bottles and then filtered into previously cleaned, glass-stoppered sample cells from a hypodermic syringe through a 220-nm Flotronics sintered filter. The sample cells have permanent glass traps built into the bottoms. The samples were centrifuged 2 hr at 3000 rpm just before being analyzed in the spectrometer; this corresponds to a field from the top of the solution to the bottom of the cell of 1400–1900 times that due to gravity. These preparations were found to give completely flat spectral measurements from pure butanone (even after 18 hr from the time of centrifuging), which indicates that dust has been effectively eliminated from the scattering volume.[4] Concentrations of 0.1–0.2 wt % polymer were selected, since it has been shown that the diffusion coefficient below this concentration range remains essentially constant for the present molecular weight polystyrenes in butanone.[4]

Spectral distributions were measured at 25° for each solution at scattering angles of 30, 45, and 60° relative to the incident beam. Higher angles were intentionally excluded from the measurements to minimize any intramolecular effects on the spectra.[14,18] Each of the spectra was least-squares fit to a single lorentzian; an example of the fit is given in Figure 3 for the phototube spectrum obtained from NBS-706 polystyrene at the 30° scattering angle. The mean values of the quantity $\Gamma_{1/2}/\sin^2(\theta/2)$ calculated from the three spectra for each sample are given in column 5 of Table VII; the numbers in parentheses are the ratios of the standard deviations to the mean values. The last column in Table VII shows the ratio D/D_w. D was calculated from eq 14, which, as mentioned earlier, assumes that the spectral distribution of the scattered light is lorentzian; this has been shown to be a satisfactory approximation for the molecular weight range of polystyrenes used here.[17] D_w was calculated from $\bar{M}_w$ using eq 6 and the values of 3.1×10^{-4} and 0.53 for C and α, respectively.[19]

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(15) H. Z. Cummins, N. Knable, and Y. Yeh, *Phys. Rev. Lett.*, **12**, 150 (1964).

(16) S. B. Dubin, J. H. Lunacek, and G. Benedek, *Proc. Nat. Acad. Sci. U. S.*, **57**, 1164 (1967).

(17) F. T. Arrechi, M. Giglio, and U. Tartari, *Phys. Rev.*, **163**, 186 (1967).

(18) O. Kramer and J. E. Frederick, *Macromolecules*, **5**, 69 (1972).

(19) N. C. Ford, Jr., F. E. Karasz, and J. E. M. Owen, *Discuss. Faraday Soc.*, **No. 49**, 228 (1970).

The last two values calculated from the experimental diffusion constant, D, are $\bar{M}_{\mathrm{wd}}$ and $\bar{M}_{\mathrm{zd}}$ given in Table VIII for the various distributions. These quantities are related to D by the following expressions.

$$\bar{M}_{\mathrm{wd}} = \left[\frac{D}{C(D_{\mathrm{c}}/D_{\mathrm{w}})}\right]^{-1/\alpha} \tag{15}$$

$$\bar{M}_{z\mathrm{d}} = \frac{\bar{M}_z}{\bar{M}_{\mathrm{c}}}\left[\frac{D}{C}\right]^{-1/\alpha} \tag{16}$$

The values of $D_{\mathrm{c}}/D_{\mathrm{w}}$ and $\bar{M}_z/\bar{M}_{\mathrm{c}}$ were obtained from Tables II–VI for each of the distribution functions using appropriate values of x, α, and $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$ for each polymer. The values of x were calculated from eq 4 assuming $nl^2/6 = \langle S^2\rangle$, the mean-square radius of gyration; for this system $\langle S^2\rangle = 3.2 \times 10^{-17}\, M$ at 22°.[20] The value of α was assumed to be 0.5 in all cases. The values of $\bar{M}_{\mathrm{wd}}$ and $\bar{M}_{z\mathrm{d}}$ calculated from the log-normal distribution for I-42, I-43, and I-45 polystyrenes were excluded from Table VIII for reasons to be given later.

Discussion

Rayleigh line broadening is becoming more popular as a means of measuring polymeric diffusion coefficients in dilute solution. The reasons for its increasing use clearly must include the accuracy of the results, the experimental simplicity, and the relatively short time required for the measurements. For the same reasons, the technique also has appeal as a characterization tool to measure moments of the distribution other than $\bar{M}_{\mathrm{w}}$ obtained from conventional light-scattering data. To do this, it is convenient to assume an analytical function to describe the polydispersity effects in polymers, for which the Schulz distribution has found the most widespread use. This is probably because it was originally derived for chain-coupling vinyl polymerization and hence has some theoretical basis, and also it has been found to fit fractionation data of many vinyl as well as condensation polymers.[6,9,21] The other three distribution functions (Tung, log normal, and two exponent) have not been used to the same extent, but were included here because much of their use has been for polymers with very broad molecular weight distributions.

Deducing the applicability of the individual distribution functions for calculating polydispersity effects in Rayleigh spectra solely on the goodness of fit to polymer fractionation results is not possible. The reason for this is that the two techniques place emphasis on different portions of the distribution curve. Fractionation experiments reported elsewhere (*e.g.*, ref 9 and 21) show that the usefulness of a distribution function to describe their results is judged on the basis of the entire molecular weight range, whereas line broadening concentrates on the high end of the function. The calculated and experimental results reported here are therefore analyzed in terms of the second and third moments of the distribution functions. For example, the data in Tables II, IV, and VI give a comparison of the calculated line-broadening diffusion constant with that of $\bar{M}_{\mathrm{w}}$ of the Schulz (Tung), log-normal, and two-exponent distributions; substitution of eq 6 into the $D_{\mathrm{c}}/D_{\mathrm{w}}$ ratio shows that this provides the same information as comparing $\bar{M}_{\mathrm{c}}$, the calculated average molecular weight obtained from line-broadening, with $\bar{M}_{\mathrm{w}}$ of the distribution functions. In a similar fashion, Tables III and V compare $\bar{M}_{\mathrm{c}}$ with $\bar{M}_z$ of the four distribution functions, and we find that the Schulz, Tung, and two-exponent distributions predict that $\bar{M}_{\mathrm{c}} \simeq \bar{M}_z$ for values of $x \leq 0.2$ over the entire range of $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$. This includes the polymers in the present investigation and most of those of practical interest. The deviations of the $\bar{M}_z/\bar{M}_{\mathrm{c}}$ values predicted by the log-normal distribution in Table V from those given in Table III for the other three distribution functions are disregarded because, as will be shown later, this function does not even qualitatively describe the results from the line-broadening measurements made on polystyrenes with broad distributions. Since $\bar{M}_{\mathrm{c}} \simeq \bar{M}_z$ of the distributions, the values of any other moments calculated from the line-broadening data would be expected to depend on the shape of the distribution function.

TABLE VIII

POLYSTYRENE MOLECULAR WEIGHTS CALCULATED FROM DIFFUSION COEFFICIENTS

Polymer	$\bar{M}_{\mathrm{w}}{}^a \times 10^{-5}$	$\bar{M}_{\mathrm{wd}} \times 10^{-5}$ Schulz	$\bar{M}_{\mathrm{wd}} \times 10^{-5}$ L-N[b]	$\bar{M}_{\mathrm{wd}} \times 10^{-5}$ T-E[c]	$\bar{M}_z{}^a \times 10^{-5}$	$\bar{M}_{z\mathrm{d}} \times 10^{-5}$ Schulz	$\bar{M}_{z\mathrm{d}} \times 10^{-5}$ L-N[b]
NBS-706	*2.58*	2.41	1.79	2.41	*3.6*	3.4	3.5
NBS-706	2.67	2.41	1.79	2.41	4.9	3.4	3.5
I-42	2.46	3.94		2.88	7.5	7.2	
I-43	5.19	9.18		6.95	13.8	16.4	
I-45	3.80	7.80		5.53	11.8	14.3	

[a] Italic values from NBS. [b] Log normal. [c] Two exponent.

The usefulness of each distribution function to accurately predict the experimental results from line-broadening measurements is judged by comparing values of $\bar{M}_{\mathrm{wd}}$ and $\bar{M}_{z\mathrm{d}}$ with $\bar{M}_{\mathrm{w}}$ and $\bar{M}_z$ measured by other means. The values of $\bar{M}_{z\mathrm{d}}$ for NBS-706 polystyrene predicted from all four distribution functions are found to agree very well with that reported by NBS (see Table VIII). This confirms that for $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}} \leq 2$, the relation $\bar{M}_{\mathrm{c}} \simeq \bar{M}_z$ is relatively insensitive to the distribution function, since the log-normal distribution is known to be much different from the other three. The sensitivity of $\bar{M}_{\mathrm{wd}}$ to the distribution function is shown by the different values reported in Table VIII from calculations using the log-normal and from those using the other distributions. Here, the Schulz distribution derived on the basis of chain-coupling vinyl polymerization would be expected to best describe the distribution of the thermally polymerized NBS-706, and indeed it does. It has been reported previously[3,4] that the difference between $\bar{M}_{\mathrm{w}}$ and $\bar{M}_{\mathrm{wd}}$ for this polymer calculated from the Schulz distribution can be reduced if the values of D_{c} were calculated from the half-widths of Lorentzians that had been least-squares fit to the theoretical spectra rather than from those measured at half maximum amplitude. Of course, the Tung and two-exponent distributions are equally applicable to NBS-706 within the limitations presented earlier.

The three other polymers listed in Tables VII and VIII were prepared by blending existing relatively narrow polystyrenes. Since no well-characterized polystryrenes were available with distributions broader than the NBS-706, this blending procedure was used as an alternate approach. Only a small quantity of each sample could be prepared (*ca.* 0.5 g) owing to the short supply of certain fractions; as a result it was necessary to rely on GPC for characterization of these samples. The GPC data of I-42, I-43, and I-45, when plotted in a fashion similar to that used for the distribution functions in Figure 1, produced curves which had an appearance similar to the Schulz (or Tung) distribution. There was a small discontinuity on the low molecular weight side of the peak of each of

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(20) C. Tanford, "Physical Chemistry of Macromolecules," Wiley, New York, N. Y., 1961, p 309.

(21) L. H. Tung in "Polymer Fractionation," M. J. R. Cantow, Ed., Academic Press, New York, N. Y., 1967, Chapter E.

the blends representing the incomplete overlap of two adjacent narrow polymers. No interference from these discontinuities is anticipated, however, since the high molecular weight sides of all three distributions are essentially smooth.

The values of $\bar{M}_{wd}$ and $\bar{M}_{zd}$ for the three polystyrene blends calculated from the log-normal distribution have been excluded from Table VIII because of variable D_c/D_w and $\bar{M}_z/\bar{M}_c$ ratios over the experimental range of x for each of these three polymers. For example, the value of $\bar{M}_z/\bar{M}_c$ from Table V for the representative values of the parameters x, α, and $\bar{M}_w/\bar{M}_n$ of 0.01–0.1, 0.5, and 5, respectively, varies from 1.07 to 1.38, almost a 30% increase; in a similar fashion the D_c/D_w values in the same range of x vary approximately 15%. Any variability in these ratios implies a change of D_c (or $\bar{M}_c$) over the angular range represented by x. This was not observed experimentally for these three polymers, as shown in Table VII by the small standard deviation of each $\Gamma_{1/2}/\sin^2(\theta/2)$ ratio. Therefore, the log-normal distribution was considered unsatisfactory for representing the polydispersity effects of these three polymers.

The other three distribution functions were found to predict constant D_c/D_w and $\bar{M}_z/\bar{M}_c$ ratios for each of the three polystyrene blends; therefore, values of $\bar{M}_{wd}$ and $\bar{M}_{zd}$ from these three functions are presented in Table VIII. There are obvious differences between the values of $\bar{M}_{wd}$ and $\bar{M}_{zd}$ compared to $\bar{M}_w$ and $\bar{M}_z$ reported by GPC, many of which can be ascribed to the limitations of the GPC measurements. These blends have significant portions of their weights above the peak value of the 1.8×10^6 molecular weight standard, the highest point on the GPC calibration curve (*i.e.*, the lowest count). Since the present investigation involves $\bar{M}_w$ and $\bar{M}_z$ of the molecular weight distributions, the high molecular weight end of the GPC calibration becomes very important. This part of the curve above the 1.8×10^6 standard was found by adjusting its location to give the best agreement to the known values of $\bar{M}_w$ for the two highest molecular weight standards (1.8×10^6 and 8.6×10^5). It was found, however, that even this method of calibration produced values of $\bar{M}_w$ and $\bar{M}_z$ for NBS-706 polystyrene significantly higher than those reported by NBS (see Table VIII). Furthermore, the values of $\bar{M}_{zd}$ measured by line broadening are much closer to the value of $\bar{M}_z$ reported by NBS than to that found by GPC. This demonstrates that line broadening is a reliable technique for measuring $\bar{M}_z$, particularly for polymers with $\bar{M}_w/\bar{M}_n \leq 2$, and that it would be a useful supplement to the present characterization methods.

Because of the limitations of the GPC results as exemplified by the NBS-706 polystyrene, any comparison between GPC and line broadening can only be qualitative. This becomes increasingly important for the three polystyrene blends, since they contain more high molecular weight species than the NBS-706. The values of $\bar{M}_{wd}$ and $\bar{M}_{zd}$ for these three polystyrene blends do agree qualitatively with $\bar{M}_w$ and $\bar{M}_z$ from GPC in that both methods rank the samples in the same order. It is believed that the values of $\bar{M}_{zd}$ are closer to the true $\bar{M}_z$ values of the blends than those reported by GPC, but this cannot be conclusively proved without well-characterized polystyrene samples with broad molecular weight distributions. A comparison in Table VIII of $\bar{M}_{wd}$ for the three blends calculated from the Schulz and from two-exponent distributions again shows the significant effect of the distribution function on the value of $\bar{M}_w$ calculated from Rayleigh spectral measurements.

Since the values of molecular weight calculated from line-broadening measurements, particularly those other than $\bar{M}_z$, are sensitive to small changes in the molecular weight distribution, it is desirable to find a procedure to analyze the data without using an analytical distribution function. In theory, this can be done from the existing data using readily available computer programs.

Summary

Rayleigh line broadening is predicted to yield a value of an average molecular weight, $\bar{M}_c$, essentially equal to $\bar{M}_z$ for polymers which are in dilute solution and which have molecular weight distributions that are relatively narrow ($\bar{M}_w/\bar{M}_n \leq 2$). This result was calculated by assuming that each of four analytical distribution functions (Schulz, Tung, log normal, two exponent) describes the effects of polydispersity and was confirmed experimentally from a solution of the well-characterized NBS-706 polystyrene ($\bar{M}_w/\bar{M}_n = 2.1$) in butanone. The value of $\bar{M}_c$ obtained from the Rayleigh spectra for this polymer is much closer to $\bar{M}_z$ reported by NBS than to that calculated from GPC results; this suggests the use of line broadening as a characterization tool for measuring $\bar{M}_z$ that can be used to complement existing techniques.

In the range of polydispersity represented by higher $\bar{M}_w/\bar{M}_n$ ratios, the predictions from the Schulz, Tung, and two-exponent distributions remain the same, *i.e.*, $\bar{M}_c \simeq \bar{M}_z$. Since no very broad polystyrenes are known to exist, three polydisperse samples were prepared by blending existing narrow polystyrenes to give $\bar{M}_w/\bar{M}_n \simeq 7$. The values of $\bar{M}_c$ from line-broadening measurements from solutions of these blends in butanone agreed qualitatively with $\bar{M}_z$ values calculated from GPC data. The line-broadening technique is believed to produce $\bar{M}_c$ values closer to the true $\bar{M}_z$ of the broad polystyrene samples than those reported by GPC, but this cannot be substantiated without highly polydisperse samples that have been carefully characterized. The log-normal distribution was totally unsatisfactory for describing polydispersity effects on the Rayleigh measurements of the three blends, and therefore its predictions in the range of higher polydispersity were disregarded.

The values of $\bar{M}_w$ calculated from $\bar{M}_c$ for the four polystyrenes were found to be dependent on the shape of the distribution function; this dependence was stronger for the greater degrees of polydispersity. This result is expected, since if $\bar{M}_c$ is essentially $\bar{M}_z$ the values calculated for other moments of the molecular weight distribution should be dependent on its shape. This also shows that if a method which did not require a distribution function could be found to evaluate the line-broadening data, moments of the distribution other than $\bar{M}_z$ could be measured.

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