polymerization) exceeded 90%.

Transesterification of Sample 1. A freeze-dried sample of sample 1 (200 mg) was dissolved in 20 mL of methanol and heated with 0.15 mL of concentrated H_2SO_4 for 24 h at 100 °C. Upon cooling (15 °C), the transesterified polymer precipitated from solution and was isolated by centrifugation. The polymer was washed with cold water (2 × 5 mL) and dried [12 h, 22 °C (0.01 mm)], affording 100 mg of a product containing 1.7% nitrogen. Repeated transesterification of the recovered polymer, five times in succession, resulted in a nitrogen content of 1.4, 1.2, 1.1, 1.1, and 1.1%, respectively. A value of 1.1% corresponds to a level of transesterification equaling ca. 85%. ^1H NMR analysis ($CDCl_3$) of the transesterified polymer confirmed the presence of the methoxy moiety of δ 3.7. Integration of the methoxy band relative to absorption bands due to CH_2N^+ and CH_3N^+ protons yielded an estimate of the extent of transesterification equaling ca. 75%. On the basis of nitrogen and ^1H NMR analyses, the extent of transesterification is estimated to be 80 ± 5%. Similar transesterification carried out under basic conditions ($KOCH_3$) resulted in a polymer which also could not be exchanged beyond ca. 80%.

Viscosity Measurements. Viscosities were determined at 25 ± 0.1 °C in $CHCl_3$ containing 0.005 M tetrabutylammonium bromide. Intrinsic viscosities determined for samples 1 and 2 were 87.5 and 12.1 mL/g, respectively.

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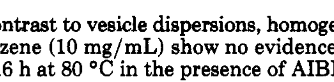
(10) Very recently, Dorn et al. have reported polystyrene equivalent molecular weights for polymers formed within bilayer vesicles comprised of the following lipid (Dorn, K.; Patton, E. V.; Klingbiel, R. T.; O'Brien, D. F.; Ringsdorf, H. *Makromol Chem., Rapid Commun.* **1983**, *4*, 513):



$$(CH_3)_2\overset{+}{N}[(CH_2)_{17}CH_3](CH_2)_6OC(=O)(CH_2)_{11}OC(=O)C(CH_3)=CH_2 \quad Br^-$$

(11) In sharp contrast to vesicle dispersions, homogeneous solutions of 1 in benzene (10 mg/mL) show no evidence of polymerization after 16 h at 80 °C in the presence of AIBN (0.1 mg/mL). We presume that the inability to polymerize 1 under these conditions is due to its very low concentration. In contrast, the "effective concentration" of 1, in vesicle form, is extremely high.
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(13) The radii, of polymerized vesicles of 1, determined from electron microscopy,[2] ranged between 100 and 350 Å. If we assume that (1) all of the vesicles are unilamellar, (2) the bilayer thickness is similar to that of saturated phospholipids, i.e., 50 Å thick, and (3) each lipid occupies an area of 70 $Å^2$, then the calculated number of lipids per vesicle is 2×10^3 to 4×10^4. This crude estimate implies that there are, to a first approximation, 3–60 polymer chains per AIBN-polymerized vesicle and 15–300 chains per UV-polymerized vesicle (see ref 10 for similar estimates).
(14) Interestingly, polymerization of large multilamellar dispersions of 1 (vortex mixed, but not sonicated) using similar procedures, afforded polymers of lower molecular weight; specific values of $\bar{M}_n$ and $\bar{M}_w$ were 8.5×10^4 and 1.1×10^6 for AIBN-induced polymerization and 5.4×10^4 and 2.1×10^5 for UV (0.5 h) polymerization. We have, at present, no clear understanding of this behavior.
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Comment on the Correct Polarization Factor for Light Scattering Photometers Employing Annular Detection

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Many types of photometers have been described for the measurement of scattered light. For studies of dilute polymer solutions, the mainstay has been the conventional goniometer, in which the detector physically rotates about the sample in a horizontal plane (Figure 1a). Both conventional and laser sources have been used. Over the past few years, a device employing a laser source and small-angle annular detection has become popular. Pioneered in the early 1970s by Kaye, McDaniel, and Havlik (KMH),[1-3] the annular design (Figure 1b) is available commercially as the Chromatix (LDC-Milton Roy) KMX-6.

In both types of photometer, factors are applied to the measured signal to correct for the effects of scattering geometry and incident beam polarization at a given scattering angle. Geometrical and polarization factors for the conventional goniometer are well-known.[4-6] While the geometric corrections for the annular device have received much attention in ref 1–3 and in the Chromatix KMX-6 instruction manual,[7] the polarization factors for the annular device are merely stated, with little supporting development. This, together with their resemblance to those for a conventional goniometer using an unpolarized incident beam, has recently led to the contention[8] that the polarization factors given by KMH and Chromatix must be incorrect. Our purpose in this brief note is to resolve this issue by developing in adequate detail the correct polarization factors for the increasingly popular annular type of instrument. We shall see that factors originally presented by KMH are correct.

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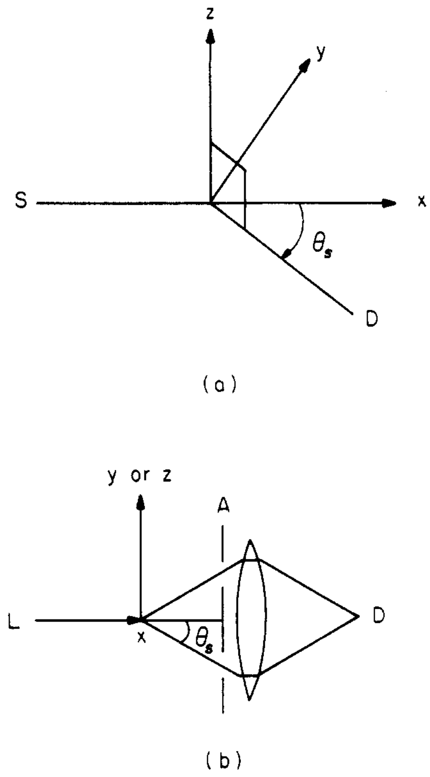

Figure 1. Essential features of light scattering photometers. z axis: vertical; xy plane: horizontal. (a) Conventional goniometer: Light from source S incident along the x axis is scattered at the origin and detected at D located in xy plane. (b) Annular photometer: Light from the laser source L (polarized along y) is scattered at the origin. The entire cone of light scattered at angle θ is θ_s by annular ring A to the detector D.

Conventional Goniometer Review

Light scattering measurements are usually expressed in terms of a Rayleigh factor, $R(\theta_s)$, which, for unpolarized detection and illumination of small independent particles, consists of four parts:[6]

$$R(\theta_s) = V_v + H_v + V_h + H_h \tag{1}$$

The upper case letter denotes the polarization detected and the subscript the incident beam polarization. For small, isotropic particles, the cross-terms V_h and H_v are zero. Thus

$$R_{iso}(\theta_s) = V_v + H_h = V_v(1 + \cos^2 \theta_s) \tag{2}$$

For small anisotropic particles, the scattering exceeds the isotropic value by the Cabannes factor, $C(\theta_s)$:

$$C(\theta_s) = R(\theta_s)/R_{iso}(\theta_s) \tag{3}$$

Cabannes factors for the conventional goniometer using an unpolarized incident beam and unpolarized detection were developed by King.[9]

$$C_u(\theta_s) = R(\theta_s)/V_v(1 + \cos^2 \theta_s) = \frac{1 + \rho_u(90) + [1 - \rho_u(90)] \cos^2 \theta_s}{(1 - \frac{7}{6}\rho_u(90))(1 + \cos^2 \theta_s)} \tag{4}$$

where the depolarization ratio is

$$\rho_u(90) = \frac{H_v(90) + H_h(90)}{V_v(90) + V_h(90)}$$

Annular Detection

In order to develop similar expressions for the annular detection scheme, we consider a cylindrically symmetric, scattering particle, small compared to the wavelength, oriented as shown in Figure 2. Let the incident beam propagate along $\hat{x}$ with $\hat{z}$ polarization. The polarizability of the cylinder is $\alpha_\parallel$, $\alpha_\perp$, and $\alpha_\perp$ along cylinder-fixed axes x', y', and z' respectively.

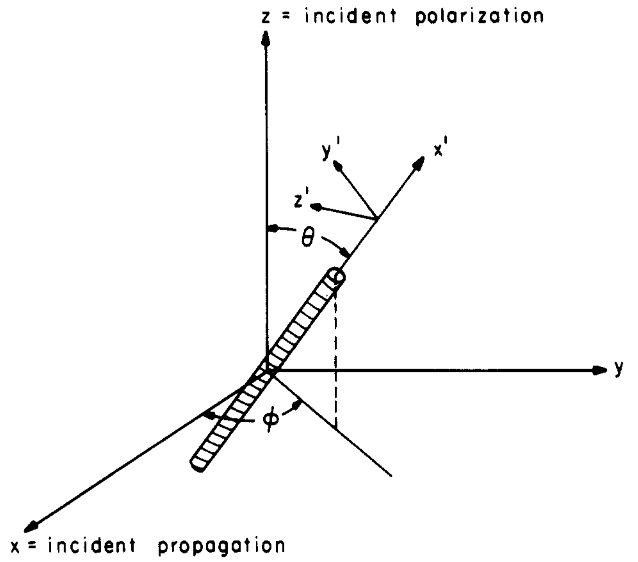

Figure 2. Orientation of scattering cylinder with internal coordinate axes x', y', z' in the laboratory frame x, y, z.

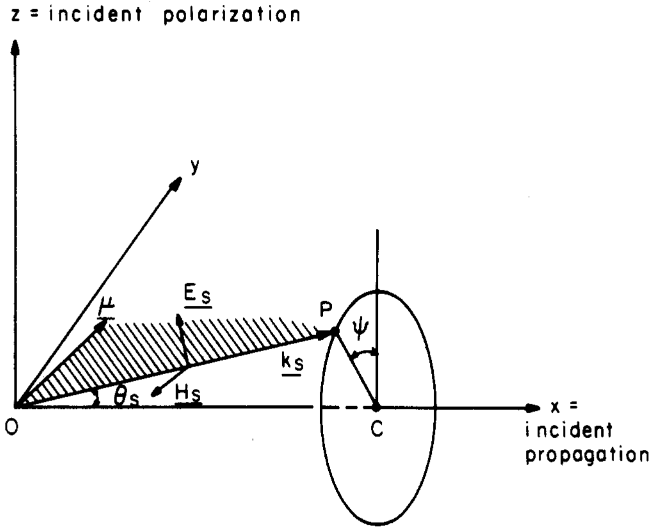

Figure 3. Scattered electric and magnetic fields for a given orientation of μ. $\mathbf{k}_s$ is the scattered wave vector.

The dipole moment induced by a unit field polarized in the $\hat{z}$ direction expressed in the laboratory frame is

$$\mu = \alpha_{xz}\hat{x} + \alpha_{yz}\hat{y} + \alpha_{zz}\hat{z} \tag{5}$$

where α_{ij} are the components of the polarizability tensor in the laboratory frames. For example

$$\alpha_{xz} = (\sin\theta \cos\phi, \quad -\cos\theta \cos\phi, \quad \sin\phi)\cdot \begin{pmatrix} \alpha_\parallel & & 0 \\ & \alpha_\perp & \\ 0 & & \alpha_\perp \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix} \tag{6}$$

Figure 3 shows the experimental geometry, with μ for a given cylinder orientation. Here, k_s is the wavevector of light scattered from a small volume at the origin O to a point P on the annulus at azimuthal angle ψ. The scattering angle at all points on the annulus, θ_s, is determined by the annular radius R and the distance OC from the origin to the center of the annulus. We may proceed by computing the *direction* of the scattered electric and magnetic fields, $\mathbf{E}_s$ and $\mathbf{H}_s$. It will not be necessary to consider time derivatives or retarded time effects. $\mathbf{E}_s$ is perpendicular to $\mathbf{k}_s$ and lies in the shaded plane defined by $\mathbf{k}_s$ and μ. $\mathbf{H}_s$ is perpendicular to $\mathbf{k}_s$, $\mathbf{E}_s$, and the shaded plane.

Thus

$$\mathbf{H}_s \propto \hat{k}_s \times \mu$$
$$\mathbf{E}_s \propto \mathbf{H}_s \times \hat{k}_s \propto \hat{k}_s \times \mu \times \hat{k}_s \tag{7}$$

where

$$\hat{k}_s = \cos\theta_s\hat{x} - \sin\theta_s \sin\psi\hat{y} + \sin\theta_s \cos\psi\hat{z} \tag{8}$$

Evaluating the cross products, one thus obtains

$$\begin{aligned}\mathbf{E}_s(\psi,\theta_s,\theta,\phi) \propto{}& \hat{x}\{\alpha_{xz}S^2 + \alpha_{yz}SC\sin\psi - \alpha_{zz}SC\cos\psi\} + \\ &\hat{y}\{\alpha_{xz}SC\sin\psi + \alpha_{yz}(S^2\cos^2\psi + C^2) + \\ &\alpha_{zz}S^2\sin\psi\cos\psi\} + \hat{z}\{-\alpha_{xz}SC\cos\psi + \\ &\alpha_{yz}S^2\sin\psi\cos\psi + \alpha_{zz}(C^2 + S^2\sin^2\psi)\}\end{aligned} \tag{9}$$

where $S = \sin\theta_s$, $C = \cos\theta_s$, and it is understood that the α_{iz} depend on θ and ϕ.

Taking the self dot product of $\mathbf{E}_s(\psi,\theta_s,\theta,\phi)$ gives a lengthy expression proportional to the scattered intensity at point P. Integrating over all ψ ($0 \rightarrow 2\pi$) gives

$$\begin{aligned}I_s^x &\propto \pi\{2\alpha_{xz}^2S^4 + S^2C^2(\alpha_{yz}^2 + \alpha_{zz}^2)\} \\ I_s^y &\propto \pi\{\alpha_{xz}^2S^2C^2 + \alpha_{yz}^2(2C^4 + 2S^2C^2 + {}^3\!/_4S^4) + {}^1\!/_4\alpha_{zz}^2S^4\} \\ I_s^z &\propto \pi\{\alpha_{xz}^2S^2C^2 + {}^1\!/_4\alpha_{yz}^2S^4 + \alpha_{zz}^2(2C^4 + 2S^2C^2 + {}^3\!/_4S^4)\}\end{aligned} \tag{10}$$

I_s^x, I_s^y, and I_s^z are the scattered intensities of light polarized parallel to x, y, and z, respectively; they depend on θ_s, θ, and ϕ. We now define Rayleigh factors for annular detection schemes in which the analyzer lies perpendicular to $\hat{x}$. The superscript "a" stands for annular detection, horizontal means parallel to $\hat{y}$, vertical means parallel to $\hat{z}$, and U means unpolarized.

$$U_v^a \propto I_s^x + I_s^y + I_s^z; \qquad H_v^a \propto I_s^x + I_s^y; \qquad V_v^a \propto I_s^x + I_s^z \tag{11}$$

Note that the I_s^x term is detected by any of these annular detection schemes, so that $U_v^a \neq H_v^a + V_v^a$. (However, in most annular devices, the angle θ_s is quite small so that $I_s^x \simeq 0$ and $U_v^a \simeq H_v^a + V_v^a$.) The survival of the small x-polarized component results from nonnormal incidence of the scattered light upon the analyzer, assumed to be a polarizing sheet with zero transmittance for light polarized along its extinction axis and zero absorbance for light polarized along either of the two axes orthogonal to the extinction axis.

For a collection of randomly oriented scatterers, we must average α_{iz}^2 over the orientations (θ, ϕ) of the scattering cylinder. Introducing $\beta = \alpha_\parallel - \alpha_\perp$ and $\alpha = {}^1\!/_3(\alpha_\parallel + 2\alpha_\perp)$ and referring to equations similar to (6), we obtain

$$\langle\alpha_{xz}^2\rangle = \langle\alpha_{yz}^2\rangle = \beta^2/15; \qquad \langle\alpha_{zz}^2\rangle = \alpha^2 + {}^4\!/_{45}\beta^2 \tag{12}$$

where the angular brackets indicate an average over θ, and ϕ. Combining eq 10–12 and simplifying, we find

$$U_v^a \propto \alpha^2(1 + C^2) + \frac{\beta^2}{45}(13 + C^2)$$
$$H_v^a \propto \alpha^2\left(S^2C^2 + \frac{1}{4}S^4\right) + \frac{\beta^2}{15}\left(2(1 - S^2C^2) + \frac{13}{12}S^4\right)$$
$$V_v^a \propto \frac{\alpha^2}{4}(3 + 5C^2 - 7S^2C^2) + \frac{\beta^2}{45}\left(8 + \frac{7}{4}S^2 - \frac{31}{4}S^2C^2\right)$$

The annular Cabannes factor for unpolarized detection reduces to

$$C^a(\theta_s) = \frac{U_v^a(\beta)}{U_v^a(\beta = 0)} = 1 + \frac{\Delta(13 + \cos^2\theta_s)}{5(1 + \cos^2\theta_s)} \tag{13}$$

Here, $\Delta = \beta^2/9\alpha^2$. Using the relation[6] $\Delta = 5\rho_u(90)/[6 - 7\rho_u(90)]$ we see that $C^a(\theta_s) = C_u(\theta_s)$. We thus obtain for the Rayleigh factor without analyzer

$$U_v^a \propto \alpha^2(1 + \cos^2\theta_s)C_u(\theta_s) \tag{14}$$

with $C_u(\theta_s)$ give by eq 4.

We now turn briefly to measurement of depolarization ratios using the annular type of instrument. In ref 3, the "average depolarization ratio", $\bar{\rho} = H_v^a/V_v^a$, is introduced, and it is "assumed" that $\bar{\rho} = (H_v + V_h)/(V_v + H_h)$. Using eq 12, one obtains a somewhat more complex expression for $\bar{\rho}(\theta_s)$, which takes into consideration that the analyzer lies perpendicular to $\hat{x}$. However, in the limit $\theta_s \rightarrow 0$, one still obtains $\bar{\rho}(0) = H_v/V_v = \rho_v$, which allows determination of $\rho_u(90) = 2\bar{\rho}(0)/(1 + \bar{\rho}(0))$.

Conclusion

Equation 14 was given without proof as eq 16 in ref 2. It is hoped that the development given above will dissuade future users of this type of instrument from using the equations set forth in ref 8. For solutions of most high polymers (with low anisotropy) the error resulting from use of the equations given in ref 8 would be quite small at any angle accessible in the KMX-6. However, an annular instrument capable of $\theta_s \sim 15°$ has been constructed and successfully used.[10] Here, the potential error approaches 7%.

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