Scattering-Angle Calibration in an Automated Small-Angle Light-Scattering Apparatus

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SYNOPSIS

Quantitative analysis in the small-angle light scattering technique for crystalline polymer studies is facilitated by the incorporation of charge-coupled detectors and image digitization and processing schemes which enable the intensity and angular dependence of scattered light to be measured. This task, however, can only be successfully achieved if a calibration procedure, where each pixel in the camera is related to its respective scattering angle component, is first implemented. In this article, a rapid and convenient calibration procedure that uses the diffraction pattern from a grating with a predetermined center-to-center distance is outlined. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Crystalline polymers scatter light due to fluctuations in density and in the orientation of correlated domains.[1] Analyses of the intensity and angular dependence of scattered light serves to characterize these fluctuations and provide information about the morphology. The original experimental layout in small-angle light scattering (SALS) involves recording the scattering pattern on a photographic film. An illustration of this is given in Figure 1. Evaluation of the entire pattern provides qualitative information about the nature and size of structures within the polymer, but quantitative information can only be obtained by determining the angular dependence of the scattering angle with a photosensitive detector. Over the last two decades, electronic photodetection in SALS had evolved from the use of point[2] to line[3] and eventually to array photodetectors.[4,5] With their improved signal-to-noise characteristics, charge-coupled detectors (CCDs) now supersede vidicons as the choice in array photodetector application.

Before quantitative information can be derived in SALS, however, it is necessary to relate each spatial picture element (pixel) in the camera to its respective scattering θ and azimuth μ angle component (see Fig. 1). A calibration step, therefore, has to be implemented before actual recording of the scattering pattern is done. Measurement of μ seldom presents a problem, but measurement of θ requires knowledge of the distance between the sample and recording plane and location of the beam center in the recording plane. In designing an appropriate calibration method, it is necessary to ensure that the accuracy of measurement is maintained and the number of calibration steps minimized. The latter factor is imperative as the distance between sample and recording plane is often adjusted in order to provide optimal coverage of the scattering pattern on the video camera. Automated study will, hence, be facilitated if a single-step calibration technique is available. In this article, such a technique that uses the diffraction pattern from a grating with a predetermined center-to-center distance is outlined.

DIFFRACTION FROM EQUIDISTANT MULTIPLE SLIT GRATINGS

Consider a grating of N slits, width b, and center-to-center separation a as illustrated in Figure 2. Assuming a Fraunhofer diffraction condition, the contribution to optical disturbance from the jth slit is given by

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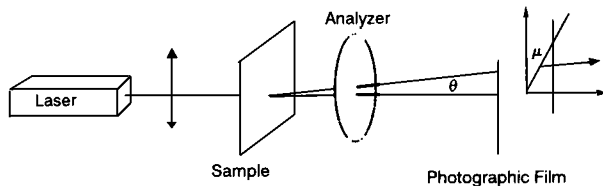

Figure 1 Small-angle light scattering experiment setup.

$$E_j = bC\left(\frac{\sin\beta}{\beta}\right)\sin(\omega t - kR + 2\alpha j) \quad (1)$$

where $\beta = (kb/2)\sin\theta$, $\alpha = (ka/2)\sin\theta$, $k = 2\pi/\lambda$, C = amplitude constant, ω = angular velocity, and t = time. The total optical disturbance is the sum of contributions from all the slits and can be described by

$$E = \sum_{j=0}^{N-1} E_j = \sum_{j=0}^{N-1} bC\left(\frac{\sin\beta}{\beta}\right) \times \sin(\omega t - kR + 2\alpha j) \quad (2)$$

This, in turn, allows expression of the imaginary part of a complex exponential in which

$$E = \mathrm{Im}\left[bC\left(\frac{\sin\beta}{\beta}\right)e^{i(\omega t - kR)}\sum_{j=0}^{N-1}(e^{i2\alpha})^j\right] \quad (3)$$

Equation (3) can be simplified by evaluating it as a geometric series to give the result

$$E = bC\left(\frac{\sin\beta}{\beta}\right)\left(\frac{\sin N\alpha}{\sin\alpha}\right) \times \sin[\omega t - kR + (N-1)\alpha] \quad (4)$$

The intensity distribution can thus be derived using

$$I(\theta) = I_0\left(\frac{\sin\beta}{\beta}\right)^2\left(\frac{\sin N\alpha}{\sin\alpha}\right)^2 \quad (5)$$

where I_0 is the intensity in the $\theta = 0$ direction. From eq. (5), it can be deduced that the waves arriving at any point beyond the grating are basically in phase and their fields add constructively. Each slit by itself would generate precisely the same intensity distribution. Superimposed, the contributions yield a multiple wave interference system modulated by a single slit diffraction envelope. Principal maxima occur when $\alpha = 0, \pm\pi, \pm 2\pi, \ldots$. Equivalently, since $\alpha = (ka/2)\sin\theta$, we have

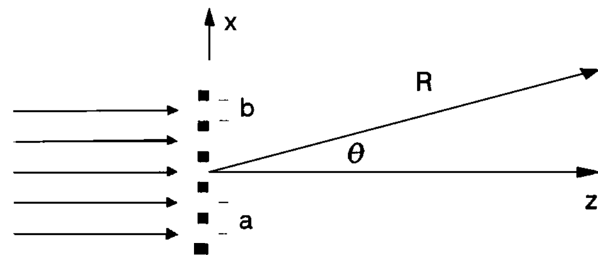

Figure 2 Optical geometry of an equidistant multislit grating.

$$a \sin\theta_m = m\lambda \quad (6)$$

with $m = 0, \pm 1, \pm 2. \cdots$. Apart from the principal maxima, subsidiary maxima are also found for $\alpha = \pm 3\pi/2N, \pm 5\pi/2N. \cdots$. The intensities of the subsidiary maxima are, however, much lower than those of the principal maxima.

TECHNIQUE DESCRIPTION

In the calibration procedure, a grating with a predetermined center-to-center distance a is placed in the sample position. The analyzer conveniently allows the intensity level of diffracted light to be adjusted. Maximum intensity is obtained when the analyzer axis is kept in a direction parallel to the input polarization, whereas minimum intensity is derived when the analyzer is oriented in a perpendicular direction. On the camera, the diffraction pattern formed is as shown in Figure 3 (for this experimentally recorded pattern, a grating with 0.05 mm center-to-center distance is used). From Figure 3, it can be clearly seen that the position of the zero scattering angle or $\theta = 0$ could be easily detected as it coincides with the position of maximum light intensity. Scattering angle calibration is done by establishing the locations of the principal maxima. Suppose that the distance between the zeroth- and mth-order principal maximum on the detector is x'.

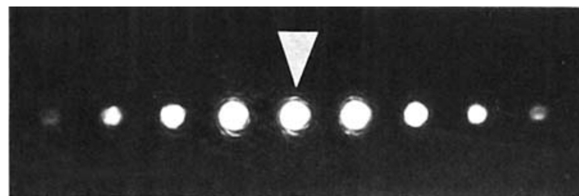

Figure 3 Experimental diffraction pattern from a grating with a center-to-center distance of 0.05 mm. The zeroth-order principal maximum is indicated with an arrow.

If the scattering angle is small, the distance between the sample and screen, d, can be calculated from eq. (6) using

$$\frac{x'}{d} = \sin \theta_m = \frac{m\lambda}{a} \tag{7}$$

Since the value of d is constant, any point on the detector that is located a distance of x_i and y_i, in the x and y directions, respectively, from the location of zeroth-order maximum, allows the scattering angle to be calculated using

$$\theta = \tan^{-1}\left(\frac{m\lambda\sqrt{x_i^2 + y_i^2}}{ax'}\right) \tag{8}$$

It should be noted that the same calibration procedure could also be applied to the diffraction pattern from a double slit rather than a grating. With a double slit, however, it would be necessary to incorporate a positioning device to locate the openings within the input laser beam; otherwise, the intensity of light transmitted would be greatly reduced or canceled. With a grating, on the other hand, there is no need to use such a device as any portion of the grating could be placed easily within the input laser beam. It should also be noted that the calibration accuracy improves when a higher-order principal maximum is used for measurement. There is, however, a limit to this alternative as the intensity decreases correspondingly with an increase in the order of the principal maximum (see Fig. 3). The choice of which order to use is therefore dependent on whether the level of intensity is detectable at that particular order. A solution to this limitation would be to use a grating with a higher interval frequency. Nevertheless, the cost of a grating generally increases with an increase in interval frequency.

CONCLUSION

Quantitative study of the scattering pattern in small-angle light scattering requires implementation of a calibration procedure, in which each pixel in the camera is related to its respective scattering angle component. In this article, a rapid and convenient calibration procedure using the diffraction pattern from a grating with a predetermined center-to-center distance is outlined. A similar calibration procedure using a double slit could also be implemented to derive an identical result but would require accurate positioning of the slits. The proposed method using gratings obviates this requirement and facilitates the quantitative study of polymers using any automated small-angle light-scattering apparatus.

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