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CD OF FILM SAMPLES: MEASUREMENT STRATEGIES

In previous reports we talked about same matter (T.R. 75, 60, 37….)
This time we would like to discuss about practical aspects on how to approach the measurement using a standard CD spectrometer.
Title indicates film samples. But it's reductive, since it applies to any sample with potential macroscopic anisotropies such as films, gels, micells and liquid crystals.
The minimum sampling accessory necessary is a rotary stage allowing to change the continuously the angle θ in the plane perpendicular to the light beam, the stage should also be routable 180° around the vertical axis to allow front and back-side measurements.

According to a recent paper[1] the apparent CD from a sample is:

$$\mathbf{CD_{app} = G_1 (P_x^2 + P_y^2) [CD + ½(LD'LB – LDLB')] + G_1(P_x^2 – P_y^2) \sin 2a (-LB\cos 2\theta + LB'\sin 2\theta)} \qquad (1)$$

Where:
G_1 is apparatus constant
P_x^2 and P_y^2 are the trasmittance of PM tube in vertical and horizontal directions
CD is the *real* CD
LD is the linear dichroism (x-y)
LD' is the 45° linear dichroism
LB is the linear birefringence (x-y)
LB' is the 45° linear birefringence
a is the azimuth angle of the PM tube in respect to the x axis
θ is the rotation angle of the sample

The above relationship is valid assuming that the PEM has a low residual static birefringence.

From above it's clear that the apparent CD signal is influenced by LD, LD', LB, LB' regardless the sample angle, while the second component is related to the θ angle when LB and LB' are not negligible.

In practical terms it means that it's necessary to measure several CD spectra of the film changing continuously the θ angle by the stage.
If CD_{app} will not change in function of the θ angle, it pays to rotate the sample 180° around the vertical axis, from front to back-side measurement..
By this operation LD and LB do not change their sign, but LD' and LB' become –LD' and –LB', so, collecting two CD_{app} spectra with front and back illumination and taking their average, a correct CD spectra can be obtained.

In contrast, if there is a change of CD_{app} in function of the θ angle, the matter is more complex.
In the paper mentioned above they try to apply further corrections measuring LB.
This can be done putting an analyzer (a good quality Glan-Taylor prism aligned exactly at same angle as the PEM via a suitable additional rotary stage will do the job) after the sample.
What we will measure is:

$$\mathbf{LB_{app} = G_3[(P_x^2+P_y^2)+(P_x^2-P_y^2) \sin 2a] [CD + ½(LD'LB – LDLB') – LB \cos 2\theta + LB' \sin 2\theta]} \qquad (2)$$

[1] Kuroda R., Harada T., Shindo Y., *Rev. Sci. Instrum.*, 72, 3802, 2001

Properly rotating the sample (θ angle), with the analyzer inserted you can find the θ angles which for LB_{max} and LB_{min} are obtained . Fixing now θ at 45° in respect to found values, we'll get a sampling angle which for LB is 0 while LB' is maximum.
Removing now the analyzer and running CD spectra Eq. 1 becomes simpler and we measure:

$$\mathbf{CD_{app} = G_1[(P_x^2+P_y^2)\,(CD\text{-}1/2LDLB') + (P_x^2\text{-}P_y^2)\,\sin 2a\ LB'\sin 2\theta} \qquad (3)$$

Now, if as before we take two measurements with the sample rotated 180° around the vertical axis and we average the two, we get the correct CD spectra, since LB' becomes –LB'.

All above measurements do not require the use of any LD accessory (to detect 100kHz signal), which is however very helpful to get right-away a quantitative idea of the LD of the sample.
Furthermore the LD accessory can be very important to align properly (by rotation) the PM tube to get the flatter natural LD baseline which will give, by definition, the best artifact free CD baseline as well (in these conditions sin2a becomes ≅ 1[2]).
The use of the analyzer may be also very important to detect the residual static birefringence of the PEM, pls note that Eq. 1 assumes that this value is negligible.
To do so the prism must be aligned in crossed position in respect to the polarization of the monochromator output. The 50KHz signal (CD) measured in air will give the residual static birefringence which should be below 0.2°.

Conclusion:
while accurate measurements may be very difficult and would call for dedicated accessories in a properly well working CD spectrometer (when not as reported in a really dedicated unit), for a preliminary approach no accessory is necessary, it's enough to sample front and back-side and to change the θ angle even approximately.
The capability to obtain also LD spectra at different θ angles would obviously further help.
Results of this preliminary approach would indicate if further, more elaborate sampling procedures are necessary; furthermore following these procedures the risk to publish incorrect data (as currently in literature) will be minimum.

[2] Shindo Y., *personal communication to E.C.*

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