Stretched polymers for X-ray linear and circular polarization

S. P. Collins

CLRC Daresbury Laboratory, Warrington WA4 4AD, UK.
E-mail: s.p.collins@daresbury.ac.uk

X-ray linear dichroism at the iodine *K*-edge of Polaroid H-sheet is explored with a view to using stretched polymers for X-ray linear-polarization analysis. The potential use of such materials as phase plates for generating elliptically polarized beams is also considered.

Keywords: linear dichroism; polarization; polymers; birefringence.

1. Background

The polarization of a scattered photon beam can contain important information about the sample, particularly in magnetic and resonant diffraction experiments. While linear-polarization analysis at X-ray frequencies is considerably harder to realize than at optical frequencies, a number of important experiments (see, for example, Gibbs *et al.*, 1991; Siddons *et al.*, 1990) have been performed by exploiting the strong linear-polarization dependence of X-ray diffraction. These experiments rely on monitoring the change in X-ray intensity, diffracted through close to 90° by an analyser crystal, as the analyser and detector are rotated carefully about the beam direction. Despite some noteworthy successes, quantitative linear-polarization analysis by crystal diffraction has proved difficult because minute changes in beam divergence, in addition to inevitable alignment errors, usually necessitate rocking of the analyser crystal. This leads to very low average intensities which remain susceptible to systematic errors.
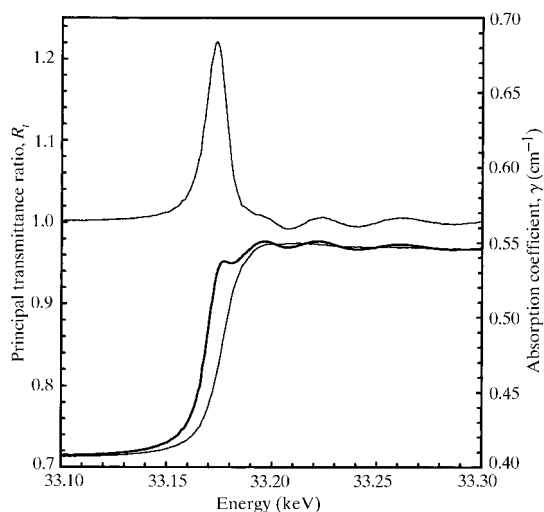
A more robust polarizer which is relatively insensitive to small variations in the beam direction would be of great advantage. To this end we have begun to explore the possibilities of using fixed-wavelength dichroic polarizers; specifically, stretched polymer films. We have studied the polarization-dependent iodine *K*-edge absorption spectrum of iodine-doped stretched polyvinyl alcohol, in the form of 100-sheet stacks of commercial Polaroid HN22 optical polarizer. The rationale for making these particular measurements is described in a previous publication (Collins, 1997), along with a detailed account of polarization measurements and calculations. Here we summarize some of the main results, and extend the calculations in order to compute the extent to which these materials can be used as sources of circular polarization.

2. Polarization-dependent absorption in polaroid HN22

Iodine *K*-edge absorption spectra were recorded on SRS Station 16.3, CLRC Daresbury Laboratory (Collins *et al.*, 1998), using an Si(111) channel-cut monochromator and a pair of Kr/He-filled ionization chambers. By rotating the Polaroids about the beam axis (normal to the film surfaces) so that the X-ray polarization changes from a parallel to an orthogonal orientation with respect to the polymer chains, we determined the principal transmittance ratio (the ratio of maximum to minimum transmission) as a function of energy (Fig. 1). The resulting spectrum is dominated by two distinct features: a single strong resonance at the *K*-edge and EXAFS-like oscillations just above it. Away from the 33.17 keV iodine *K*-edge the sample had no discernible effect on the X-ray polarization.

From a practical point of view, we conclude that a 100-layer stack of Polaroid H-sheet makes a modest fixed-wavelength X-ray polarizer, with a polarization dependence of a little over 20% and around 25% total transmission. While the polarization sensitivity of the commercial material (Fig. 2) is not huge, an increase by a factor of two or three would surely make a very useful device for X-ray polarization analysis. Indeed, absorption in the as-bought samples is due largely to the relatively thick protective layers. A polarizer constructed specifically for X-ray work with, perhaps, a higher dopant concentration and no backing layers should
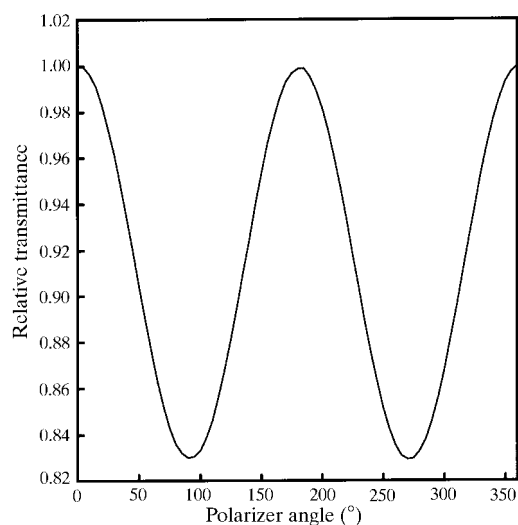

Figure 1
Above: the principal transmittance ratio (the ratio of maximum to minimum transmission) near the iodine *K*-edge for 100 layers of Polaroid HN22 sheet polarizer. Below: linear-absorption coefficients with the beam polarization parallel (thick line) and orthogonal (thin line) to the polymer chains.

Figure 2
The measured variation in transmitted intensity of a plane-polarized X-ray beam at the iodine *K*-edge as the polarizer is rotated about the beam axis.

improve the situation considerably. Moreover, even the HN22 polarizer has already been put to use in a measurement of the height-dependent beam polarization on Station 16.3 (Collins, 1997).

Returning to the absorption data, the main features of the transmittance-ratio spectrum are elucidated by plotting, in Fig. 1, the linear-absorption coefficient separately with polarization parallel and orthogonal to the polymer axis. The central resonance can be viewed as a 7.6 eV energy-shift in the K-edge for the two states of polarization. Between the edges, X-rays with one linear-polarization state are absorbed more than those of the other, leading to a sharp peak in the transmittance ratio. The origin of the EXAFS oscillations, too, becomes clear. With the electric vector along the stretch direction, iodine p-state photoelectrons are emitted preferentially along the polymer chains, and encounter a periodic arrangement of polymeric iodine neighbours. When the polarization and photoelectrons are orthogonal to the chains, no heavy (iodine) ions are present, leaving an almost total absence of EXAFS signal, as noted by Yokoyama et $al.$ (1995).

3. X-ray birefringence and circular polarization

Dichroism in the resonant signal leads inevitably to birefringence, or polarization-dependent dispersion, through the Kramers–Kronig transform. This immediately suggests the possibility of using dichroic polarizers as phase plates to convert a plane-polarized X-ray beam to a state of elliptical polarization. In this section, we extend earlier calculations (Collins, 1997; Lovesey & Collins, 1996) to compute the extent to which the Polaroid H-sheet sample can generate circularly polarized X-ray beams.

Polarization density-matrix calculations for stretched polymers are described in detail in the earlier publications. Briefly, the response of a sheet polarizer to a beam of photons normal to the plane of the sheet can be written in terms of a transmission amplitude matrix

$$A = \begin{pmatrix} \exp(-\Delta\tilde{\gamma}t/2) & 0 \\ 0 & 1 \end{pmatrix}, \tag{1}$$

where $\Delta\tilde{\gamma}$ is the difference between the (complex) linear absorption coefficients with polarization orthogonal and parallel to the polymer chains, and t is the sample thickness. (Note that, for brevity, we have neglected factors which are common to both polarization states.) The complex absorption difference can be written in terms of its real and imaginary parts,

$$\Delta\tilde{\gamma} = \Delta\gamma + i\Delta\gamma', \tag{2}$$

where the real part represents difference in the familiar linear-absorption coefficient, and the imaginary part determines the polarization-dependent phase change on passing through the medium. It is the latter which is responsible for birefringence. The polarization of the transmitted beam is characterized by the polarization density matrix

$$\mu' = (A\mu A^\dagger)/\text{Tr}(A\mu A^\dagger), \tag{3}$$

which depends on the transmission matrix and the initial polarization density matrix. (In the above expression $\dagger$ is the Hermitian conjugate.) The denominator is simply the new intensity, and is required to normalize the density matrix, which is defined as having a trace of unity. For convenience, one can write the density

matrix in terms of Stokes parameters,

$$\mu = \frac{1}{2}\begin{pmatrix} 1 + P_3 & P_1 - iP_2 \\ P_1 + iP_2 & 1 - P_3 \end{pmatrix}, \tag{4}$$

where P_1, P_2 and P_3 represent, respectively, linear polarization at 45° to the polymer chains, circular polarization, and linear polarization orthogonal to the chains. The Stokes parameters for the transmitted beam are easily obtained from the polarization density matrix using

$$P_j' = \text{Tr}(\sigma_j\mu'), \tag{5}$$

where σ_j are the Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \ \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{6}$$

To compute the induced circular polarization, we arrange for the incident beam to be plane-polarized at 45° to the polymer chains, by inserting $P_1 = 1$, $P_2 = P_3 = 0$ into equation (4) and applying the above expressions. The result is pleasingly simple:

$$P_2' = \sin(\Delta\gamma't/2)/\cosh(\Delta\gamma t/2) \simeq \Delta\gamma't/2. \tag{7}$$

The final task before calculating the circular polarization induced by the Polaroid sample is to extract the real and imaginary dichroic differences $\Delta\gamma t$ and $\Delta\gamma' t$ from experimental data. The real part is simply the natural logarithm of the principal transmittance ratio

$$\Delta\gamma t = \ln(R_t). \tag{8}$$

The imaginary part is then obtained by application of the Kramers–Kronig transform (Jackson, 1975)

$$\Delta\gamma't(E) = (2/\pi)P\int_0^\infty dE' E' \Delta\gamma t(E')/(E'^2 - E^2), \tag{9}$$

where P denotes the principal part of the integral. Generally, such a calculation is hampered by the infinite extent of the energy spectra involved. The present case is more straightforward since the dichroism is negligible for all energies apart from a narrow range in the vicinity of the iodine K-edge. To evaluate the transform over a uniform grid of experimental data points with energy
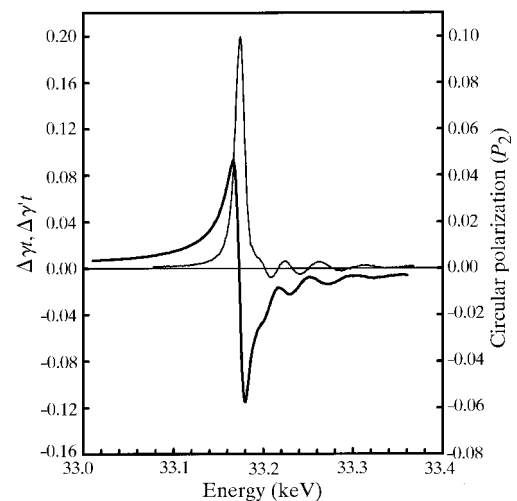

Figure 3
The real (thin line) and imaginary (thick line) parts of the dichroic absorption difference. The right-hand axis gives the calculated circular polarization.

increment ΔE, one can employ the rectangular-rule approximation

$$\Delta\gamma' t(E) \simeq (2/\pi)\Delta E \sum_{E'=E_{min}}^{E'=E_{max}} \frac{E'(1-\delta_{E',E})}{(E'^2-E^2)+\delta_{E',E}} \Delta\gamma t(E'). \qquad (10)$$

Here, the Kramers–Kronig transform is evaluated over the same grid points as the original data, and the Kronecker delta serves to eliminate infinities which should contribute nothing to the integral.

The final result of these calculations is shown in Fig. 3. Clearly, the circular polarization in this case is extremely small. Nonetheless, working just below the K-edge where absorption is reduced, one could employ a substantially thicker sample. Combined with the possible improvements discussed earlier, it is quite conceivable that one could construct a useful device for producing reversible elliptically polarized X-rays, suitable for experiments where the required degree of circular polarization is modest, *e.g.* non-resonant magnetic diffraction from ferromagnets (Lovesey & Collins, 1996).

4. Conclusions

It seems likely that stretched doped polymers can play a useful role in X-ray linear-polarization analysis at fixed wavelengths. The potential of these materials as phase plates for producing elliptically polarized beams is less clear, but they may find application where the required degree of circular polarization is modest.

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