A simple electric field birefringence cell

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A simple inexpensive electric field birefringence cell is described. This cell has a low strain birefringence, low cell volume and is particularly suited to studies on macromolecular solutions and pure liquids. The correct functioning of the cell is illustrated by measurements on poly(γ-benzyl-L-glutamate) solutions. Further improvements are suggested.

INTRODUCTION

Pulsed electric field birefringence (the Kerr effect) has recently become increasingly popular as a method of studying macromolecules in solution. In this technique an otherwise optically isotropic solution, or suspension, is rendered optically anisotropic under the action of an applied pulsed electric field. By measuring this induced birefringence (Δn) and its time dependence, molecular characterizations may be made.

Experimentally, plane polarized light passes through the sample cell with its polarization direction at an angle of 45° to the applied electric field[1] (E). This field induces two net refractive indices parallel and perpendicular to it in the fluid and the emergent beam becomes elliptically polarized. In practice, the phase difference (δ) between the resolved components (parallel and perpendicular to the electric field) of the incident light beam is measured and then related to the birefringence in the following way[2]:

$$\delta = \frac{2\pi l \Delta n}{\lambda_0} = \frac{2\pi n l K_{sp} c_v \langle E^2 \rangle}{\lambda_0}$$

where l is the optical path length, n is the mean refractive index, λ_0 is the vacuum wavelength of the measuring light, c_v is the volume fraction of the macromolecules in solution, and K_{sp} is the specific Kerr constant, which is a function of the electrical and optical properties of the macromolecule. Thus for sensitivity in the apparatus it is desirable to have a low λ_0 value but high values of l and $\langle E^2 \rangle$, given a solution of fixed concentration and specific Kerr constant. Further, if the solute macromolecule is of very low birefringence, δ is consequently small and the stray birefringence in the Kerr cell becomes critical.

Several descriptions of apparatus suitable for birefringence measurements have been published[2–4], and while the main components (light sources, polarizers, electric field generators and detectors) are all commercially available, the sample or Kerr cell itself remains a matter of personal choice. As was recently pointed out[5] the designs of such cells are often complex, and utilize large sample volumes; the second point is critical when only small amounts of rare polymer are available. It is the purpose of this paper to present the design of a Kerr cell that is not only quick and inexpensive to fabricate using readily available components, but also simple, satisfies the above criteria for maximizing δ, and (more importantly) has a very low strain birefringence.

EXPERIMENTAL

A schematic diagram of the present cell is shown in *Figure 1*. The main body (A) is machined in one unit from PTFE (polytetrafluoroethylene) which is electrically insulating and also chemically inert. The dimensions of the cell were chosen so that it could accept electrodes (B) made from standard microscope slides (75 x 25 x 1 mm) or from precut stainless steel sheet. The slot for the electrodes was cut 4 mm wide so that with a 2 mm wide spacer (C) the electrodes were held firmly parallel and in place. This also ensures that the electric field is homogenous throughout the optical path length, and field strengths of several kV per cm are supportable. The sample volume is approximately 1.5 cm^3. The optimum optical path length depends on the electrical and optical properties of the solution being studied, commensurate with detectivity. However, for typical polymer

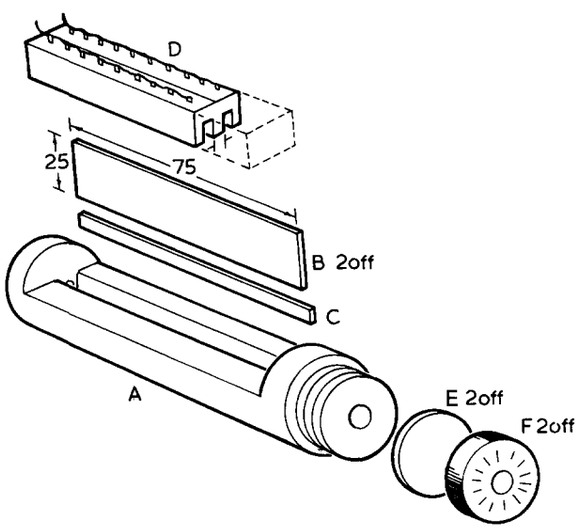

Figure 1 Schematic of the Kerr cell (dimensions in mm). A, main PTFE body; B, electrodes; C, PTFE spacer; D, electrode contacts; E, windows; F, thermoplastic

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solutions of the type described here, a path length of 75 mm was found to be a good compromise. The electrodes are held in position at their upper edges by a double-edge connector. These connectors are commercially available as contacts for printed circuit boards of various standard lengths, and give a very good electrical contact with the electrodes. In the present work two such connectors are used and bonded together with an epoxy resin to give an electrode spacing at the top edge of 2 mm, thus further ensuring that the electrodes are parallel. Both the microscope slides and the stainless steel electrodes are vacuum coated with a thin gold film giving a highly conductive and inert surface.

The cell windows (E), 2 mm thick and 25 mm in diameter, have been attached to the body (A) by means of heat shrinkable tubing (F). This tubing*, which is made from an irradiated polyolefin, shrinks diametrically by approximately 50% and longitudinally by between 5 and 7% when heated. Each end of the main body tube is machined flat at the face and grooved along the barrel. This grooving gives a good purchase for the thermoplastic tube which, on heating shrinks, and firmly presses the cell window to the main body. To the author's knowledge this is the first time such a joint has been used for a Kerr cell, the principal advantage being the negligible strain birefringence induced in the window. Previous designs have used screw mountings or epoxy resins etc, which tend to strain the window in a given direction[6]. This straining depolarizes the probe light beam and lowers the signal-to-noise ratio. These windows allowed the measurement of birefringences as small as 10^{-9} under pulsed electric fields with a time constant in the detecting circuits of <0.2 μsec (i.e. with a photomultiplier load resistance of 1 kΩ). Detectivity can be improved by using long time constants in the detecting photomultiplier circuits but this limits the range of relaxation times that can be monitored. The cell is filled via a syringe through holes machined in the corner of the slot in the main cell body.

RESULTS AND DISCUSSION

In order to test the cell, measurements were made on nitrobenzene and then two poly(γ-benzyl-L-glutamate) (PBLG) solutions. These measurements were made on an otherwise standard electric field birefringence system[7]. A Kerr constant, defined by $B = \Delta n/\lambda_0 E^2$, was determined for nitrobenzene, and found to be 2.53×10^{-12} mV^{-2} at $\lambda_0 =$ 633 nm. This is in good agreement with values published elsewhere, when corrected for wavelength[3,8]. The measurements on two solutions of PBLG of molecular weight 48 000 (PBLG I) in dimethylformamide (DMF) and 260 000 (PBLG II) in dioxane illustrate the use of the cell for conducting and non-conducting solutions, respectively. Typical results are given in *Figure 2*. The inset shows a tracing of the photographically recorded transient, while the graphs give the dependence of birefringence on applied field. Particle rotary relaxation times may be determined from the transient decay, and dipole moments calculated from the field dependence.

Analysis of the decay curves using the peeling method[10] gives one relaxation time for PBLG I in DMF and two for PBLG II in dioxane. These times may be taken as indicative of the particle size in solution, and assuming PBLG to behave as a rigid rod, and using Broersma's equations[11], they

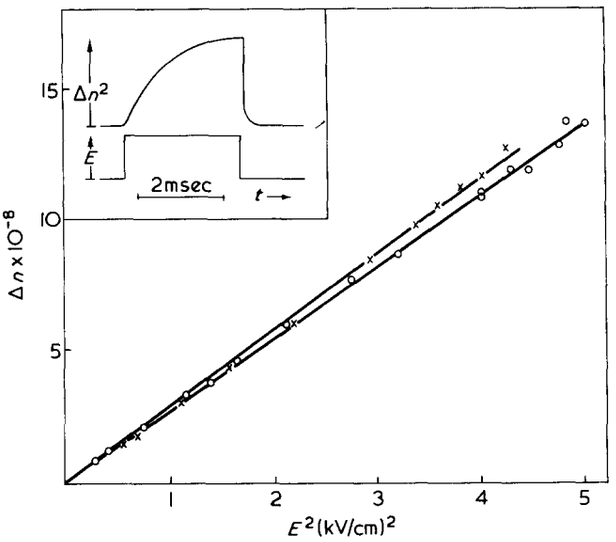

Figure 2 Birefringence vs. field dependence studies for the PBLG solutions. O, PBLG I, $c_v = 1.7 \times 10^{-3}$ cm^3/cm^3; X, PBLG II, $c_v = 1.85 \times 10^{-3}$ cm^3/cm^3. The inset shows a typical birefringence transient by quadratic detection for PBLG II where $\Delta n = 11 \times 10^{-8}$ and $E = 2$ kV/cm, and the thickness of the trace is indicative of the noise on the signal

give lengths of 360 Å for PBLG I and between 1620 and 2770 Å for PBLG II. Using Peterlin and Stuart's equation[12] and an assumed optical anisotropy factor $(g_1 - g_2)$ of 2.8×10^{-3} for both solvents[13], dipole moments of 1730 Debye (PBLG I) and 1700 Debye (PBLG II) are obtained. These results agree well with those obtained by others[13–15] and the low value of the dipole moment for PBLG II may indicate an anti-parallel aggregation taking place with dioxane as a solvent[15].

These measurements have all been made with the cell as described above; however, it is worth mentioning further improvements that may be made. Firstly, the need for cell windows can be effectively eliminated by using disc polarizers or conventional glass polarizers suitably mounted. The polarizer and analyser prisms become the windows, and may be adjusted to their correctly crossed position before the thermoplastic is finally heat shrunk. Secondly, by using a tubular design, the whole cell can be conveniently placed in a cylindrical thermal jacket for temperature dependence studies.

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