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DYNAMIC OPTICAL BIREFRINGENCE
New possibilities in polymer characterisation

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Abstract

The measurements of dynamic optical birefringence is described, together with instrumentation for this purpose. Complex birefringence, stress- and strain-optical coefficients are determined simultaneously with complex mechanical properties ($E'$and tan δ_m). Results are shown for poly(vinyl chloride) comparing data obtained in this study with earlier measurements. Optical birefringence is shown to be a very sensitive probe for molecular motions and is therefore a useful structural elucidation tool.

Keywords: DMTA, dynamic optical birefringence, polymer characterisation

Introduction

Optical birefringence has been used for many years to study stress state and structure in polymeric solids. The work presented here aims to show how the dynamic-optical birefringence measurements give more information than the dynamic mechanical (DMTA), measurements alone. Such measurements are possible on a fully automated instrument, with little knowledge required by the operator.

Dynamic techniques for relaxational spectroscopy

A brief summary of the principles of relaxational techniques will be given. In all relaxational measurements the time dependence of a microscopic or macroscopic deformational mechanism is measured. This is most commonly achieved by applying a periodic stimulus to a sample and recording the response and the phase lag between them. As energy is dissipated by a relaxation process, the phase lag will increase. Thus relaxations arising from molecular motions can be studied by varying the temperature and the applied frequency.

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Theory of birefringence measurement

Birefringence occurs when polarised light travels through a sample exhibiting anisotropy of refractive index. The origin of the anisotropy can be manifold, for example form (two-phase structure with specific geometry), orientational and stress-induced. The latter are of specific interest and can give a powerful insight into molecular deformation processes. The text below describes how optical birefringence is measured and how it can show extra information on previously well studied materials.

Birefringence is defined as the difference in refractive indices between two perpendicular axes, 1 and 2, in a sample.

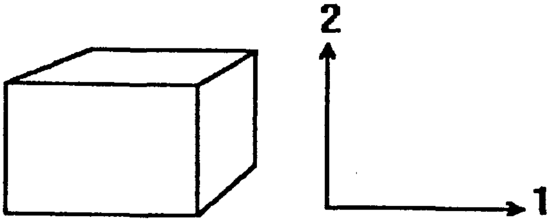

Fig. 1 Definition of birefringence. $\Delta n = n_1 - n_2$ – where n_1 is the refractive index parallel to axis 1, n_2 is the refractive index parallel to axis 2

Birefringence is measured using the Sènarmont method, which is described below.

Plane polarised monochromatic light is passed through the sample, with the plane of polarisation at 45° to axes 1 and 2. This can be thought of as the resultant electromagnetic wave, produced by two component waves, travelling parallel to the axes, and in phase with each other (Fig. 2).

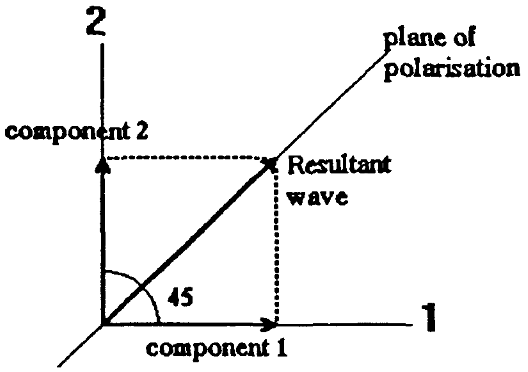

Fig. 2 Components of polarised light beam

As the beam enters the sample, the velocity of each component changes according to the refractive index along that axis, so the two component waves travel at different speeds through the sample. Consequently, when they re-emerge, there is a phase shift between the component waves, so that the resultant wave becomes elliptically polarised (Fig. 3).

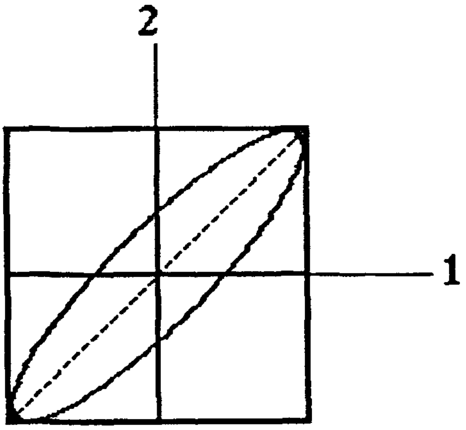

Fig. 3 Elliptically polarised light

A quarter wave plate, with its optical axis parallel to the original plane of polarisation, converts this elliptically polarised beam back into a plane polarised beam. The new plane of polarisation is shifted through a phase angle from the original beam, and this angle corresponds to a retardation of R wavelengths between the two component waves within the sample (Fig. 4)

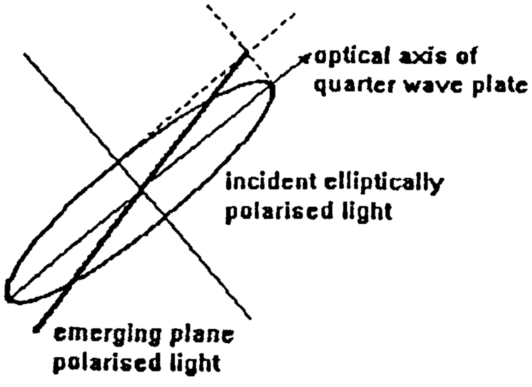

Fig. 4 Relative retardation as seen by rotation of plane of polarisation

This phase angle can be measured by using a second polariser, positioned after the quarter wave plate. Before the sample is introduced, this polariser is set fully crossed with the first, so that the output intensity is at its minimum. The angle through which this polariser must be rotated to restore the minimum after the sample has been introduced corresponds to the phase angle. The relative retardation, R, is this phase angle expressed as a fraction of a wavelength (phase angle/180°). The birefringence is then given by

$$\Delta n = \frac{R\lambda_o}{d}$$

where λ_o is the wavelength of the incident radiation (m) and d is the sample thickness (m).

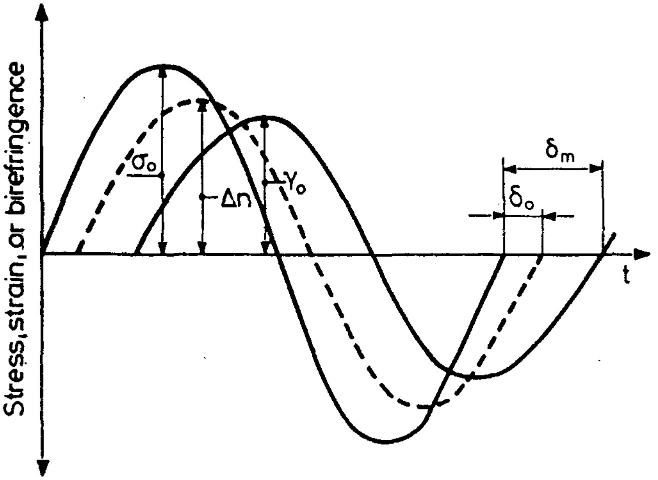

Fig. 5 Phase relationship between stress (σ_o), birefringence (Δn) and strain (γ_o)

This technique has been combined with existing dynamic mechanical thermal analysis techniques to produce an instrument which is capable of simultaneous mechanical and optical measurements. In DMTA experiments, an oscillating stress is applied to the sample, which results in a strain, lagging behind the stress by a phase angle, δ_m. Similarly, the dynamic birefringence (Δn^*) of the sample lags behind the stress by a phase δ_o (Fig. 5). Therefore the combined instrument can yield dynamic birefringence, stress- and strain-optical coefficients, as well as the mechanical modulus, damping factor and sample displacement.

Experimental

The PL-DMTA Mk III and Mk II combined heads can be retro-fitted to enable birefringence measurement on samples mounted in tension. Birefringence

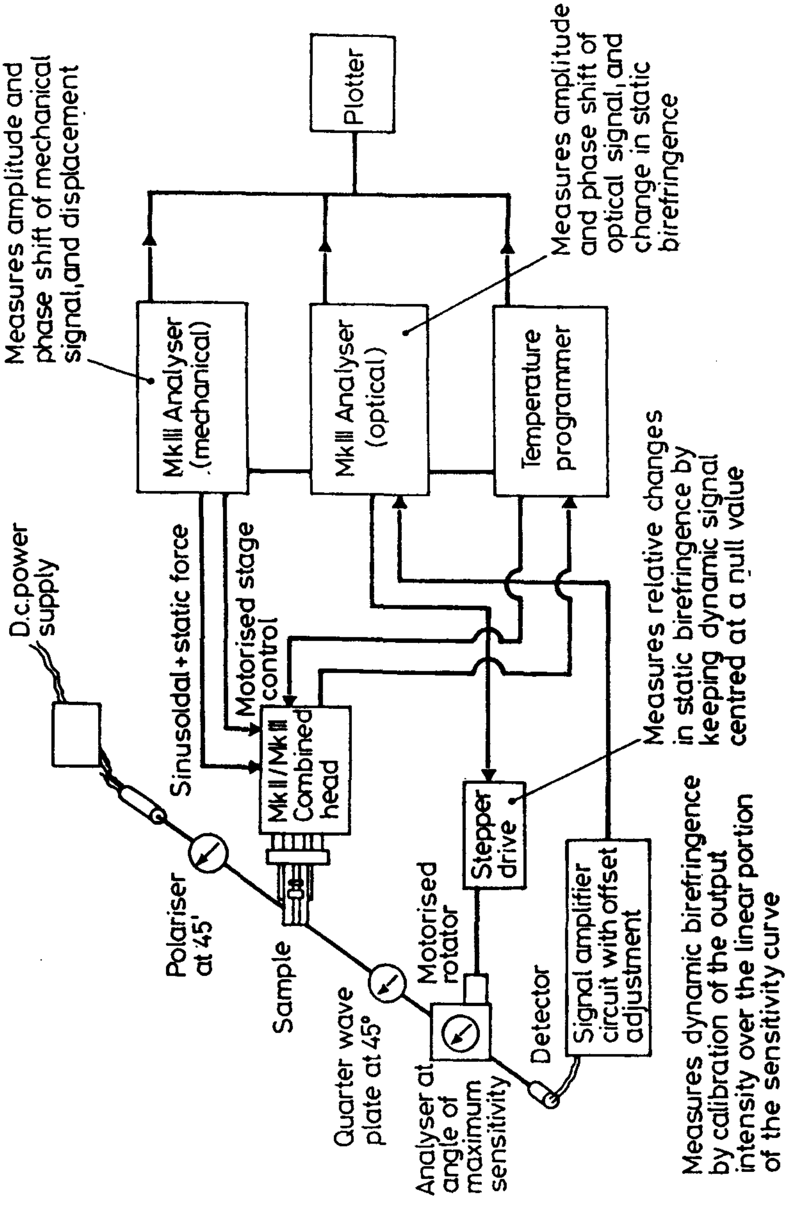

Fig. 6 Schematic diagram of experimental set-up

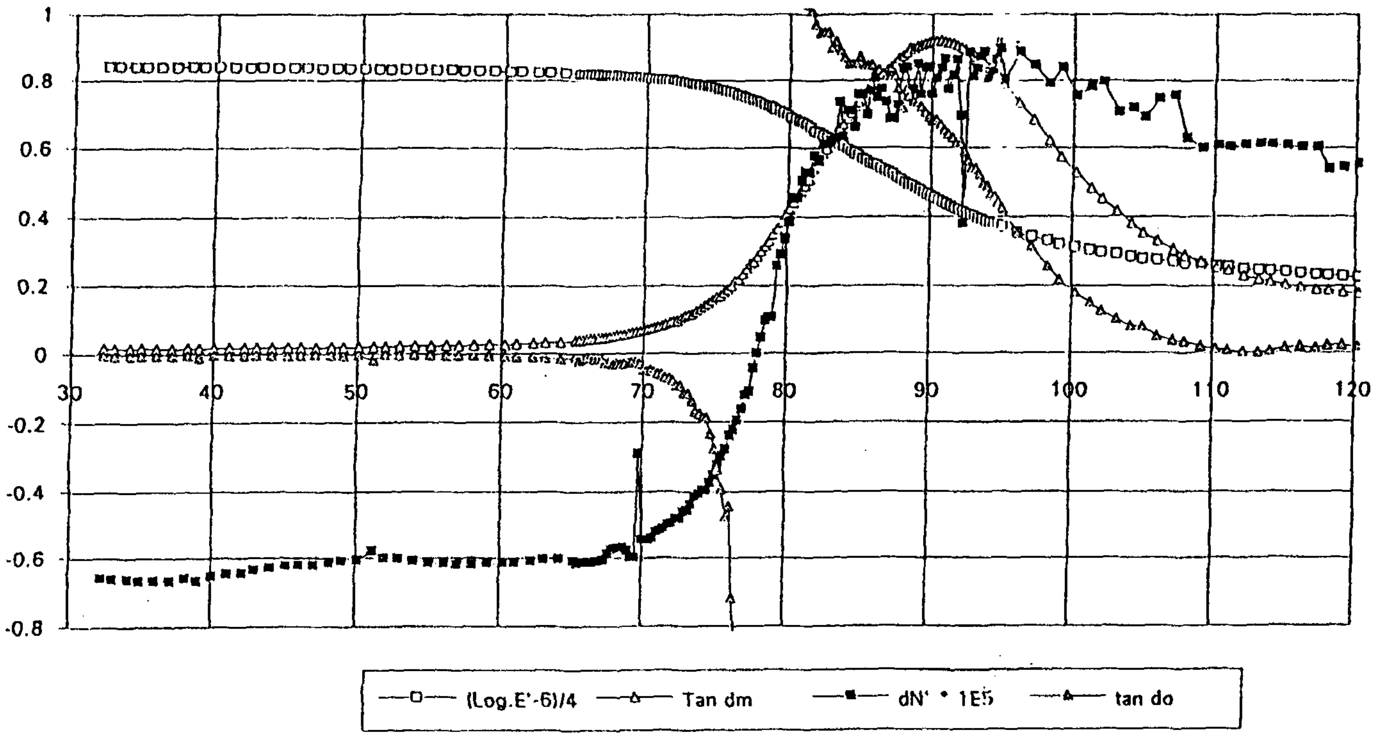

Fig. 7 Complex mechanical and optical data

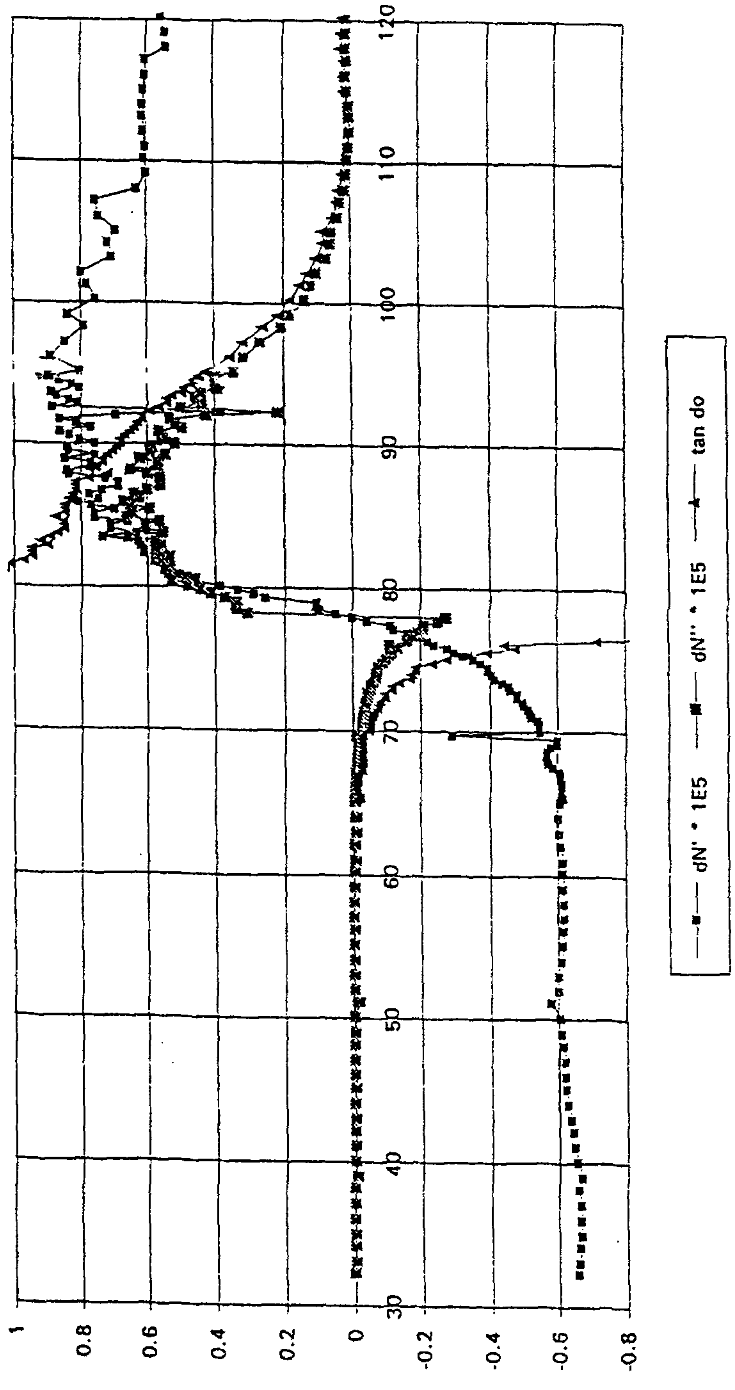

Fig. 8 dN' and dN'' dynamic optical birefringence for PVC, together with tan δ

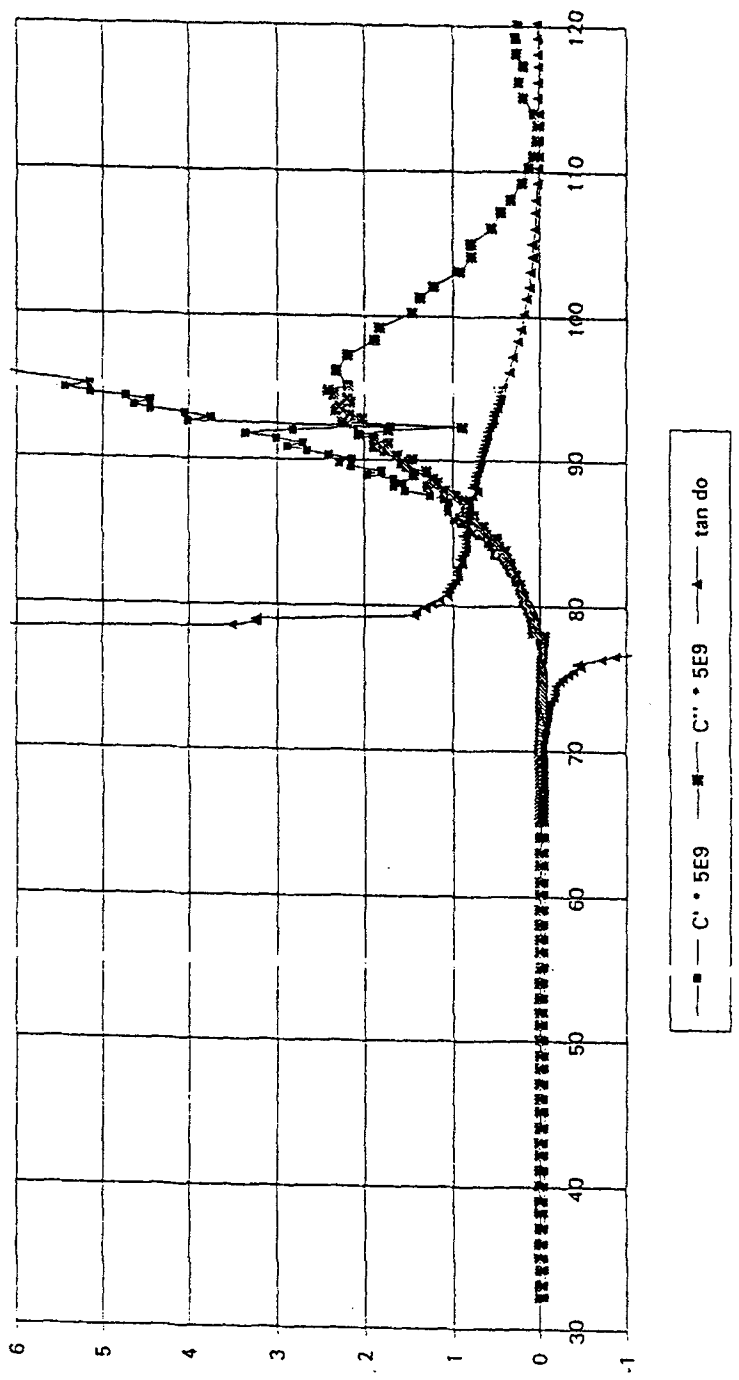

Fig. 9 Real (C') and imaginary (C'') dynamic stress-optical coefficients for PVC together with tan δ

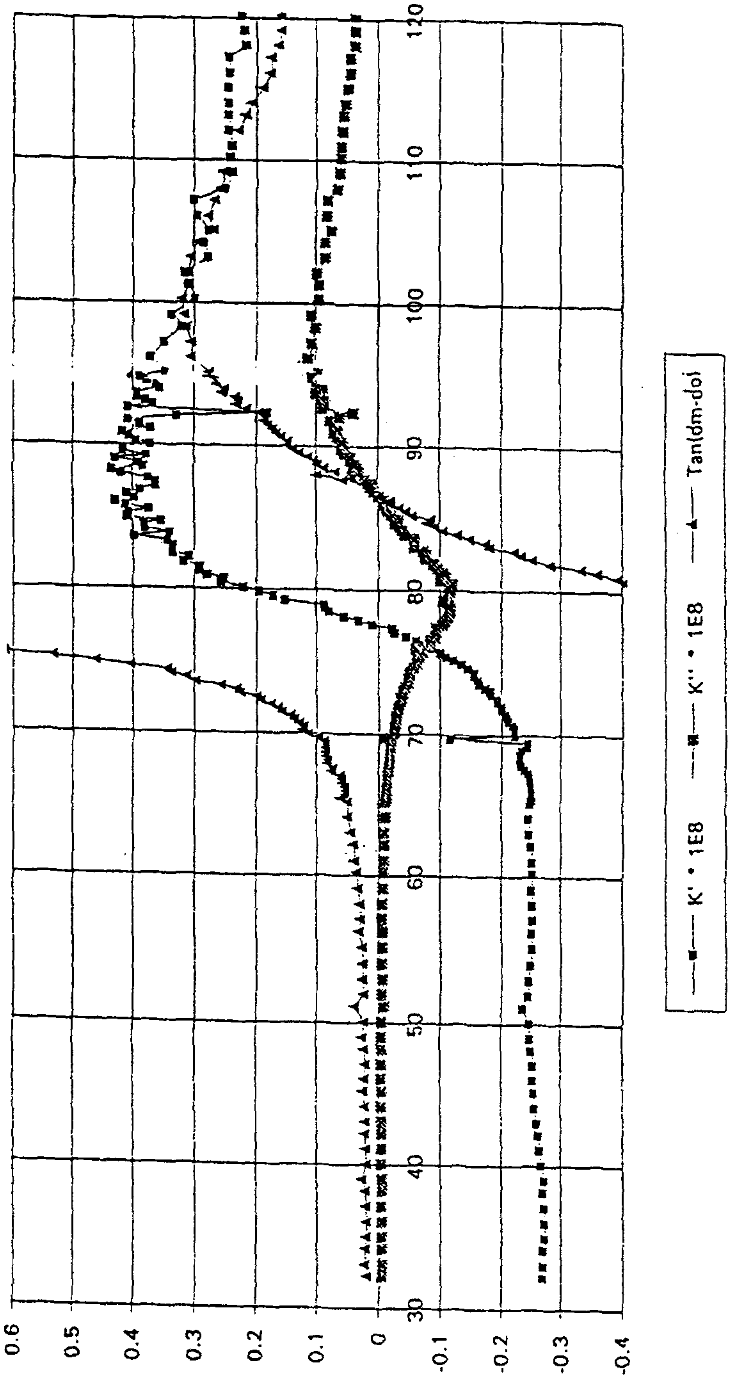

Fig. 10 Real (K') and imaginary (K'') dynamic strain-optical coefficient for PVC, together with tan(dm-do)

is measured simultaneously with the mechanical properties, thereby enabling evaluation of the complex stress- and strain-optical coefficients. Dynamic birefringence due to the applied stress is measured directly, whilst the change in residual birefringence is tracked with varying temperature. Measurements on transparent samples are possible over a temperature range of –150 to 500°C, at frequencies between 0.1 and 200 Hz.

Figure 6 shows the birefringence apparatus attached to a combined head. A monochromatic beam with polarisation vector at 45° to the horizontal emerges from the transmitter, passes through the access holes in the temperature chamber, through the sample and into the birefringence monitor. The device is self-calibrating and automatically produces dynamic birefringence and change of residual birefringence with no operator intervention.

Results

Figure 7 shows the in-phase birefringence ($\Delta n'$) and phase lag (tan δ_o, with respect to applied stress) values of poly(vinyl chloride), together with the moduli (E') and damping factor (tan δ_m). Two factors immediately apparent are

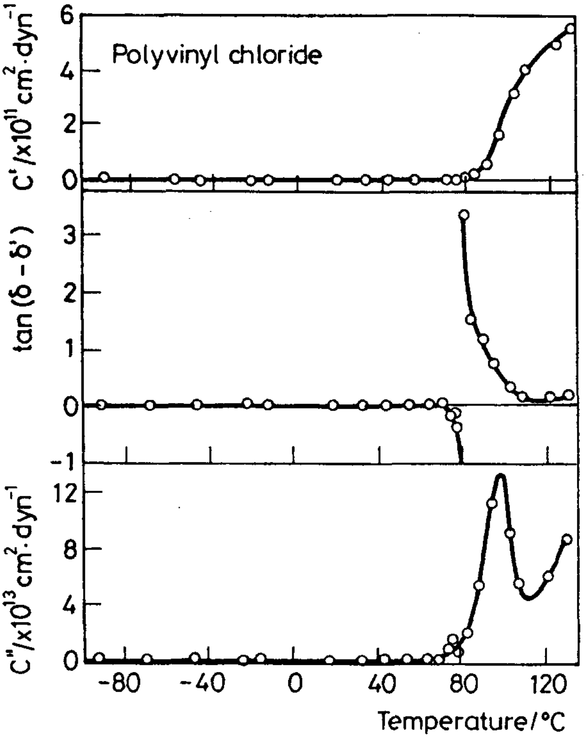

Fig. 11 Temperature dependence of C', tan (δ–δ'), and C'' for PVC at 8 c/s

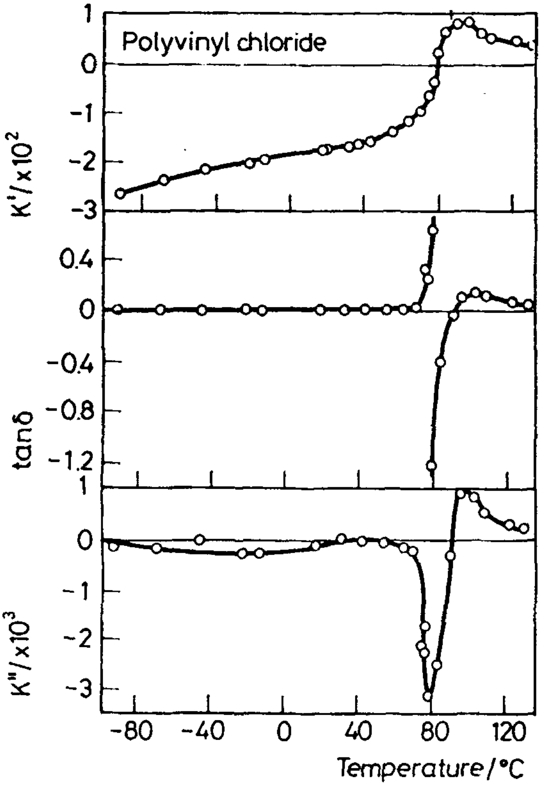

Fig. 12 Temperature dependence of K', tan δ', and K'' for PVC at 8 c/s

that the birefringence can be either positive or negative, and than tan δ_o is normally close in magnitude to tan δ_m.

The birefringence, and therefore stress- and strain-optical coefficient are negative whilst the polymer is glassy (Figs 8–10). At the glass transition the birefringence changes sign, as evidenced by the sharp discontinuity in tan δ_o. Note that this peak in tan δ_o (78°C) occurs at a lower temperature than tan δ_m peak (90°C), even though these are simultaneous measurements at the same frequency, 10 Hz. This is due to the relative probe size of each technique, the optical method probing a smaller scale than the mechanical measurements. This is in good agreement with dielectric measurements where the tan δ_{de} peak occurs at 77°C at 10 Hz for this material. This is not surprising since the origin of the birefringence is in the local molecular electric fields, however the optical birefringence is much more sensitive than the dielectric technique and it does not suffer from conductive processes that occur above T_g.

Similar measurements made earlier by Read [1] are shown in Figs 11 and 12. Agreement is very good.

The stress- and strain-optical coefficients are constant before and after the transition region for this material. However the sign change suggests that the molecular deformational mechanism is quite different for the glassy and rubbery state.

Conclusions

Dynamic birefringence is a useful probe into molecular motion processes and also macroscopic phenomena, such as phase structure within a semicrystalline polymer or a blend. Structural relaxations can be separated from molecular relaxations. This could be of considerable importance for understanding new and traditional polymers, for example epoxies, poly(imides) and poly(ethers). In these more complex systems, the additional dynamic parameter will give a better understanding of the molecular motional processes occurring during deformation.

Reference

1 B. E. Read, Proceedings of the Fifth International Congress on Rheology, Vol. 4 1970.

Zusammenfassung — Es werden Messungen – einschließlich Gerätschaft – der dynamischen optischen Doppelbrechung beschrieben. Simultan zu komplexen mechanischen Eigenschaften (E' und tan δ_m) wurden die komplexe Doppelbrechung, spannungs- und dehnungsoptischer Koeffizient bestimmt. Ergebnisse für Polyvinylchlorid werden anhand eines Vergleiches der Daten aus vorliegender Untersuchung mit früheren Messungen gegeben. Es wurde gezeigt, daß die optische Doppelbrechung eine sehr empfindliche Prüfsonde für Molekularbewegungen und somit ein hilfreiches Instrument zur Strukturaufklärung ist.