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Anisotropic Properties of Strained Viscoelastic Fluids. I. A Method for Measuring Strain Birefringence*

STANLEY J. GILL

Department of Chemistry, University of Colorado, Boulder, Colorado

INTRODUCTION

The study of anisotropic properties of materials has long been an important aspect in the characterization of physical systems. The anisotropic state is not limited to crystalline or even solid materials. Anisotropy can be induced in all systems through the effect of an external field, such as an electric field, a shear field, or a force field. The induced orientation caused by an external field naturally depends upon the physical and molecular properties of the system. The magnitude of induced anisotropy and its direction also depend upon the nature and magnitude of the applied field. The application of this general approach has long been known through such studies as the Kerr effect, streaming birefringence, photoelasticity, the Faraday effect, and so on.

This paper describes a new method for producing a temporary anisotropic state in viscous polymer solutions. In contrast to crystalline solids, viscoelastic solutions and elastomers have the notable ability of undergoing very large strains without internal destruction. Elastic stress develops when the polymer in such a material is strained. This anisotropic stress has been measured for polymer solutions subjected to either continuous shear[1,2] or to a sudden removal of shear with a consequent measurement of stress relaxation.[3,4] The elastic forces can be measured in these experiments, but the state of molecular strain is not available, although it must be large to account for the measured stress. Our attention was therefore directed toward a measurement which would yield some information about the state of molecular strain. It also seemed desirable to consider a method capable of producing relatively large strains.

The theoretical implications of the anisotropic state of polymer fluids are found in theories on rubber elasticity[5] and relaxation effects.[6-8] The experimental application of these ideas to fluid materials has generally involved measurements on the properties of elastic waves. The method described in this paper is based upon suddenly straining the material to a known extent and measuring the anisotropy and its decay by the induced birefringence. In this way the initial state of strain can be estimated from geometrical considerations. It is further possible to vary the amount of initial strain.

The purpose of this paper is to describe the principle of the straining mechanism, its construction, and its use in the measurement of strain birefringence. The application of this apparatus to the study of the induced anisotropic state will be the subject of subsequent papers in this series.

PRINCIPLE OF INTRODUCING A SUDDEN STRAIN BY A ROTATING ELLIPSE

It is possible to introduce a sudden strain into a polymeric liquid by distorting the shape of a flexible tube which functions as a container for the fluid. The flow pattern will be greatly simplified if the distortion takes place at constant area. This latter requirement is neatly met by the use of an elliptical sleeve around the container tube. If the ellipse is allowed to rotate about the fixed flexible tube, the area remains constant, but the material within the tube is strained. Continuous rotation of the sleeve would provide either a continuous state of rotating strain or an oscillatory strain, depending upon the relaxation time of the material, the speed of rotation, and the time after initiating rotation. Some of these possibilities are under current investigation. In the present application, the ellipse rotates a limited number of degrees and stops. The state of strain and its relaxation are followed by the measurement of the induced birefringence.

Suppose an ellipse is oriented with its major axis of half-length a along the coordinate x and with its minor axis of half-length b along the coordinate y.

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What will be the state of strain if the original ellipse is deformed to one of the same dimensions, but oriented with the major axis at an angle α from the x direction? To answer this question, consider a hypothetical process where a deformation on the original ellipse leads to a circle which is then deformed to the state of the second ellipse at an angle α from the x axis.

The initial ellipse is defined by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 \tag{1}$$

and it has an area of πab. A circle of equal area will be given by

$$\frac{x'^2}{ab} + \frac{y'^2}{ab} = 1 \tag{2}$$

and the transformation from the circle to the ellipse is given by

$$x' = \frac{1}{a}(ab)^{1/2}x$$

$$y' = \frac{1}{b}(ab)^{1/2}x \tag{3}$$

The problem, then, is to deform the circle to that of the ellipse oriented at an angle α. The coordinates given by a rotation of α degrees are

$$x'_\alpha = x' \cos\alpha + y' \sin\alpha$$

$$y'_\alpha = -x' \sin\alpha + y' \cos\alpha \tag{4}$$

Extend x'_α and contract y'_α by factors which give the dimensions of original ellipse, but now oriented α degrees from x:

$$x'_\alpha \frac{a}{(ab)^{1/2}} = x_{\alpha_1}$$

$$y'_\alpha \frac{b}{(ab)^{1/2}} = y_{\alpha_1} \tag{5}$$

The point $(x_{\alpha_1}, y_{\alpha_1})$ is then given in terms of the original axial directions by

$$x_{\alpha_1} = x_1 \cos\alpha + y_1 \sin\alpha$$

$$y_{\alpha_1} = -x_1 \sin\alpha + y_1 \cos\alpha \tag{6}$$

We thus have the necessary relations for the transformation of a point (x, y) to (x_1, y_1) when the elliptical shape rotates an angle α. This transformation is

$$x_1 = \left[1 - \left(\frac{a-b}{a}\right)\sin^2\alpha\right]x + \left[\left(\frac{a-b}{b}\right)\sin\alpha\cos\alpha\right]y$$

$$y_1 = \left[\left(\frac{a-b}{a}\right)\sin\alpha\cos\alpha\right]y + \left[1 + \left(\frac{a-b}{a}\right)\sin^2\alpha\right] \tag{7}$$

which has the form

$$x_1 = (1 + a_{11})x + a_{12}y$$

$$y_1 = a_{21}x + (1 + a_{22})y \tag{8}$$

where

$$a_{11} = -\left(\frac{a-b}{a}\right)\sin^2\alpha$$

$$a_{12} = \left(\frac{a-b}{b}\right)\sin\alpha\cos\alpha$$

$$a_{21} = \left(\frac{a-b}{a}\right)\sin\alpha\cos\alpha \tag{9}$$

$$a_{22} = \left(\frac{a-b}{b}\right)\sin{}^2\alpha$$

The strain is homogeneous and will approach pure strain when a nearly equals b, i.e., for cases of small ellipticity.

The practical application of the rotating ellipse requires an ellipse of reasonably small ellipticity. The analysis of strain is greatly simplified for this practical case and applies to the instrument which will be described in this paper.

The coefficients a_{11}, a_{12}, a_{21}, a_{22} of eq. (8) define a deformation which is represented by the tensor $[a_{ij}]$[9]. If the deformation tensor is antisymmetrical, a rotation is indicated. The deformation tensor can be separated into a symmetrical tensor and an unsymmetrical tensor. The strain is given by the symmetrical tensor and the rotation by the antisymmetrical tensor. Let

$$[a_{ij}] = [\epsilon_{ij}] + [\omega_{ij}] \tag{10}$$

where the symmetrical tensor is

$$[\epsilon_{ij}] = [{}^1/_2(a_{ij} + a_{ji})] \tag{11}$$

and the antisymmetrical tensor is

$$[\omega_{ij}] = [{}^1/_2(a_{ij} - a_{ji})] \tag{12}$$

When the differences $a_{ij} - a_{ji}$ are small, the unsymmetrical tensor indicates an angular rotation from x to y of ${}^1/_2(a_{21} - a_{12})$ radians. A rotation from x to y will be considered counterclockwise.

The eqs. (10) through (12) may now be used with the coefficients of eqs. (9) to find the amounts of strain and the direction of the principal strains in the strained state. The symmetrical tensor is first diagonalized by considering a counterclock wise rotation of θ radians. The condition placed on θ to achieve diagonalization is

$$\tan 2\theta = \frac{a_{12} + a_{21}}{a_{22} - a_{11}} \tag{13}$$

The two diagonal elements are given by the Mohr circle construction as

$$S_1 = {}^1/_2(a_{11} + a_{22}) - R$$

and

$$S_2 = {}^1/_2(a_{11} + a_{22}) + R \tag{14}$$

where

$$R = [{}^1/_4(a_{22} - a_{11})^2 + {}^1/_4(a_{12} + a_{21})^2]^{1/2} \tag{15}$$

Substituting the coefficients of eqs. (9) into these expressions and simplifying gives

$$\tan 2\theta = \cot \alpha \tag{16}$$

and in the first quadrant

$$2\theta = (\pi/2) - \alpha \tag{17}$$

Also

$$S_1 = {}^1/_2(a - b) \sin \alpha \,[((1/b) - (1/a)) \sin \alpha - ((1/a) + (1/b))]$$
$$S_2 = {}^1/_2(a - b) \sin \alpha \,[((1/b) - (1/a)) \sin \alpha + ((1/a) + (1/b))] \tag{18}$$

The angle θ gives the directions of the principal axes described by the diagonalized tensor of eq. (11). The direction of the principal axes of strain in the strained state have been rotated by the angle ${}^1/_2(a_{21} - a_{12})$. Thus the angle γ, that gives a principal axis in the strained state, is

$$\gamma = \theta + {}^1/_2(a_{21} - a_{12}) \tag{19}$$

With eqs. (9) and (17)

$$\gamma = \frac{\pi}{4} - \frac{\alpha}{2} - \frac{(a - b)^2}{4ab} \sin 2\alpha \tag{20}$$

The other axis is orthogonal to the first. For practical cases where a is comparable to b, the rotation term is indeed very small, which justifies this type of analysis.

The principal extension ratios λ_1 and λ_2 are found easily from the equation

$$\lambda_1 = 1 + S_1$$
$$\lambda_2 = 1 + S_2 \tag{21}$$

To a first approximation

$$\lambda_1 = 1 - {}^1/_2 \frac{a^2 - b^2}{ab} \sin \alpha$$

and

$$\lambda_2 = 1 + {}^1/_2 \frac{a^2 - b^2}{ab} \sin \alpha \tag{22}$$

If the deformations are exceptionally large, then the analysis does not conclude with such simple expressions. If very large strains can be practically produced without rotary disturbing effects, the strained state can be analyzed from the theory of large deformations. (See for example Love.[9a]) For present purposes the eqs. (17) and (19) will suffice.

STRAIN APPARATUS

Several models of apparatus based on the principles of a rotated ellipse have been constructed. The apparatus described here is the final development of initial trial models and is illustrated in Figures 1 and 2.

The polymer solution is placed within a 0.3-inch diameter Teflon tube of 0.020-inch wall thickness. End fittings hold optical windows. The Teflon tube and end windows are held in position by a Lucite container. The Lucite case also functions as the holder for the straining mechanism. This mechanism (Fig. 2) consists of an elliptically shaped piece (a) of telescopic tubing, which fits snugly around the Teflon tube. The elliptical tube is soldered to a turned steel piece or armature (b) which is subjected to a force causing rotation by two symmetrically placed springs (c). The armature is positioned by two nylon bearings (d). Stops have been placed on the armature and also on a ring which is held stationary (e). End rings (f) hold the nylon bearings and fix the position of the springs. These rings can be rotated and anchored with set screws to adjust the tension so that the armature is driven against the stops. The armature can be cocked to a position of 90° or less from the final stopped position and is held by a simple trigger (g). When released, the armature turns α degrees and impinges against the stops. In order

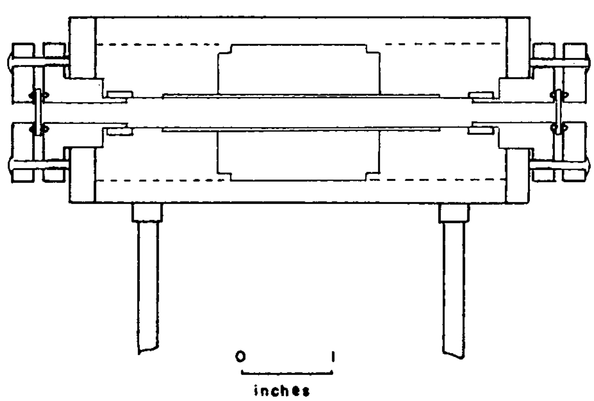


Fig. 1. Lucite container with end fittings and strain mechanism.

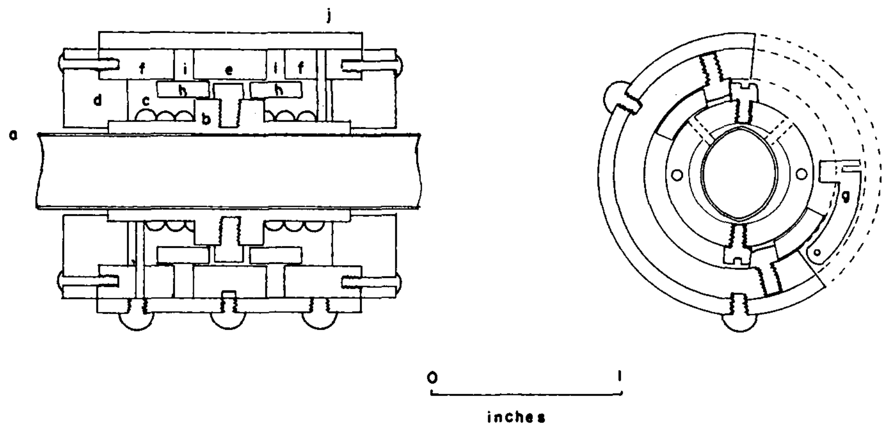


Fig. 2. Strain mechanism.

to remove some of the shock of this process, a cylinder of similar moment of inertia as the armature and elliptical sleeve is built into the apparatus so that momentum is transferred through the stops to this cylinder (h). The cylinder is guided by nylon rings (i). The springs which drive the mechanism are wound from $^1/_{16}$-inch diameter piano wire and consist of approximately four turns with a diameter of $^5/_8$ inch. All of this mechanism is assembled within a sleeve (j), and set screws anchor the end rings and stops in place. Access to the armature for cocking is attained through a slot in the stopping ring and sleeves. The straining assembly is held with set screws within the Lucite container with the Teflon tube running through the elliptical sleeve.

The Lucite container is fixed on rods so that it can be attached to the optical bench. This container can also function as a liquid reservoir for maintaining the temperature of the material within the Teflon tube at values different from room temperature.

With this apparatus, a rotation of 90° is obtained in nearly 1 millisecond, which corresponds to an average speed of rotation of about 15,000 revolutions per minute. The straining time is therefore quite small.

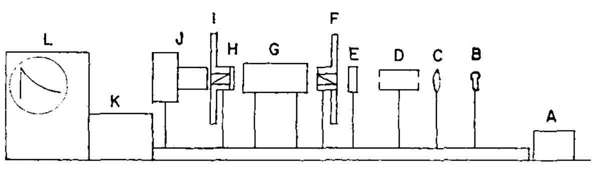


Fig. 3. Schematic arrangement of apparatus for measuring birefringence decay: (A) storage battery; (B) lamp; (C) condensing lens; (D) collimator with $^1/_8$-in. diameter holes; (E) mercury line filter; (F) Nicol prism mounted in rotable graduated circle; (G) fluid cell and straining mechanism; (H) quarter-wave plate; (I) same as (F); (J) photomultiplier tube and mount; (K) high-voltage supply; (L) oscilloscope.

APPLICATION OF ROTATED ELLIPSE TO MEASURE STRAIN BIREFRINGENCE

There are several possibilities for measuring birefringence as a function of time. In cases in which the birefringence changes rapidly with time, visual observation with a Babinet compensator is not feasible, and a photoelectric method is necessary. Photoelectric techniques have been used in the study of electrical and magnetic birefringence effects.[10–12] The optical arrangement of Chauvin is used in our work.[13]

The optical set-up is illustrated in Figure 3. Collimated light from a battery-connected, 6-volt tungsten-filament lamp is filtered by a mercury-line (5461 A.) interference filter. The light then passes through a Nicol prism oriented at 45° to the strain axes, through the strained material, and through a quarter-wave plate (also at 45° to the strain axes) and Nicol prism in the crossed position with respect to the original prism. When the material is unstrained, no light passes through the analyzing prism. When the material is strained, however, light reaches a 6292 Dumont photomultiplier tube, and an electrical signal is observed with an oscilloscope. The trace on the scope can be photographed. The photomultiplier is supplied with negative voltage so that a d.c. output can be obtained. A Baird-Atomic High Voltage Supply Model 312 is used as the voltage source. The amplification of the photomultiplier tube is sufficient to give satisfactory current and voltage without preamplification. Further amplification is obtained from the vertical amplifier of a Tektronix 531 scope. The optical components are mounted on an optical bench, and the Nicol prisms are held in rotatable mounts with a divided circle and vernier (+1′).

When the isotropic material is strained, it becomes birefringent. The optical arrangement with oriented quarter-wave plate and crossed Nicols permits detection of the birefringence effect as a plane polarized beam at an angle $\delta/2$ radians from the optical axis of the analyzing Nicol. The retardation is given by

$$\delta = \frac{2e(n_2 - n_1)}{\lambda} \quad (23)$$

where e is the length of the path through the birefringent material, λ the wave length of the light, and n_1 and n_2 the refractive index along the principal strain axes. The intensity of light which passes through the system is

$$I = I_0 \sin^2 \delta/2 \quad (24)$$

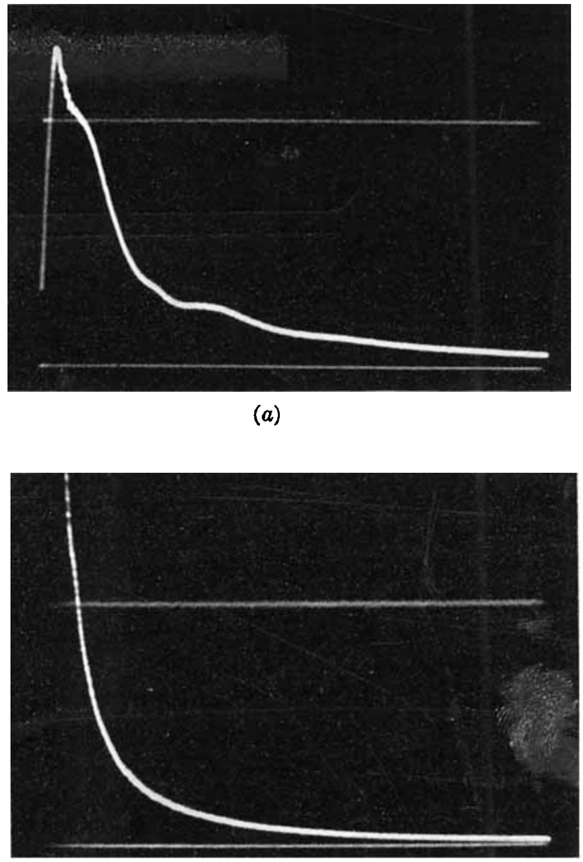
The optical system can be calibrated easily by rotating the polarizing Nicol an angle β degrees with the unstrained material in the optical path. In this case,

$$I = I_0 \sin^2 \beta \quad (25)$$

from which I_0 may be obtained. The advantage of this calibration method is that the absorption and reflection effects are nearly the same in the strained and unstrained measurements, since no part of the optical arrangement is radically changed. The disadvantages are found in the requirement that the strain axes must be set at 45° to the crossed Nicols. This requirement could be eliminated by introducing a second quarter-wave plate after the polarizer and orienting both quarter wave plates to give circularly polarized light. In this case, the axes of orientation of the strained material are unimportant, but calibration procedures are not so direct as in the first method.

The method based on eqs. (24) and (25) has proved satisfactory, since the axes of strain can be established by rotating the crossed Nicols and quarter-wave plate until no light passes through the strained material. The Nicols are then set at 45° from this zero position. This strain-axis calibration will depend upon the angle through which the ellipse is rotated.

Some results obtained with this apparatus are illustrated in photographs of the 'scope trace showing the induced birefringence. The photographs include a base line indicating zero degrees of birefringence and calibration lines of $\beta = 50°$, $\beta = 15°$ for Figures 4*a* and 4*b*, respectively. The decay curves are a measure of the birefringence induced by the straining mechanism. Both of these pictures are for a 1.4% solution of carboxymethylcellulose; Figure 4*a* was made with a sweep of 5 msec./cm. and Figure 4*b* with higher amplification and 50-msec./cm. sweep. The sweep distance in both



(*a*)

(*b*)

Fig. 4. Strain birefringence relaxation of 1.4% carboxymethcellulose: (*a*) baseline sweep time of 41 msec. with calibration line of $\beta = 50°$; (*b*) baseline sweep time of 410 msec. with calibration line of $\beta = 15°$. The vertical scale is proportional to $\sin^2 \delta/2$.

photos is 8.2 cm., and the sweep rate was calibrated against a time-mark generator. There are several points worth comment. In the first photograph (Fig. 4*a*) we see how rapidly birefringence is induced by the straining mechanism, i.e., of the order of 1 msec. More viscous materials will reduce strain time for this particular apparatus. The decay in the short-time region to 15 msec. is slightly obscured by apparatus vibration which was more pronounced in the first models of the apparatus and was greatly reduced by the counter-momentum rotor and nylon bearings.

END EFFECTS ON THE GEOMETRY OF STRAIN

The state of strain developed with the Teflon tube is constant along the length of the elliptical sleeve, but varies at the ends, where the shape of the Teflon tube goes from elliptical to circular. Figure 5 illustrates the situation. The end of the tube is circular with a radius r and gradually assumes the elliptical shape with major axis $2a$ and minor axis $2b$ at

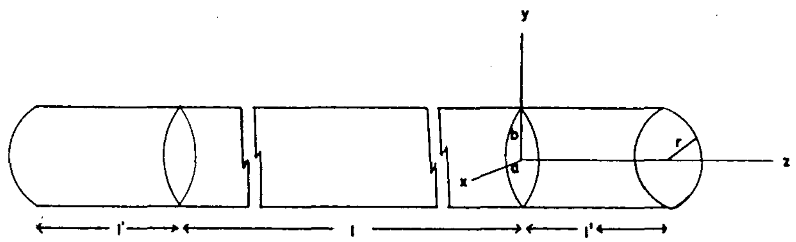


Fig. 5. Geometry of distorted Teflon tube.

a distance l' from the end. Provided the ellipse at the center of the tube is of reasonably small ellipticity, we may assume the end regions are characterized by the elliptical shape at $(1/2)l'$. The half-major axis of this intermediate ellipse is $(r + a)/2$, and the half-minor axis is $(r + b)/2$. This gives

$$\lambda_{1(\text{end average})} \cong 1 - \frac{1}{2}\left[\left(\frac{r+a}{r+b}\right) - \left(\frac{r+b}{r+a}\right)\right] \sin \alpha$$

$$\lambda_{2(\text{end average})} \cong 1 + \frac{1}{2}\left[\left(\frac{r+a}{r+b}\right) - \left(\frac{r+b}{r+a}\right)\right] \sin \alpha \quad (26)$$

which applies over a length $2l'$. The total contribution of the strained volume within the tube is the sum of the ends of length $2l'$ and the middle section of length l:

$$(2l' + l)\lambda_{1(\text{average})} = 2l'\left\{1 - \frac{1}{2}\left[\left(\frac{r+a}{r+b}\right) - \left(\frac{r+b}{r+a}\right)\right] \sin \alpha\right\} + l\left[1 - \frac{1}{2}\left(\frac{a^2 - b^2}{ab}\right) \sin \alpha\right]$$

$$(2l' + l)\lambda_{2(\text{average})} = 2l'\left\{1 + \frac{1}{2}\left[\left(\frac{r+a}{r+b}\right) - \left(\frac{r+b}{r+a}\right)\right] \sin \alpha\right\} + l\left[1 + \frac{1}{2}\left(\frac{a^2 - b^2}{ab}\right) \sin \alpha\right] \quad (27)$$

The optical path e is thus given by

$$e = 2l' + l \quad (28)$$

The equations describing the state of strain of a viscoelastic solution apply to sudden application of strain, since the polymer will relax to its average undistorted shape unless permanent junction points are present within the material. For the case of a rubberlike material, some of the junction points are permanent. If the relaxation is slower than the time to strain the system initially (t_1 sec.), eq. (27) should approximate the state of strain also at the molecular level at t_1 seconds. The molecular strain and, therefore, the birefringence of the system will decay from this maximum initial value. The birefringence can be followed from this time and indicates the molecular strain of the relaxing system. It would also seem feasible to apply these methods for stress measurements, and an attempt is being made in this direction.

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Synopsis

A mechanism has been devised for the purpose of introducing a sudden strain of calculable amount into a viscoelastic fluid. The principle of the apparatus relies upon the deformation caused by the rotation of an elliptical sleeve about a flexible tube containing polymer solution. An apparatus has been constructed which can produce a 90°

rotation (with consequent deformation) in the period of one millisecond. The detection of the strained state is accomplished by means of strain birefringence. In this way, relaxation can be studied in concentrated solutions for a time range beyond one millisecond.

Résumé

On a mis au point un mécanisme en vue d'introduire brusquement une tension de valeur calculable dans un fluide viscoélastique. Le principe de l'appareil est basé sur la déformation causée par la rotation d'un manchon elliptique dans un tube flexible contenant la solution de polymère. On a construit un appareillage qui peut produire une rotation de 90° (aved déformation subséquente) en une période d'un milliseconde. La détection de la tension est faite par biréfringence d'étirement. Ainsi la relaxation peut être étudiée en solutions concentrées sur un espace de temps inférieur d'une milliseconde.

Zusammenfassung

Eine Vorrichtung zur Einführung einer plötzlichen Spannung von berechenbarer Grösse in eine viscoelastische Flüssigkeit wurde angegeben. Das Prinzip des Apparates beruht auf der Deformation, die durch die Rotation einer elliptischen Hülse um ein flexibles Rohr erzeugt wird, das die Lösung des Polymeren enthält. Es wurde ein Apparat konstruiert, der eine Rotation um 90° (mit darauffolgender Verformung) im Zeitraum einer Millisekunde erzeugen kann. Die Bestimmung des Spannungszustandes erfolgt mittels der Spannungsdoppelbrechung. Auf diese Weise kann die Relaxation in konzentrierten Lösungen in Zeiträumen von Millisekunden bestimmt werden.

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