# Molecular orientation behaviours of uniaxially stretched poly (vinyl chloride) film: 3. Effect of molecular orientation on anisotropy of Young's modulus in uniaxially stretched poly(vinyl chloride) film

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Using uniaxially stretched, unplasticized PVC film as an example of non-crystalline polymer film, an aggregation model is assumed consisting of a structural unit having an elastic compliance of the same value as that of an ideal sample, uniaxially stretched and with orientation of the structural unit that conforms to that of the molecular chain axis. By using orientation factors evaluated from polarized fluorescence measurements the anisotropy of Young's modulus on the surface of the sample is investigated. The results of theoretical calculation explain the elastic anisotropy observed. The dependence of the anisotropy of Young's modulus on draw ratio can be specified by the molecular orientation regardless of the temperature, above or below the glass temperature, at which the sample was stretched.

## INTRODUCTION

It is well known that the short time response to an infinitesimal deformation in polymer solids represents elasticity. In crystalline polymers in particular, the basic methods for the evaluation of Young's moduli have been developed by using molecular orientation functions with respect to the main chain in a crystallite on the basis that the elasticity depends mainly on that of crystallites[1–3]. Elastic anisotropy of stretched crystalline polymer films has been evaluated by means of the orientation factors obtained by X-ray diffraction, and the results have been compared with the measured values[4–6].

For non-crystalline polymers, Kashiwagi, Folkes and Ward[7] have explained the anisotropy of the elastic modulus in poly(methyl methacrylate) in terms of the molecular orientation factors evaluated from measurements by broadline nuclear magnetic resonance. However, little work has been reported on the evaluation of the elastic anisotropy of stretched non-crystalline polymer film in terms of the molecular orientation owing to the difficulty of quantitative evaluation of the molecular orientation.

In a previous paper in this series[8], the second and the fourth moments of molecular orientation in poly(vinyl chloride) (PVC) film have been evaluated by using polyene and carbonyl radicals formed in the heat-treated samples as fluorescent radicals, and the results were found to be reasonably in agreement with experiment. In this paper, uniaxially stretched PVC film was chosen as an example of non-crystalline polymer and its elastic anisotropy was investigated by birefringence and polarized fluorescence intensity measurements.

## EVALUATION OF YOUNG'S MODULUS BY POLARIZED FLUORESCENCE

Since the sample consists only of non-crystalline chains having cylindrical symmetry about the extension axis, an equivalent aggregation model was used which consisted of the structural unit with cylindrical symmetry about the $X_3^u$ axis (the molecular chain axis) in the structural unit. The elastic compliance of the structural unit is:

$$\begin{bmatrix} S_{11}^u & S_{12}^u & S_{13}^u & 0 & 0 & 0 \\ & S_{11}^u & S_{13}^u & 0 & 0 & 0 \\ & & S_{33}^u & 0 & 0 & 0 \\ & & & S_{44}^u & 0 & 0 \\ & & & & S_{44}^u & 0 \\ & & & & & 2(S_{11}^u - S_{12}^u) \end{bmatrix} \qquad (1)$$

The coordinate system $0\text{-}X_1, X_2, X_3$ is set in the sample by making the $X_3$ and $X_1$ axes parallel to the initial draw direction and the thickness direction of the sample, and the coordinate system $0\text{-}X_1^u, X_2^u, X_3^u$ is fixed in a reference structural unit.

Under the condition that the sample is subjected to uniform stress conforming to Reuss's model, Young's modulus in the $X_3$ axis direction is derived in terms of the elastic compliance elements from the relation :

$$E_{33}^{-1} = \langle a_{3i}a_{3j}a_{3k}a_{3l}\rangle S_{ijkl}^u \qquad (2)$$

where the elastic compliance element $S^u_{ijkl}$ corresponds to $S^u_{pq}$ in engineering notation, and $a_{ij}$ is the direction cosine between the $X_i$ and $X^u_j$ axes (the angular brackets denote the space average of the structural units). Similarly, Young's modulus in an arbitrary direction on the surface of the film (the $X'_3$ direction, say) is given by:

$$E^{-1}_{3'3'} = \langle a'_{3i}a'_{3j}a'_{3k}a'_{3l}\rangle S^u_{ijkl} \tag{3}$$

where $a'_{3k}$ is the direction cosine between the $X'_3$ and $X^u_k$ axes. If $m_{3j}$ is the direction cosine between the $X'_3$ and $X_j$ axes, the value of $a'_{3k}$ is:

$$a'_{3k} = m_{3p}a_{pk} \quad (m_{3l} = 0)$$

Substituting each element of equation (1) into equation (3) and modifying the average $\langle a'_{3i}a'_{3j}a'_{3k}a'_{3l}\rangle$ by the additive theory of Legendre functions, we arrive at[3]:

$$\begin{aligned}[E(\beta)]^{-1} = {} & \frac{1}{35}\{8F_{400}P_4(\cos\beta) + 20F_{200}P_2(\cos\beta) + 7\}S^u_{33} \\ & + \frac{8}{105}\{3F_{400}P_4(\cos\beta) - 10F_{200}P_2(\cos\beta) + 7\}S^u_{11} \\ & + \frac{2}{105}\{-12F_{400}P_4(\cos\beta) + 5F_{200}P_2(\cos\beta) + 7\} \times \\ & (2S^u_{13} + S^u_{44})\end{aligned} \tag{4}$$

In the above equation, $\beta$ is the angle between the $X'_3$ and $X_3$ axes and $F_{l00}$ ($l = 2, 4$) are the second and the fourth orientation factors of the molecular chain ($X^u_3$ axis) about the $X_3$ axis.

When the fluorescence intensity pattern is measured both for polarizer and analyser being parallel (denoted by ∥) and normal (denoted by ⊥), the orientation factors $F_{200}$ and $F_{400}$ can be evaluated by the following equations[8]:

$$F_{200} = \frac{(n+1)(3y - 4x + 3)}{[nP_2(\cos\Theta_1) + P_2(\cos\Theta_2)]\ (8x + 12y + 3)} \tag{5}$$

$$F_{400} = \frac{3(n+1)(x - 6y + 1)}{[nP_4(\cos\Theta_1) + P_4(\cos\Theta_2)]\ (8x + 12y + 3)} \tag{6}$$

$$x = I_{\parallel}(90^\circ)/I_{\parallel}(0^\circ) \tag{7}$$

$$y = I_{\perp}(0^\circ)/I_{\parallel}(0^\circ) \tag{8}$$

The notations (0°) and (90°) in equations (7) and (8) designate the principal values of the fluorescence intensity corresponding to the two cases in which the extension direction, $X_3$ axis, of the sample is parallel with, or perpendicular to, the polarizer.

The fluorescence intensities $I_{\parallel}(\beta)$ and $I_{\perp}(\beta)$, in which the $X_3$ axis makes an arbitrary angle $\beta$ with the polarizer, are theoretically derived from:

$$\begin{aligned}I_{\parallel}(\beta) = {} & \frac{k}{35}\ [n\{8P_4(\cos\beta)P_4(\cos\Theta_1)F_{400} \\ & + 20P_2(\cos\beta)P_2(\cos\Theta_1)F_{200} + 7\} \\ & + \{8P_4(\cos\beta)P_4(\cos\Theta_2)F_{400} \\ & + 20P_2(\cos\beta)P_2(\cos\Theta_2)F_{200} + 7\}]\end{aligned} \tag{9}$$

$$\begin{aligned}I_{\perp}(\beta) = k\ \Bigg[n\ \Bigg\{ & -\frac{8}{35}P_4(\cos\beta)P_4(\cos\Theta_1)F_{400} \\ & + \frac{2}{21}P_2(\cos\beta)P_4(\cos\Theta_1)F_{400} + \frac{2}{105}P_4(\cos\Theta_1)F_{400} \\ & + \frac{1}{21}P_2(\cos\Theta_1)F_{200} + \frac{1}{15}\Bigg\} \\ & + \Bigg\{-\frac{8}{35}P_4(\cos\beta)P_4(\cos\Theta_2)F_{400} \\ & + \frac{1}{21}P_2(\cos\beta)P_4(\cos\Theta_2)F_{400} + \frac{2}{105}P_4(\cos\Theta_2)F_{400} \\ & + \frac{1}{21}P_2(\cos\Theta_2)F_{200} + \frac{1}{15}\Bigg\}\Bigg]\end{aligned} \tag{10}$$

where $k$ is a constant relating to the apparatus, and constants $\Theta_1$, $\Theta_2$ and $n$ are concerned with the fluorescent radicals formed in the sample. Because the fluorescence intensity is obtained through polyene and carbonyl radicals formed in the sample, the constants relevant to the fluorescent radicals are as follows: $n$ is the ratio of polyene to carbonyl, and $\Theta_1$ and $\Theta_2$ are the contact angles of the fluorescent radicals to the main chain axis.

The polarized fluorescence method, including the practical use of equations (5), (6), (9) and (10), was verified and used in the previous paper[8] to evaluate the second and the fourth orientation factors: $\Theta_1 = 20^\circ$, $\Theta_2 = 90^\circ$ and $n = 2.0$. Therefore, if all the elastic compliance elements $S^u_{pq}$ are known, we can calculate Young's modulus in the arbitrary direction of angle $\beta$ with the draw direction in the film, by substituting the evaluated $F_{200}$ and $F_{400}$ into equation (4) as will be described later.

## PREPARATION OF SAMPLE

PVC film ($P_n$ = 1300) was produced by the T-die method and used for initial stretching after assuring that it was in the non-oriented state by the birefringence method. The film was heat-treated at 150° ± 1°C for 30 min in a constant temperature chamber in order to increase its fluorescence intensity, and then uniaxially stretched at a constant rate of 10%/min to specified extension ratios under the following conditions. The draw temperature was 65° and 110°C – below and above the glass temperature ($T_g$ = 85°C) – and the film was cut in the shape of a dumb-bell 15 cm long and 10 cm wide.

## METHOD OF MEASUREMENT

### *Birefringence*

The value of birefringence was derived from the retardation with a polarizing microscope (Nihon-Kogaku PX–OH-2) equipped with a Berek compensator.

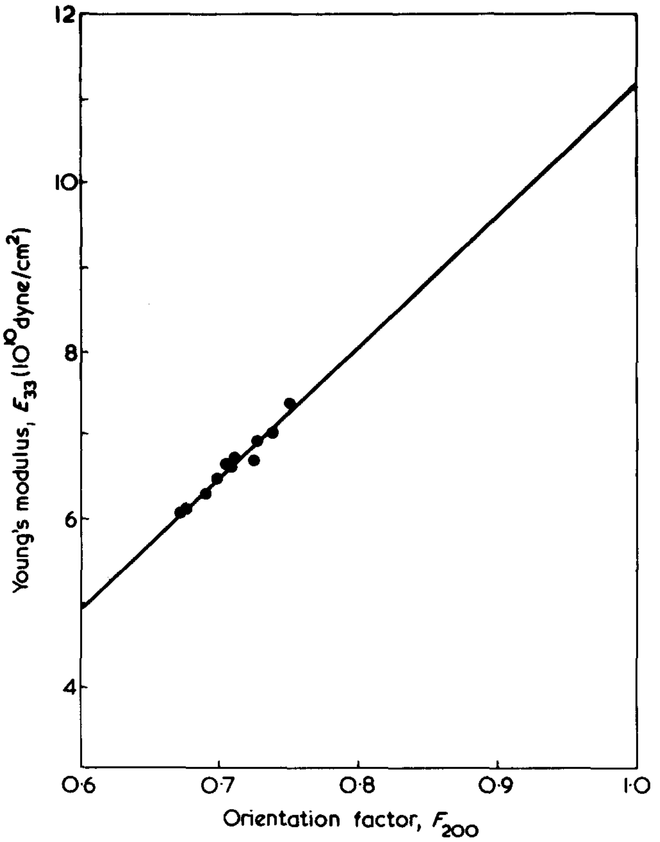

*Figure 1* Method of estimation of $E^u_{33}$ in the structural unit, 11.2 x $10^{10}$ dyne/cm$^2$ being estimated by extrapolation at $F_{200} = 1$

*Polarized fluorescence intensity*

The measurement was performed by the reflection method with a polarized fluorometer (Nihon-Bunko FOM-1).

*Young's modulus*

Test pieces 35 mm long, 0.5–1.0 mm wide and 0.1–0.2 mm thick were cut in all directions of 15° between $\beta$ = 0° and 90°, and then measured at 23° ± 1°C and 110 Hz with a Vibron DDV-II (Toyo Measuring Instrument Co.).

## ESTIMATION OF ELASTIC COMPLIANCES IN STRUCTURAL UNIT

The elastic compliance is assumed to be the same as that of a perfectly uniaxially stretched sample and the value of the compliance is supposed to be kept constant during the uniaxial stretching process at different draw temperatures. Furthermore, it is postulated that the orientation of the structural unit conforms to that of the molecular chain axis.

The compliance elements of the structural unit shown in equation (1) are determined as follows. Young's moduli in the initial draw direction (draw ratio 2.5 to 4.0) were first plotted as shown in *Figure 1* against the orientation factor $F_{200}$, and the elastic compliance element $S^u_{33}$ was estimated as the reciprocal of the extrapolated value at $F_{200} = 1.0$. Similarly, the reciprocal of the extrapolated Young's modulus in the transverse direction was taken as $S^u_{11}$. Since the samples used were too thin to determine the value of $S^u_{44}$ by direct measurement, the following indirect method was applied[5]. If we take a parameter $\epsilon$, the relation $(2S^u_{13} + S^u_{44}) = \epsilon(2S^u_{12} + S^u_{66}) = 2\epsilon S^u_{11}$ is true for the structural unit with cylindrical symmetry about the $X^u_3$ axis. The value of $(2S^u_{13} + S^u_{44})$ was therefore evaluated from $S^u_{11}$ after determining the values of $\epsilon$ and $S^u_{13}$. The values of $S^u_{12}$ and $S^u_{13}$ were calculated on the assumption that Poisson's ratios $\nu_{12}$ and $\nu_{13}$ are equal to 0.46 by referring to the values presented by Hennig[9], and the value of $\epsilon$ was determined experimentally as will be shown later.

## RESULTS AND DISCUSSION

*Figure 2* shows the experimental results for birefringence, and the curves (A and B) derived from the calculation described in the first paper of this series: curve A conforms to the affine deformation of a rigid molecular chain and curve B follows from the mixture of rigid molecular chain and Langevin chain proposed by Roe and Krigbaum[10]. Good agreement between the curves and the points shows that the assumption regarding the molecular orientation function and the characteristic parameters may be acceptable. The parameters used for this sample are as follows: the segment number in the Langevin chain is 10 and the ratio of rigid chain to Langevin chain is 70:30.

It is evident from this Figure that samples drawn above and below the glass temperature have different molecular orientations for the same draw ratio, and comparison of the results of the samples annealed at 120°C with those annealed at 150°C shows that the effect of heat treatment cannot be appreciable.

The determination of the ratio *n* (polyene to carbonyl) is carried out as shown in *Figure 3*. The fluorescence intensity ratio $I_{\|}(90°)/I_{\|}(0°)$ is taken as the ordinate and curves, calculated from equation (9) for different value of the parameter *n* using the postulated orientation factors. Comparison of these curves with the measured values leads to $n = 2.0$.

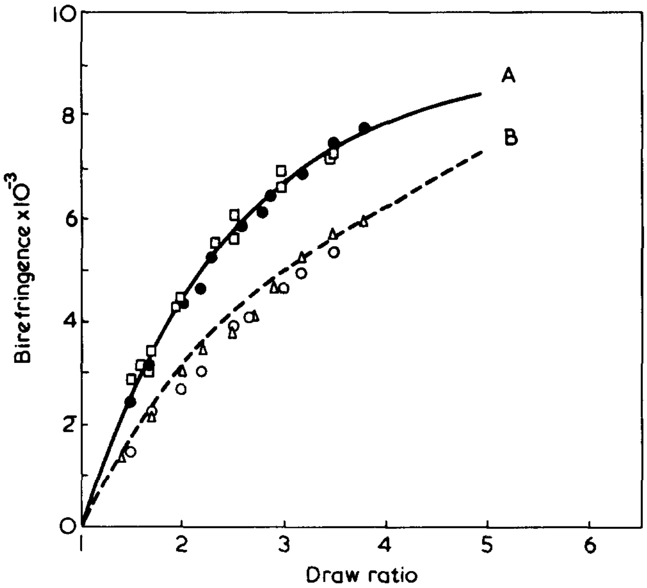

*Figure 2* Change of birefringence with draw ratio; A (affine) and B (affine + Langevin) are calculated from the distribution functions indicated in this Figure. ●, Draw temperature 65°C, annealed temperature 120°C; △, draw temperature 110°C, annealed temperature 120°C; □, draw temperature 65°C, annealed temperature 150°C; ○, draw temperature 110°C, annealed temperature 150°C

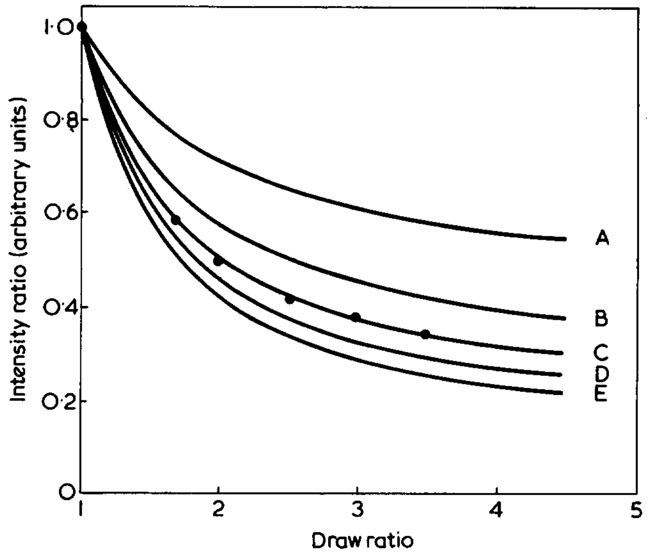

*Figure 3* Estimation of value of $n$; A–E are calculated with specified value of $n$ and the one having $n = 2.0$ is the best fit. A, $n = 1.0$; B, $n = 1.5$; C, $n = 2.0$; D, $n = 2.5$; E, $n = 3.0$

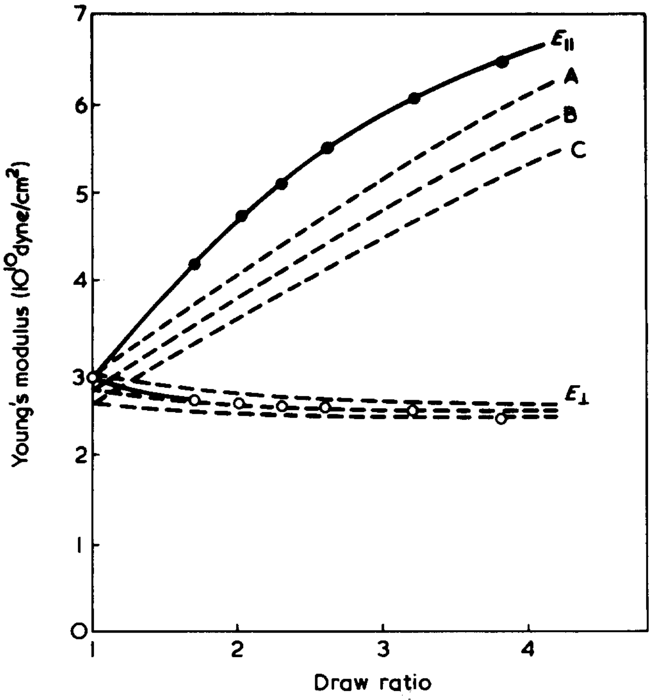

*Figure 4* Change in Young's modulus in the initial draw direction and the transverse direction with draw ratio for the samples drawn below $T_g$: — — — —, calculated with parameter $\epsilon$; ●, $E_{\parallel}$; ○, $E_{\perp}$. A, $\epsilon = 1.0$; B, $\epsilon = 1.2$; C, $\epsilon = 1.4$

Therefore, we can evaluate the orientation factors $F_{200}$ and $F_{400}$ from equations (5), (6), (7) and (8) by using the measured fluorescence intensity at an arbitrary extension of the sample.

In *Figure 4* the plotted points are measured values of Young's modulus in the initial stretch direction and in the transverse direction for the film drawn at 65°C; the broken curves are results of the substitution of numerical values of the elastic compliance parameter $\epsilon$ and $F_{l00}$ into equation (4). According to the theory of Hill[11], the calculated Young's modulus using the assumption of uniform stress field should not be larger than that of the true value, the value of $\epsilon = 1.2$ was determined from *Figure 4* and this value of $\epsilon$ was used for the calculation of Young's modulus.

The values of the elastic compliance elements are tabulated together with Hennig's results, in *Table 1*. The value of $S^u_{33}$ is smaller than that of Hennig's values because of the difference in the state of the film; the sample in our calculation is a perfectly drawn sample contrary to Hennig's case where the sample was stretched by 150%. In the calculation of the curves denoted by broken lines in *Figures 5* to *7*, the evaluated numerical values listed in *Table 1* are used in equation (4). Taking into account Hill's restriction, we see from *Figures 4* to *7* that the calculated curve adequately explains the dependence of the measured Young's modulus on the change in draw ratio and measuring direction.

Since the structural unit has been assumed to be independent of draw ratio and draw temperature, it appears from equation (4) that the draw ratio dependence of Young's modulus and its anisotropy may be defined by the degree of molecular orientation alone. The result shown in *Figures 8* and *9*, which were derived as described in the following paragraphs, support this conclusion.

Values of draw ratio of samples drawn at 65° and 110°C, with the same birefringence value, were selected from *Figure 2*; for example, a draw ratio of 1.7 for the sample drawn at 65°C is equivalent to 2.2 for the one drawn at 110°C. Each measured value of Young's modulus, corresponding to the equivalent draw ratio is picked out and then replotted in *Figure 8* by taking the values for draw tempera-

*Table 1* Numerical values of elastic compliance elements estimated in this paper, and the values proposed by Hennig[9]

| Compliance, $S^u_{ji}$ (cm$^2$/dyne) | This paper | Hennig |
|---|---|---|
| $S^u_{33}$ | $0.89 \times 10^{-11}$ | $2.0 \times 10^{-11}$ |
| $S^u_{22}$ | 4.01 × | 3.7 × |
| $S^u_{44}$ | 10.44 × | 7.1 × |
| $S^u_{12}$ | −1.84 × | −1.7 × |
| $S^u_{23}$ | −0.41 × | −0.93 × |

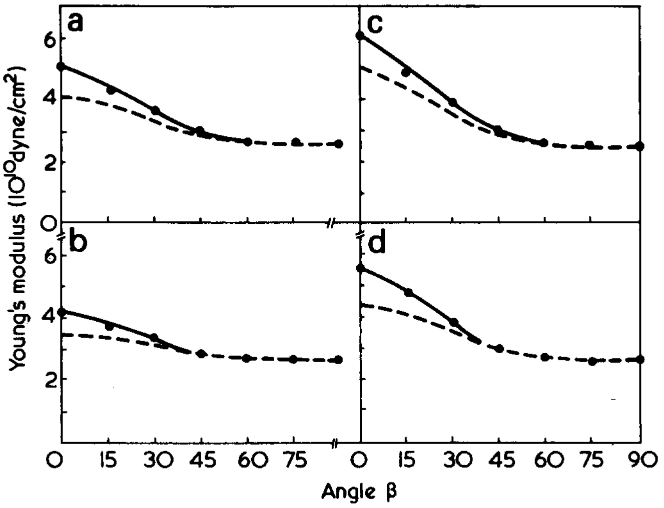

*Figure 5* Anisotropy of Young's modulus for the samples drawn below $T_g$ up to different draw ratios, the broken lines being calculated values. (a) *DR* 2.3; (b) *DR* 1.7; (c) *DR* 3.2; (d) *DR* 2.6

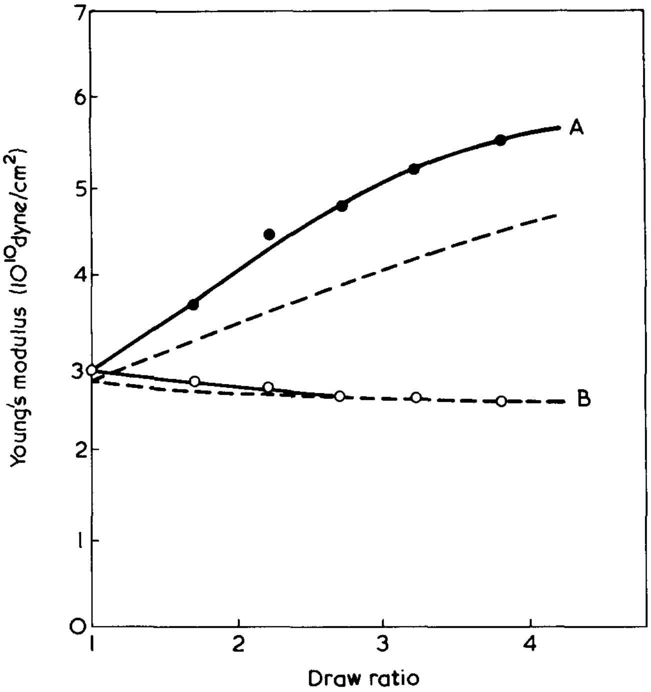

*Figure 6* Change in Young's modulus parallel with and perpendicular to the initial draw direction with draw ratio for the samples drawn above $T_g$. A, $E_{\parallel}$; B, $E_{\perp}$; – – – –, calculated (affine, Langevin)

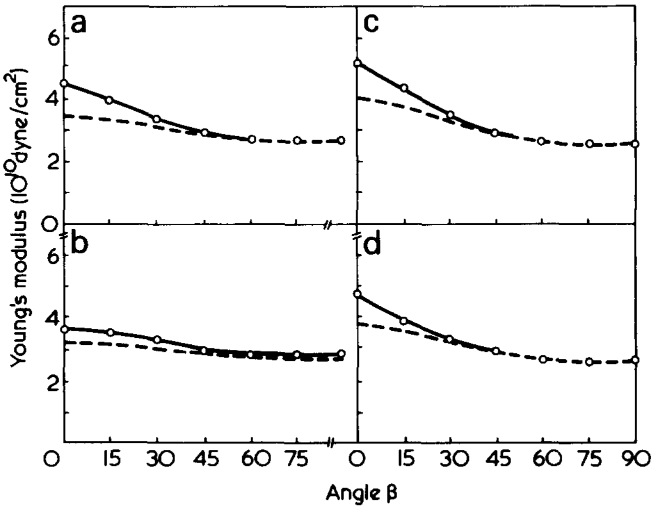

*Figure 7* The anisotropy of Young's modulus for the samples drawn above $T_g$. (a) *DR* 2.2; (b) *DR* 1.7; (c) *DR* 3.2; (d) *DR* 2.7

ture 65°C as abscissa and those for 110°C as ordinate. The result shows that each point lies on the bisector. If we plot the Young's moduli in the directions $\beta = 0°$ and 90° against the change of birefringence value for the two samples, the points lie on the corresponding two curves as shown in *Figure 9* independent of the draw temperature. Accordingly, Young's modulus of uniaxially stretched PVC film appears to be defined by the second moment of molecular orientation alone and irrespective of the structural element defining the molecular orientation – rigid rod-like chain or segment in Langevin chain in our assumed orientation distribution function.

However, it is apparent from equation (4) that Young's modulus is a function of the molecular orientation through $F_{400}$ as well as $F_{200}$, so that the result in *Figure 9* seems to reflect the structural feature of PVC films stretched uniaxially. In these films the significant difference is so small – the value of $\langle\cos^2\Theta\rangle$ is slightly larger than that of $\langle\cos^4\Theta\rangle$ (refer to Figure 5 in part 2[8]) – that only the second moment appears to govern the value of Young's modulus. The result calculated from equation (4) by using $F_{200}$ for the corresponding terms is shown in a dot–dash line in *Figure 10* in order to establish this fact.

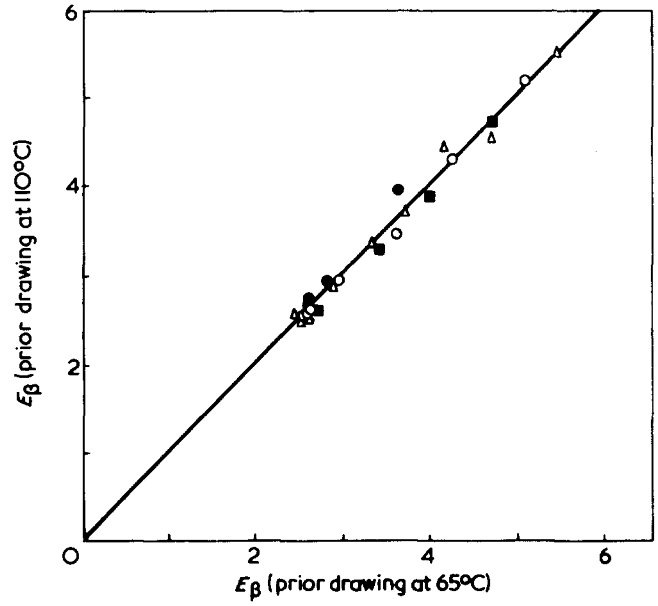

*Figure 8* Correlation between Young's moduli of the samples with the same birefringence value, drawn above and below $T_g$. ●, 65°C (x1.7) vs. 110°C (x2.2); ■, 65°C (x2.0) vs. 110°C (x2.7); ○, 65°C (x2.3) vs. 110°C (x3.2); △, 65°C (x2.6) vs. 110°C (x3.8)

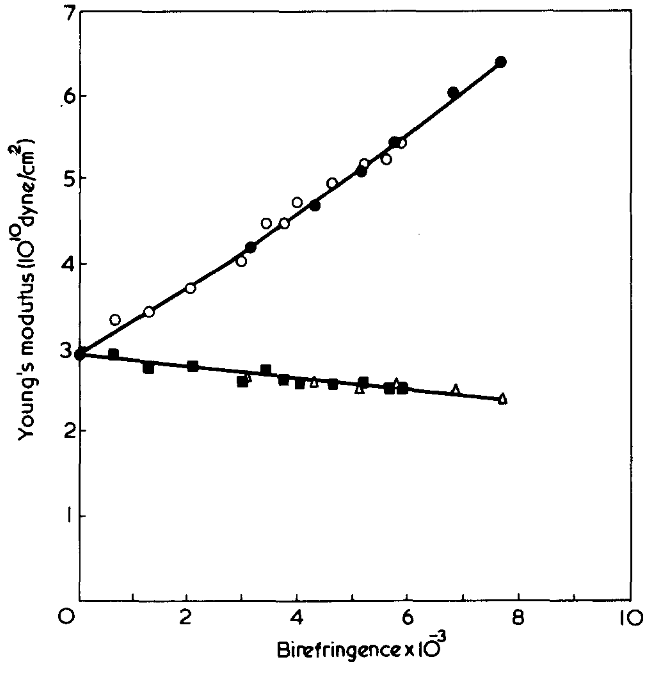

*Figure 9* Dependence of Young's modulus, in the directions parallel with and normal to the initial draw driection, upon birefringence. ●, $E_{\parallel}$, 65°C; △, $E_{\perp}$, 65°C; ○, $E_{\parallel}$, 110°C; ■, $E_{\perp}$, 110°C

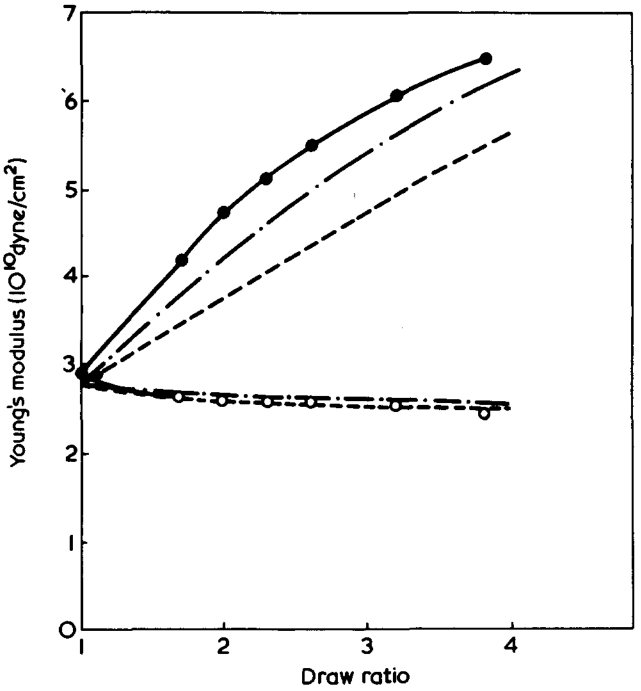

*Figure 10* The effect of substitution of $F_{200}$ for $F_{400}$ in the calculation of Young's modulus for the sample drawn below $T_g$: —·— shows the result from using $F_{200}$ alone; — — — —, indicates the ordinary one having $\epsilon = 1.2$ quoted from *Figure 4*. ●, $E_{\parallel}$; ○, $E_{\perp}$

## CONCLUSIONS

An aggregation model consisting of a structural unit having elastic compliance which is obtained by extrapolation to the perfectly, uniaxially, stretched sample, is applicable to evaluate Young's modulus in uniaxially stretched PVC film when orientation of the structural unit is taken to conform to the orientation of the molecular chain axis. In addition it is found that the orientation factors $F_{200}$ and $F_{400}$ evaluated from the results of polarized fluorescence intensity are valid for this calculation. Considering the fact that the structural unit used in this mechanical model is kept constant without relating to the draw ratio and the draw temperature, Young's moduli and their anisotropy in the uniaxially stretched PVC film may be uniquely specified by the second and fourth moments.

As pseudo-affine deformation is the prevailing factor in the molecular orientation in these samples, the difference between the second and the fourth moments, $\langle\cos^2\Theta\rangle$ and $\langle\cos^4\Theta\rangle$, does not become large under the experimental conditions of this work, and thus the value of Young's modulus appears to be governed by the second moment (birefringence) alone. Although molecular interpretation of the structural unit is scarcely touched upon in this paper, it is important to consider this in future studies in order to investigate the relationship between the nature of elastic compliance in the structural unit and the molecular configuration or conformation.

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