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Studies of the Effect of Orientation on the Elastic Constants of Stretched and Hydrostatically Extruded Poly (Chlorotriflouroethylene): A Model of Affine Orientation in Semi-Crystalline Polymers

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STUDIES OF THE EFFECT OF ORIENTATION ON THE ELASTIC CONSTANTS OF STRETCHED AND HYDROSTATICALLY EXTRUDED POLY (CHLOROTRIFLOUROETHYLENE): A MODEL OF AFFINE ORIENTATION IN SEMI-CRYSTALLINE POLYMERS

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ABSTRACT

A model of affine orientation of polymer solids is given. The solid is described as a collection of small, orientable units. The elastic constants of the oriented polymer are given as a combination of the elastic constants of the orientable units and of the orientation parameters $\langle \overset{\text{sub}}{P_2}(\cos \overset{\text{theta}}{\theta})\rangle$ and $\langle \overset{\text{sub}}{P_4}(\cos \overset{\text{theta}}{\theta})\rangle$. The elastic constants of stretched and hydrostatically extruded samples of poly (chlorotriflouroethylene) are obtained with Brillouin light scattering. These are fitted to the model and the orientation parameters are calculated. The elastic constants from the extruded samples are fit well by the model but the fit to the stretched film is less satisfactory by the model. Hydrostatic extrusion in polymers is thus assumed to be an affine orientation process in the amorphous phase and the stretching process is non-affine.

INTRODUCTION

In solid polymers the distribution of molecular chain orientation has a strong effect on macroscopic physical properties of those samples. To characterize the degree of chain orientation which is produced by deformation processes such as stretching or extrusion a variety of techniques have been employed. The techniques include x-ray diffraction, polarized Raman spectroscopy,[1] wide line NMR,[2] and birefringence measurements, and give information that is specific to certain regions of the poly microstructure. For example, x-ray diffraction is generally used to determine the orientation distribution of the crystalline regions. The polarized Raman technique can give the information about the orientation distribution of polymers in both the amorphous and crystalline regions, and from each individual region, depending on the nature of the Raman band that is analyzed.

The various analytical methods give different amounts of information about the orientation depending on the physical property that is measured. X-ray and birefringence methods can give the second moment of the orientation distribution function. In principle, Raman methods give the second and fourth moments while NMR methods can supply up to the sixth moment of the distribution function, but in practice, Raman and NMR are limited by experimental difficulties.

Sonic methods have also been used to determine the second moment of the distribution. The model proposed by Moseley[3] relates the sound velocity along the orientation axis of a fiber to the degree of orientation of the chains within the sample. The analysis includes rather severe approximation and it accounts only for the elastic constant C_{33} rather than the full set of elastic constants.

Ward has derived a model[4] to relate the elastic stiffness (C_{ab}) or the elastic compliances (S_{ab}) to the extension ratio of oriented polymers. This model assumes the polymer to be an aggregate of small, cylindrical units. The elastic constants of the material are determined by the elastic constants of the material and the degree of orientation of the polymer. This model has been moderately successful in predicting qualitatively the elastic constants of oriented polymers;[5,6] however, it does not provide the orientation parameters which characterize the orientation distribution of the polymer. A drawback in testing this model is that the elastic constant data used haved been imprecise due to large errors inherent in the available measurement techniques.

We have recently developed a technique using Brillouin light scattering to measure accurately the various elastic constant tensor components of oriented polymer samples.[7] Brillouin light scattering occurs by the inelastic scattering of light from the accoustic phonons in a given medium. The Brillouin spectrum consists of the Rayleigh line, which is centered at the laser frequency, and one or more sets of doublets which are shifted higher and lower in frequency from the Rayleigh line. The Brillouin frequency shift in a birefringent medium is related to the hypersonic velocity in the sample by the expression:

$$V_s = \frac{f_B \lambda_i}{(n_i^2 + n_s^2 - 2n_i n_s \cos\theta)^{\frac{1}{2}}} \qquad (1)$$

where f_B is the measured Brillouin frequency, λ_i is the incident wavelength in vaccuo, n_i and n_s are the refractive indices along the incident and scattered directions and θ is the scattering angle.

Poly(chlorotrifluoroethylene) (PCTFE) is a semi-crystalline polymer which has a spherultic superstructure when annealed near the crystalline melt point and a superstructure consisting of a random array of small disordered crystallites when quenched from the melt.[8] X-ray diffraction of PCTFE films has shown that as the films are stretched the orientation of the crystalline regions occurs affinely in the melt quenched samples. In other samples which have a spherultic superstructure, the crystalline regions within the spherulites interact so that the deformation does not occur affinely.

Two of the methods of orienting solid polymers that are used extensively in fabrication processes are stretching and extrusion. Each of these processes are known to cause the polymer chains in both the amorphous and crystalline regions to align with the orientation axis. However, the mechanism involved in stretching a film and forcing a polymer billet through a dye may be quite different and we should expect to observe some difference in the morphology produced by each process.

In this work we described a theoretical model which relates the orientation of polymer chains to the macroscopically observed elastic constants. From this model we obtain the second and fourth moments, $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$, of the orientation distribution. This model is then used to compare the morphology of stretched films and hydrostatically extruded rods of PCTFE using the elastic constants obtained with Brillouin scattering.

Theoretical

In this model the structure of a solid polymer is described as a collection of small orientable units, which are similar to those in the model of Ward.[4] It is assumed that the size of the units is smaller than the phonon wavelength (~5000 Å), and that the density of the sample does not change with orientation. For simplicity we also assume that each basic unit has cylindrical symmetry in which the x and y axes are equivalent and the z axis is unique. The collection of the basic units when perfectly oriented has the elastic constant tensor given by:

$$\underset{\approx}{C}^{\circ} = \begin{pmatrix} C^{\circ}_{11} & C^{\circ}_{12} & C^{\circ}_{13} & & & \\ C^{\circ}_{12} & C^{\circ}_{11} & C^{\circ}_{13} & & & \\ C^{\circ}_{13} & C^{\circ}_{13} & C^{\circ}_{33} & & 0 & \\ & & & C^{\circ}_{44} & & \\ & & 0 & & C^{\circ}_{44} & \\ & & & & & C^{\circ}_{66} \end{pmatrix} \qquad (2)$$

where $C^{\circ}_{66} = \frac{1}{2}(C^{\circ}_{11} - C^{\circ}_{12})$. The collection of the perfectly orientated basic units have the ultimate elastic constants which are heretofore referred to as intrinsic (elastic) constants. In the unoriented sample, the basic units are randomly oriented and the elastic constant tensor of such an unoriented sample does not have the form of Eq.(2). instead it has a structure of an isotropic solid. When the polymer is deformed the basic units are oriented in the material so that the z-axes of the units are aligned with the axis of orientation. The elastic constants of the deformed polymer are then a linear combination of the intrinsic elastic constants of the perfectly oriented sample. In this model, we neglect the process of plastic deformation, and the deformation only occurs affinely.

The elastic constant tensor is of fourth rank and when subject to orientation it obeys the transformation law:

$$C_{efgh} = a_{ej} a_{fk} a_{gl} a_{hm} C^{\circ}_{jklm} \qquad (3)$$

where the a_{ij} are the rotation matrix elements which relate the original coordinate axes to the deformed axes. The C°_{jlkm} are the intrinsic tensor components in the original coordinate system, and

C'_{efgh} is the transformed tensor component in the new coordinate system. The new coordinate system is defined in accordance with the deformed system. The operation sympolized by Eq. (3) is facilitated with the Bond (M) matrix method.[9]

To accomplish the calculation as expressed by Eq. (3), we start with the basic units which are aligned perfectly with the material coordinate system so that the z axis of the units is along the Z axis of the deformed material. The units are rotated collectively about the Y axis through an angle θ, as illustrated in Figure 1 Using Eq. (3) and evaluating the a_{ij}'s, we have found that the transformed elastic constant tensor has the following form:

$$C'_{ba} = \begin{pmatrix} C'_{11} & C'_{12} & C'_{13} & 0 & C'_{15} & 0 \\ C'_{12} & C^{\circ}_{11} & C'_{23} & 0 & C'_{25} & 0 \\ C'_{13} & C'_{23} & C'_{33} & 0 & C'_{35} & 0 \\ 0 & 0 & 0 & C'_{44} & 0 & C'_{46} \\ C'_{15} & C'_{25} & C'_{35} & 0 & C'_{55} & 0 \\ 0 & 0 & 0 & C'_{46} & 0 & C'_{66} \end{pmatrix} \qquad (4)$$

where, the elastic constant tensor elements are functions of the intrinsic elements and θ. For example, $C'_{11} = C^{\circ}_{11} \cos^4\theta + C^{\circ}_{33} \sin^4\theta + 2C^{\circ}_{13} \sin^2\theta \cos^2\theta + C^{\circ}_{44} \sin^2 2\theta$.

We then transform C_{ij} using an equation similar to Eq. (3) by rotating the units around the Z axis of the material through the angle ϕ, as shown in Figure 1 Since the deformed sample has cylindrical symmetry, all angles of ϕ are equally probable; we thus perform an average on each component of the transformed elastic constant over ϕ by integration over the full range of ϕ. Furthermore, since each basic unit will be oriented differently with respect to the Z-axis of the original coordinate system, we also need to average the orientation angle θ over an orientational distribution function. The resultant elastic constant tensor of the deformed sample is:

$$C''_{ab} = \begin{pmatrix} C''_{11} & C''_{12} & C''_{13} & 0 & 0 & 0 \\ C''_{12} & C''_{11} & C''_{13} & 0 & 0 & 0 \\ C''_{13} & C''_{13} & C''_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C''_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C''_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C''_{66} \end{pmatrix} \tag{5}$$

where the various elastic constant tensor elements are given by:

$$\begin{aligned} C''_{11} = {} & 1/21(8C^{\circ}_{11} - 2C^{\circ}_{13} - 6C^{\circ}_{33} - 4C^{\circ}_{44}) \langle P_2 \rangle \\ & + 1/35(3C^{\circ}_{11} - 6C^{\circ}_{13} + 3C^{\circ}_{33} - 12C^{\circ}_{44}) \langle P_4 \rangle \\ & + 1/15(8C^{\circ}_{11} + 4C^{\circ}_{13} + 3C^{\circ}_{33} + 8C^{\circ}_{44}) \end{aligned} \tag{6}$$

$$\begin{aligned} C''_{33} = {} & 1/21(4C^{\circ}_{13} - 16C^{\circ}_{11} + 12C^{\circ}_{33} + 8C^{\circ}_{44}) \langle P_2 \rangle \\ & + 1/35(8C^{\circ}_{11} = 16C^{\circ}_{13} + 8C^{\circ}_{33} - 32C^{\circ}_{44}) \langle P_4 \rangle \\ & + 1/15(8C^{\circ}_{11} + 4C^{\circ}_{13} + 3C^{\circ}_{33} + 8C^{\circ}_{44}) \end{aligned} \tag{7}$$

$$C''_{44} = 1/21(C^{o}_{11} + C^{o}_{33} - 2C^{o}_{13} + 3C^{o}_{44} - 7C^{o}_{66}) \langle P_2 \rangle$$
$$+ 1/35(8C^{o}_{13} - 4C^{o}_{11} - 4C^{o}_{33} + 16C^{o}_{44}) \langle P_4 \rangle$$
$$+ 1/15(C^{o}_{11} + C^{o}_{33} - 2C^{o}_{13} + 6C^{o}_{44} + 5C^{o}_{66}) \tag{8}$$

$$C''_{13} = 1/21(C^{o}_{11} + C^{o}_{33} + 5C^{o}_{13} - 4C^{o}_{44} - 7C^{o}_{12}) \langle P_2 \rangle$$
$$+ 1/35(8C^{o}_{13} + 16C^{o}_{44} - 4C^{o}_{11} - 4C^{o}_{33}) \langle P_4 \rangle$$
$$+ 1/15(C^{o}_{11} + C^{o}_{33} + 8C^{o}_{13} - 4C^{o}_{44} + 5C^{o}_{12}) \quad . \tag{9}$$

where $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are Legendre polynomials of order 2 and 4. They are related to $\cos^2\theta$ and $\cos^4\theta$ by

$$\begin{aligned} \cos^2\theta &= (2P_2 + 1)/3 \\ \cos^4\theta &= (20P_2 + 8P_4 + 7)/35 \end{aligned} \tag{10}$$

The angular brackets denote average over the orientational distribution function $f(\theta)$. For an oriented polymer chain, the orientational distribution function can be expanded in terms of Legendre polynomials. $P_K(\cos\theta)$ as [10]

$$f(\theta) = \sum A_K P_K(\cos\theta) \tag{11}$$

where the expansion constants A_K are the orientational parameters which are given by

$$A_K = \int_0^{\pi} f(\theta) P_K(\cos\theta) \sin\theta d\theta = \langle P_K \rangle \; . \tag{12}$$

Since the C''_{ab} can be determined experimentally from the Brillouin frequency shifts, the orientational parameters $<P_2>$ and $<P_4>$ as well as the intrinsic elastic constants corresponding to the perfectly oriented polymer chain can be obtained by using Brillouin scattering.

One notes that these equations satisfy the conditions that in the fully oriented sample in which $<P_2> = <P_4> = 1$, C''_{ab} reduces to the intrinsic elastic constants, i.e.,

$$C''_{ab} = C^{\circ}_{ab} \quad . \tag{13}$$

Equations (6) and (8) are identical to those of Ward,[4] and Reuss and Voight[11,12] for an unoriented sample, where $<P_2> = <P_4> = 0$. In the unoriented sample the equations reduce to the isotropic consistency relation:

$$C^{u}_{44} = \frac{1}{2}(C^{u}_{11} - C^{u}_{13}) \tag{14}$$

where:

$$C^{u}_{12} = C^{u}_{13} \tag{15}$$

and

$$C^{u}_{11} = C^{u}_{33} \quad . \tag{16}$$

Experimental

The extruded samples used in these experiments are made from PCTFE having the trade name Diaflon which is supplied to us by the courtesy of Dr. H. Kanetsuna (Japan).

The extrusion temperature was 110°C and the extrusion pressure ranged between 440 Kg/cm^2 and Kg/cm^2 for samples of low and high extrusion ratios.[13] Samples with extrusion ratios of 1.00, 1.94, 2.80 and 3.66 were prepared. The samples used for the light scattering experiments are cut from the extruded rod samples on a diamond-wheel saw in the form of thin plates. The plates are cut so the extrusion axis and the faces of the plates are parallel. The plate faces are polished to an optically smooth finish. The samples vary from translucent in the unextruded sample to transparent in the high extrusion ratio.

The film samples are prepared from Kel-F, KF-6061 PCTFE supplied by the courtsey of the 3-M Company. The PCTFE in powder form was melt pressed into films at 270°C and 1 metric ton of pressure. The molten polymer was quenched in ice water to limit the growth of crystallinity. Rectangular pieces of the film were stretched with a film stretcher in a water bath at 80°C to draw ratios of 1.00, 1.80, 2.28, 2.88 and 3.50. The films did not neck as they were stretched. All films are of equally good optical quality, and are transparent.

The density of the samples was measured in a density gradient column with a dibromemethane-tetrachloroethane mixture. The densities of all extruded samples are the same and were measured to be 2.132 g/cc. This corresponds to a 47% crystalline fraction. The stretched sample densities were also unchanged by stretching and the stretched sample density is measured to be 2.093 g/cc which corresponds to a crystalline fraction of 20%.

A piezoelectrically scanned five pass Fabry Perot interferometer is used to resolve the Brillouin spectrum. The free spectral range (FSR) is 30 GHZ and the instrumental finnesse is above 60. The 4880 Å line from an Ar-ion laser is the incident light source. The polarization of the scattered light is selected with a Glan-Thompson prism polarizer and all spectra reported here are obtained in the VV polarization configuration.

The elastic constants of both the extruded and stretched samples, were obtained using the same experimental technique developed in our laboratory. The experimental details have been explained previously.[7] Briefly, the film or plate sample is mounted on a goniometer. The sample is rotated so that the scattering vector, $\vec{q}$, lies in the x-z plane of the film at some angle, α, to the orientation axis (or z axis). The Brillouin spectra are recorded at a series of angles between 0° ($\vec{q}$ along z) and 90° ($\vec{q}$ along x). From the Brillouin frequencies, the sound velocities of the quasilongitudinal and quasitransverse waves are calculated. The sound velocities in each sample are then fitted with a computer routine to elastic theory as a function of the angle α. The elastic constants C_{11}, C_{33}, C_{44} and C_{13} which provide the best fit of the theoretical velocity contours to the experimental contours are thus obtained.

In previous experiments[14] the four elastic constants in extruded polymer samples were measured using three scattering configurations. The error in the elastic constants C_{13} and C_{44} measured in this way are large, due to the method of analysis and uncertainties in the refractive index. The method used in this work eliminates the difficulty with optical birefrigence.[15] All of the elastic constants are reported with an equal degree of uncertainty and the elastic constant measurements from the extruded and stretched samples are of equal precision.

Results and Discussion

The sound velocity contours were measured in the stretched and extruded samples. The contours of the samples with the highest stretch and extrusion ratios are shown in Figure 2. The solid dots are the experimental points and the curve contours are theoretical curves calculated using equations given previously.[7] These are:

$$\begin{aligned} 2\rho V_{\pm}^{2} = {} & (C_{11}\ell_x^{2} + C_{33}\ell_z^{2} + 2C_{44}) \pm \{(C_{11}\ell_x^{2} + C_{33}\ell_z^{2} + 2C_{44})^{2} \\ & - 4[(C_{11}\ell_x^{2} + C_{44}\ell_z^{2})(C_{44}\ell_x^{2} + C_{33}\ell_z^{2}) \\ & - \ell_x^{2}\ell_z^{2}\,(C_{13} + C_{44})^{2}]\}^{\frac{1}{2}}\,, \qquad (17) \end{aligned}$$

where $\ell_x = \sin\alpha$ and $\ell_z = \cos\alpha$ are the direction cosines of $\vec{q}$ along the film coordinate axes, ρ is the sample density and $V_{\pm}$ are the velocities of the quasilongitudinal and quasitransverse waves, respectively.

It is evident that for similar deformation ratios stretching produces a higher modulus along the orientation axis. The velocity contour of the unextruded sample showed that this sample has a small degree of orientation. The velocity contour of the unstretched film sample is circular in shape indicating that it is fully isotropic.

The elastic constants obtained by fitting the experimental contours to elastic theory are plotted versus deformation ratio in Figure 3 In the stretched samples C_{33} is seen to increase linearly with stretch ratio (Figure (3a) and in the extruded samples to increase non-linearly (Figure (3b). C_{11} decreased linearly in both samples. C_{44} is constant with deformation in both samples. We have found that C_{44} remains constant with deformation in other deformed polymers, [7,14,15,16] so this appears to be a general result. C_{13} follows a different trend in each process. In the extruded samples C_{13} decreases with deformation while in the stretched samples C_{13} increases with deformation. An increase of C_{13} has been found two other stretched polymers.[7,16] The decrease of C_{13} in extruded polypropylene was also found,[14] although in that work the experimental uncertainty was large. The elastic constants with deformation that are found in PCTFE appear to be typical of the semicrystalline polymers.

To obtain the orientation parameters from the experimentally measured elastic constant using the model described earlier we must first determine the intrinsic elastic constants of the perfectly oriented units. Experimentally we have found that the elastic constant C_{11} of an oriented polymer is less than the elastic constant of the unoriented polymer. Namely, $C^{\circ}_{11} < C^{u}_{11}$, where C^{u}_{11} is measured in the unoriented polymer. Thus, it is convenient to define:

$$C^{\circ}_{11} = A\, C^{u}_{11} \qquad (18)$$

where A is a parameter which is less than unity. Similarly, C_{33} in the oriented sample is always greater than C^u_{11}, therefore:

$$C^o_{33} = B\,C_{11} \qquad (19)$$

where B is a parameter greater than unity.

The value of C_{44}, as mentioned earlier, has been found to remain constant with deformation in several polymers. This appears to be a general results, therefore we assume that:

$$C^o_{44} = C^u_{44} \qquad (20)$$

The values of C^o_{13} and C^o_{12} can be found from Eqs. (6) and (8) for the case where $\langle P_2\rangle = \langle P_4\rangle = 0$, and Eqs. (18), (19) and (20), so that:

$$C^o_{13} = 15/4\, C^u_{11} - 3/4\, C^o_{33} - 2C^o_{11} - 2C^u_{44} \qquad (21)$$

$$C^o_{12} = 3C^o_{11} - 3C^u_{11} + C^o_{33} - 2C^u_{44} \qquad (22)$$

When the condition stated by Eq. (20) holds, the first two terms on the right side of Eq. (8) must add to zero for all values of $\langle P_2\rangle$ and $\langle P_4\rangle$. When the intrinsic constant set is substituted into the two terms in Eq. (8), we find an important result:

$$\langle P_2\rangle = \langle P_4\rangle\ . \qquad (23)$$

Substituting Eq. (6) into Eqs. (6), 7) and (9), we obtain simple expressions for the various elastic constants:

$$C''_{11} = (1 - \langle P_2\rangle)\, C^{u}_{11} + C^{\circ}_{11}\, \langle P_2\rangle \qquad (24)$$

$$C''_{33} = (1 - \langle P_2\rangle)\, C^{u}_{11} + C^{\circ}_{33}\, \langle P_2\rangle \qquad (25)$$

$$C''_{13} = (1 - \langle P_2\rangle)\, C^{u}_{13} + C^{\circ}_{13}\, \langle P_2\rangle \qquad (26)$$

The oreintation parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ that have been measured in polymers with various experimental methods are found to have similar values[10] however, the general result given in Eq. (23) is found first by us in the present paper.

To obtain the orientation parameters, the experimental elastic constants are fit to this model on a computer by the following scheme: we first make initial guesses of the values A and B, which, along with the unoriented elastic constants determine a full set of intrinsic constants. The value of $\langle P_2\rangle$ for each sample is then calculated from the experimental values C_{11} and C_{33} with the help of Eqs. (24) and (25). C''_{11}, C''_{33}, C''_{44} and C''_{13} are then calculated from Eqs. (6) - (9) letting $\langle P_2\rangle = \langle P_4\rangle$. The calculated results are compared with the experimental results and the process is repeated, varying A and B to minimize the difference between the experimental results and the calculated results.

Figure 4 shows the orientation parameter $\langle P_2\rangle$ plotted versus deformation ratio for the stretched and extruded samples. One notes that $\langle P_2\rangle$ increases linearly in the stretched samples, whereas, the increase is slower in the extruded samples which approach a limiting value at high extrusion ratios. The unextruded sample is slightly oriented as determined from the sound velocity contour, therefore $<P_2>$ for this sample is greater than zero.

The intrinsic constants calculated from the data fitting are listed in Table I. There is some difference in the elastic constants for the stretched and extruded samples although the relative magnitudes are similar. The parameters A and B which are the ratios $C^{\circ}_{11}/C^{u}_{11}$ and $C^{\circ}_{33}/C^{u}_{11}$, respectively, are also given in Table I. In Morsely's model of the sonic modulus[3] the value of A was taken to be 0.67 and B was infinity. This approximation in light of our result appears clearly invalid.

Discussion of Choice of Orientation

The elastic constants calculated from the intrinsic constants and the orientation parameters, Eqs. (6) - (9), are shown in Figure 3. The agreement between calculation and experiment is fairly good for each elastic constant in the extruded samples; furthermore, the model also correctly predicts the decrease of C_{13}. However, in the stretched samples while the model correctly predicts the trends of C_{11} and C_{33}, it does not predict the correct C_{13} result. Experimentally C_{13} is found to increase with stretching, in contrast to the result predicted by the model. Thus, the change in the polymer morphology produced by extrusion appears to be well characterized by our model, and in the stretched film the model is less satisfactorily.

Although for polymers above T_g, the effect of the crystallinity on the sonic velocity has not been studied in detail, it has been found that the sonic velocity in semicrystalline polymers is independent of the crystallinity at temperatures below the T_g.[3] The

T_g of PCTFE is 45°C. All of the measurements reported here were made at room temperature. Thus the behavior of the sound velocity presented here is expected to be predominantly influenced by the amorphous phase.

In our model we have assumed that the basic unit is a polymer chain segment of some length that is located in the amorphous region and that during the deformation event each unit is oriented independently of the units surrounding it. This ideal case constitutes an affine deformation. In the extrusion process the pressure of extrusion is evenly distributed at every point in the polymer solid so the orienting force is the same for each unit. Since this process produces a morphology which fits the prediction of our model of affine deformation (Figures 3a and 3b), it is reasonable to assume that in the amorphous phase of the extruded PCTFE sample each chain is oriented independently of its neighbors. This can occur most easily if the polymer chains are folded at short intervals and if each unit consists of an oriented segment of the folded chain, as illustrated in Figure 5. The observed behavior of the elastic constant C_{13} is consistent with this morphology for the reason that C_{13} measures the efficiency of a compressional stress along the 1 (x or y) axis for creating a compressional strain along the 3 (or z axis. As the polymer becomes more highly extruded the chain folding should reduce the C_{13} stress-strain coupling efficiency.

The deformation in the stretching process is produced by tension on the ends of the film. This process differs from the extrusion process in that the tensional force on individual amorphous phase chains is not necessarily the same for every chain in the solid. The deformation in this case is due to the tensional forces on the chains and to interaction forces between neighboring chains. A tensional force should reduce the number of chain folds and elongate the chains in the stretch direction. This would account for the large linear increase in C_{33} in the stretched samples. If the interaction of neighboring chains are in the form of cross-ties between chains the linkage between the oriented units would improve as the polymer is stretched to higher ratios. This linkage of the amorphous phase chains can be envisioned as an elongated chain network as shown in Figure 5. The increase in C_{13} with stretching is thus expected for such a morphology. It should be mentioned that the same idealized morphology has been proposed to account for the large piezoelectric coefficient d_{31} in PVF_2.[15]

X-ray studies of PCTFE have shown that the stretching process orients crystalline regions affinely when the crystallinity is poorly developed and non-affinely when the superstructure is spherulitic.[8] Our melt-quenched films have poorly developed crystallinity, thus the bulk of the material is amorphous. Since the degree of crystallinity in PCTFE can be controlled by thermal treatment it would be interesting to study the amorphous deformation in highly crystalline stretched films in which the amorphous chains are less concentrated and to see whether the amorphous deformation is affine in this condition.

Conclusion

In conclusion, we have developed a model which accounts for the change in the elastic constants of oriented polymers due to deformation by considering the polymer to consist of a collection of basic orientable units. The elastic constants of the oriented material are expressed in terms of the intrinsic elastic constants of the perfectly oriented basic units and the orientation parameter $<P_2>$ and $<P_4>$. The elastic constants of hydrostatically extruded and stretched poly(chlorotrifluoroethylene) are obtained with Brillouin light scattering. These results are consistant with the model and show that the hydrostatic extrusion process deforms the amorphous phase of the polymer affinely, whereas, the stretching process produces a less-affine amorphous deformation. Further, we have found that in the oriented polymer systems the orientation parameters $<P_2>$ and $<P_4>$ are identical.

ACKNOWLEDGEMENT

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TABLE I

Intrinsic Constants of the Fundamental Units for the Two Orientation Processes

	Stretched	Extruded
C°_{11}	4.44[a]	2.12[a]
C°_{33}	24.0[a]	30.4[a]
C°_{44}	1.40[a]	1.40[a]
C°_{13}	0.305[a]	0.167[a]
C°_{12}	10.5[a]	9.95[a]
A	0.555	0.265
B	3.00	3.80

[a] Units of the elastic constants are: $(\times 10^{10})$ dyn/cm^2

FIGURE CAPTIONS

1. The fundamental unit of the model. θ is the average angle between the unit and the orientation axis. ϕ is the angle of rotation of the unit about the orientation axis.
2. Sound velocity at various angles relative to the stretch axis, plotted in polar coordinates. $\alpha = 0$ is the stretch direction, the points are the measured velocities and the curve is the theoretical fit. The highest extrusion and draw ratios are shown.
3. Elastic Constants of: a) stretched and b) extruded samples. The solid points are experimental, open points are the fit of the affine deformation model.

○ , ● - C_{33}
□ , ■ - C_{11}
△ , ▲ - C_{13}
⬡ , ⬢ - C_{44}

The lines are only to indicate the trends of the experimental data.

4. Orientation parameter $\langle P_2 \rangle$ versus deformation ratio;

● - stretching

■ - extrusion

5. Diagrams showing the essential features of the proposed stretched and extruded polymer chain morphology that would be consistent with the experimental results.

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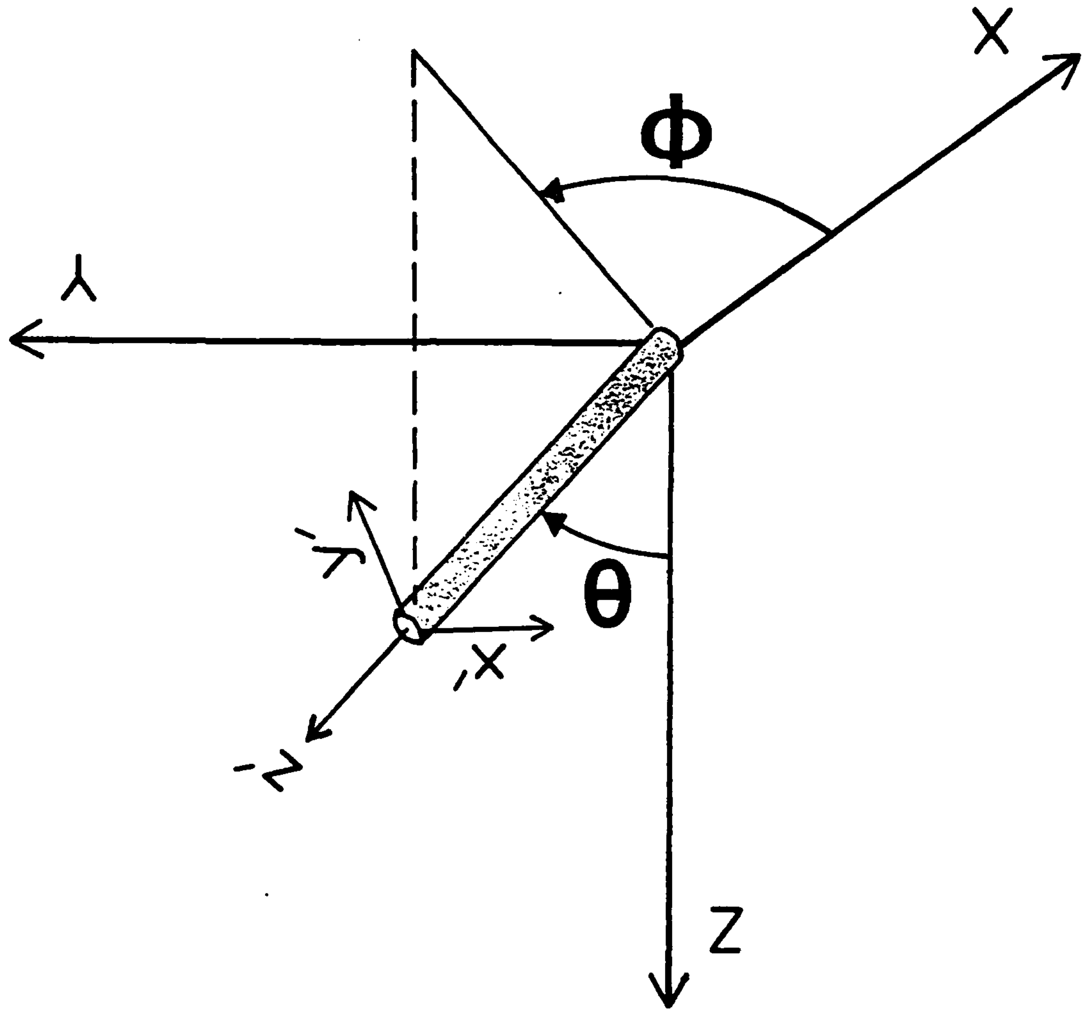
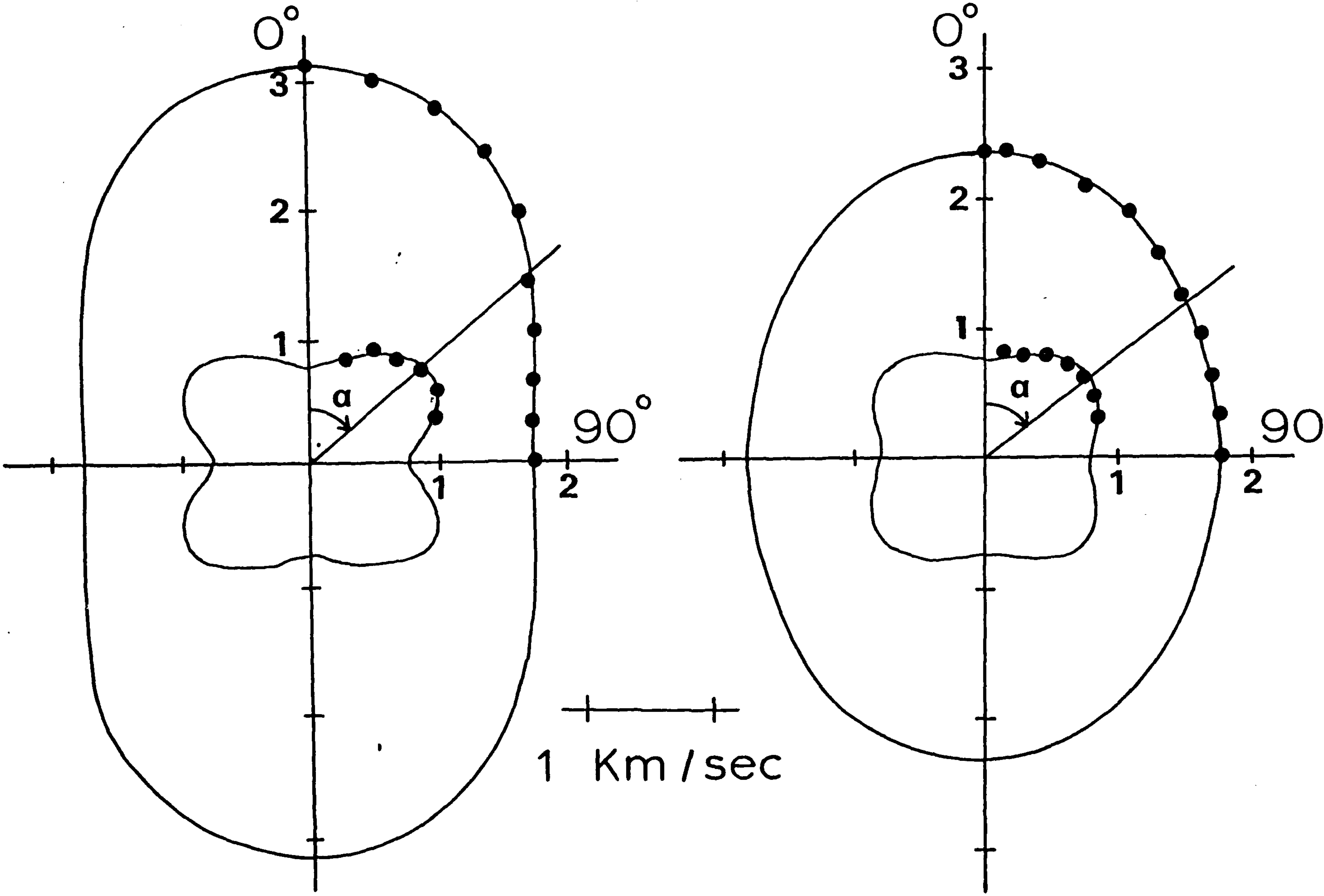
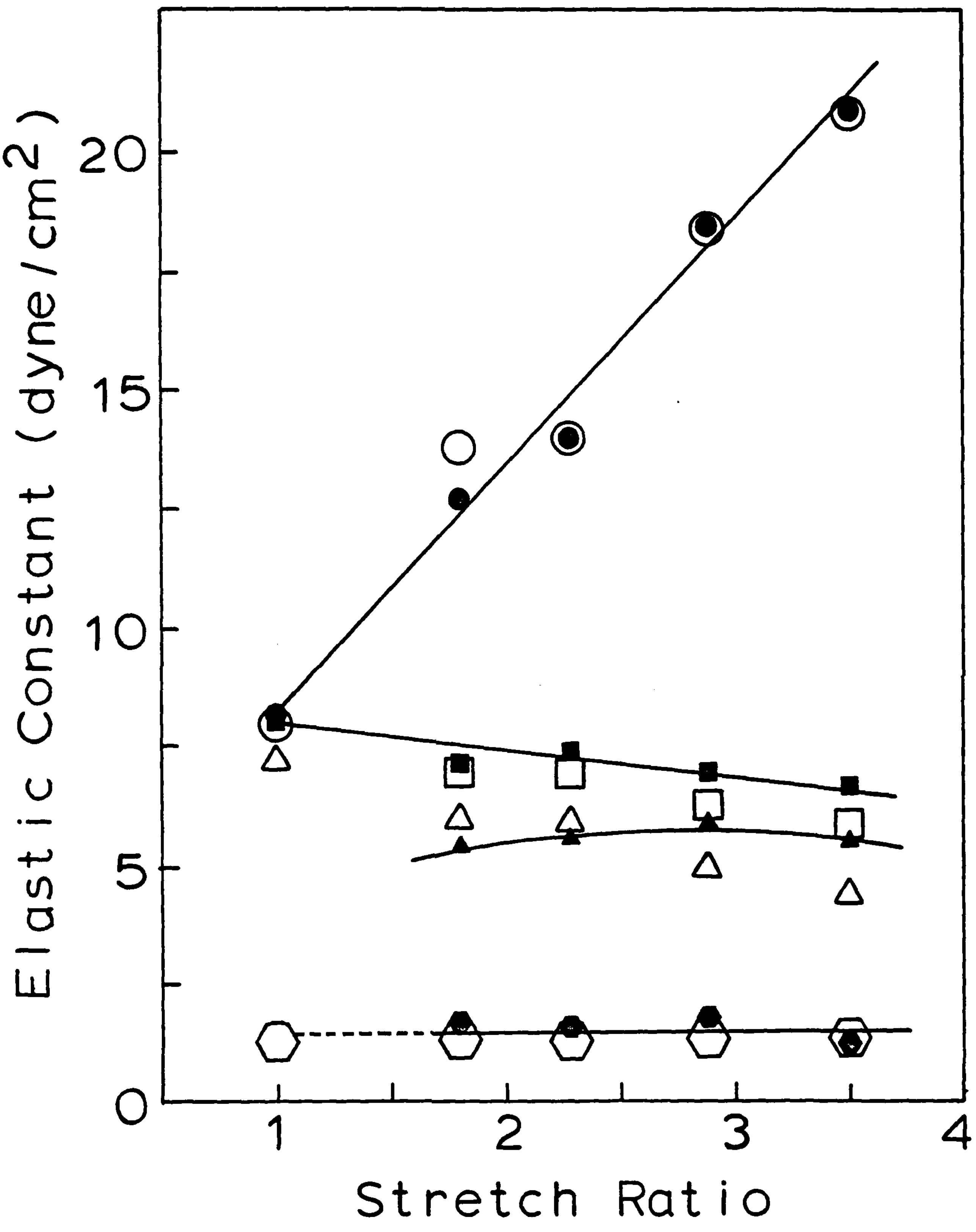

X
Φ
Y
θ
Y'
X'
Z'
Z

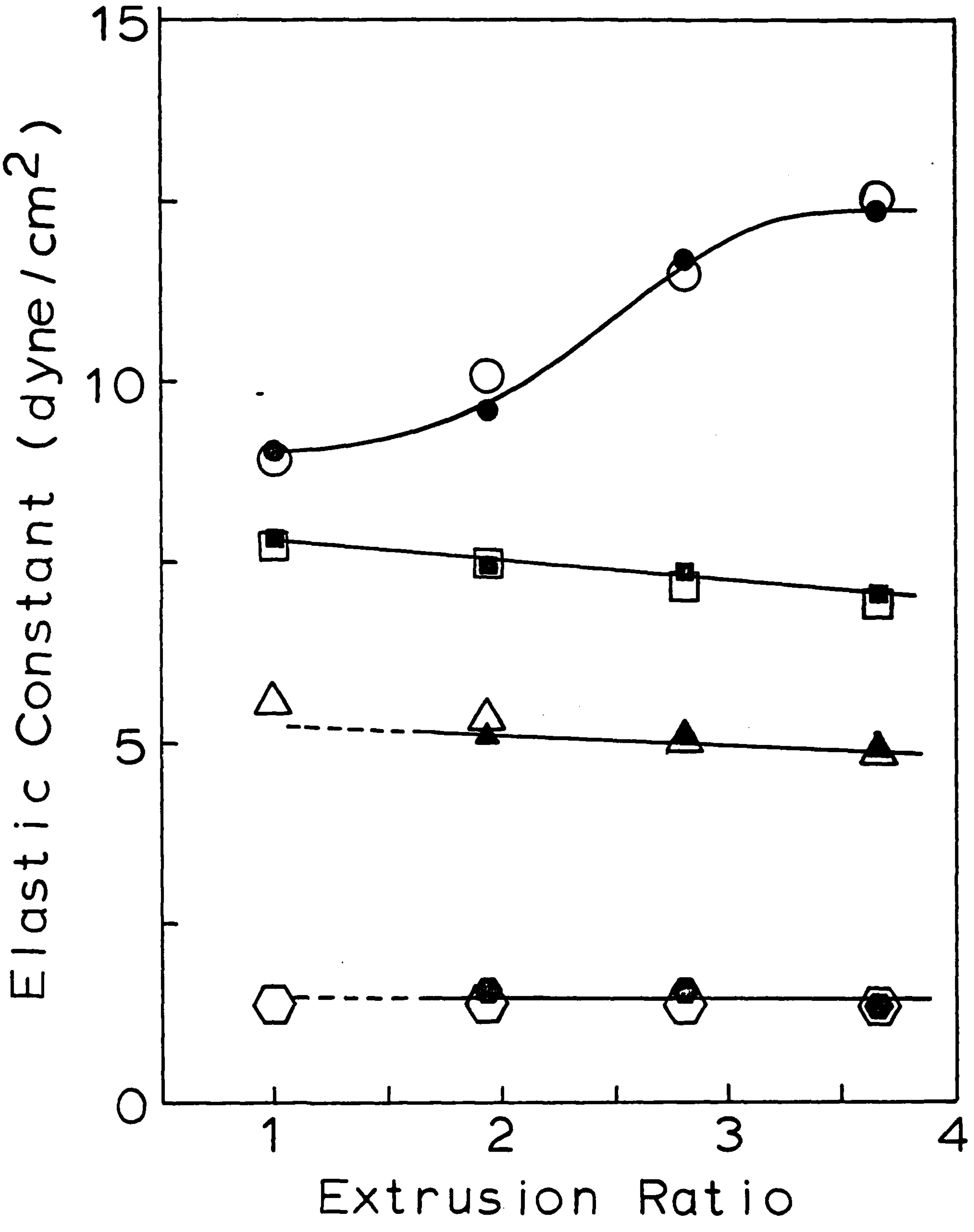


stretched
$R_s = 3\cdot5$

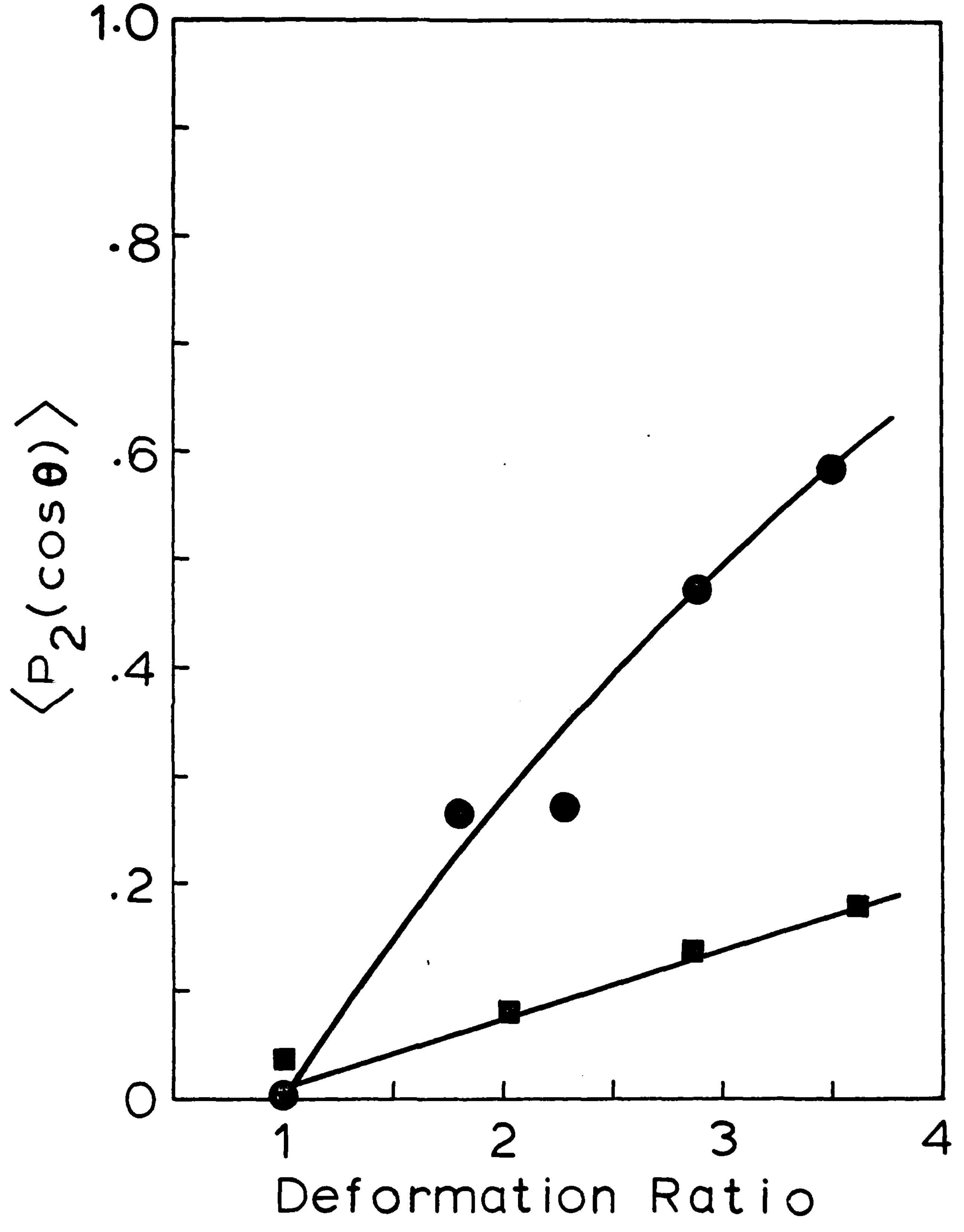
extruded
$R_e = 3\cdot7$



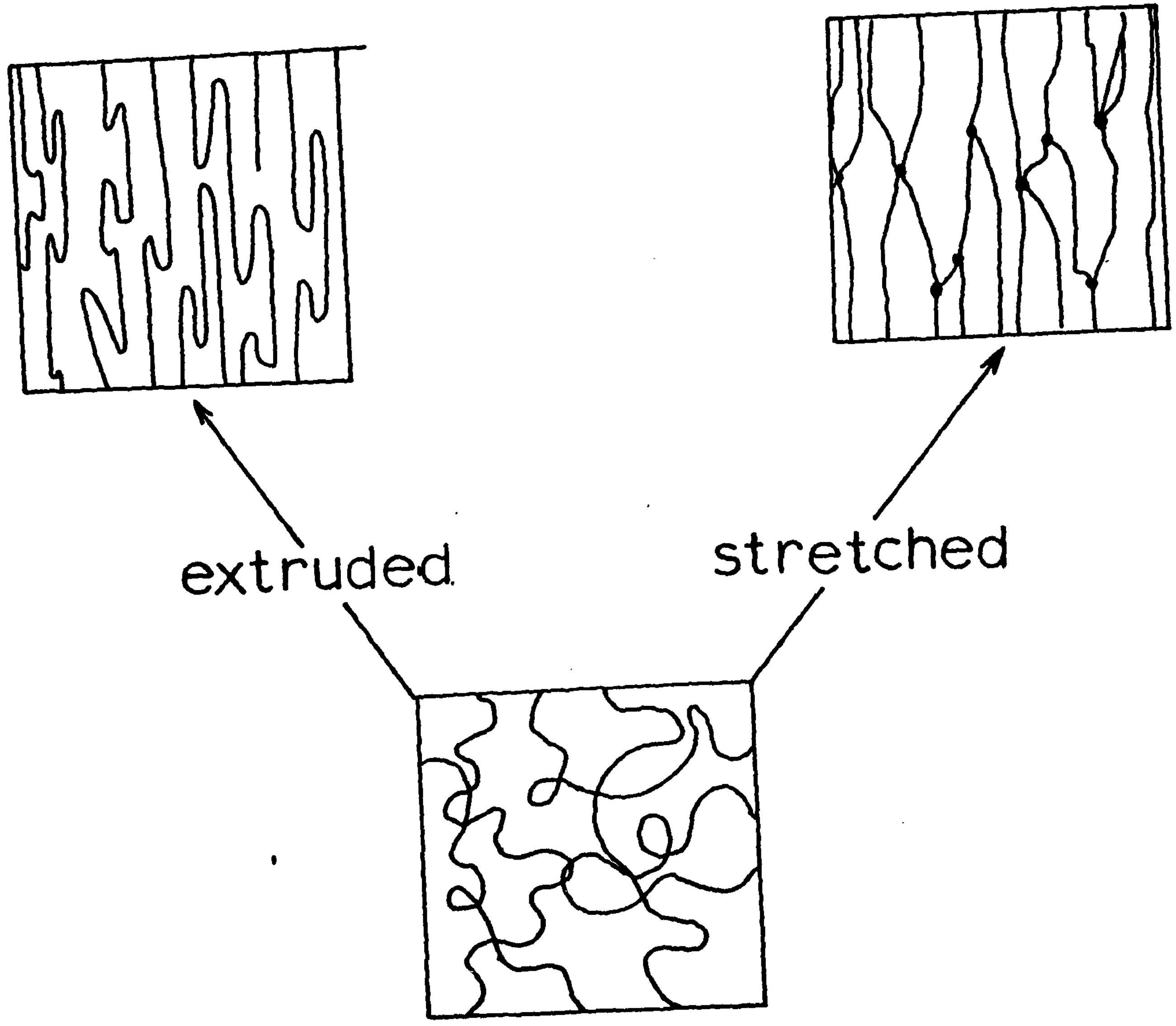
Elastic Constant (dyne/cm^2)
0
5
10
15
20
1
2
3
4
Stretch Ratio



15
10
5
0
Elastic Constant (dyne/cm^2)
1
2
3
4
Extrusion Ratio



1.0
.8
.6
.4
.2
0
1
2
3
4
$\langle P_2(\cos\theta)\rangle$
Deformation Ratio



F.5

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