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POLARIZED RAMAN SCATTERING STUDIES OF CHAIN ORIENTATION IN HYDR--ETC(U)
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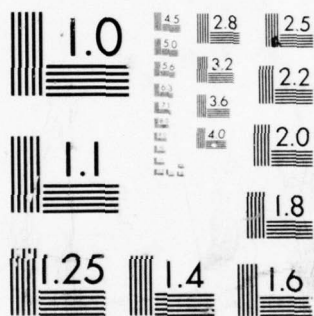
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POLARIZED RAMAN SCATTERING STUDIES
OF CHAIN ORIENTATION IN
HYDROSTATICALLY EXTRUDED POLYPROPYLENE

by

Sushil K. Satija and C. H. Wang

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Abstract

Polarized Raman scattering measurements have been used to study chain orientation statistics in uniaxial hydrostatically extruded isotactic polypropylene. By investigating the CH_2 twisting mode at 1256 cm^{-1} , quantitative results for $\langle P_2(\cos\theta) \rangle$ and $\langle P_4(\cos\theta) \rangle$ have been obtained. Functions $\langle P_2(\cos\theta) \rangle$ and $\langle P_4(\cos\theta) \rangle$ are the second and fourth moments of the orientational distribution function, where θ is the angle between the chain axis and the direction of extrusion. Alignment of polymer chains has been found to increase with the increase of extrusion ratio. The measured $\langle P_2 \rangle$ values are found to be in good agreement with the birefringence data. Values of orientational order parameter $\langle P_4 \rangle$ for an extruded polymer are reported for the first time.

Introduction

It is now established that imposition of hydrostatic pressure can cause substantial changes in the mechanical behavior of polymers.^{1,2} Hydrostatic extrusion has in recent years become a practical technique for altering the mechanical properties of polymers in a controllable manner. Hydrostatic extrusion gives rise to the plastic deformation of polymers and results in changes in molecular orientation as well as texture. At a high extrusion ratio (which is defined as the ratio of cross sectional area of the virgin specimen to that of the extrudate through the die) the extruded samples are known to have highly oriented fiber structure in which stacks of folded chain crystallites are present.^{3,4,5}

As the extent of polymer-chain orientation is closely related to the mechanical and optical properties of a polymer there is a considerable interest in determining the orientational state of the molecules in polymers. To date x-ray diffraction, sonic modulus and birefringence studies have been used to determine the degree of molecular orientation in extruded samples of polyethylene.⁴ Williams has recently studied the tensile and torsional moduli of the hydrostatically extruded polypropylene.³ It was found that the molecular orientation of the extruded polypropylene increases with increasing extrusion ratio. An increase in molecular orientation is reflected by an increase in the degree of transparency. Recently Yoon et al.⁶ have also reported a study of the properties of extrudates of polypropylene. It has been found that the c-axis orientation of chains occur upon extrusion and that the extent of c-axis orientation is enhanced with increasing the extrusion ratio at a given temperature.^{5,6}

Observation of Raman spectra and Raman intensity ratios of various vibrational modes at several scattering geometries is another attractive method

for obtaining molecular structure information in polymer solids. In a series of papers Bower and coworkers⁷ have shown that it is possible to obtain detailed quantitative information about orientational order parameters $\langle P_2(\cos\theta) \rangle$ and $\langle P_4(\cos\theta) \rangle$ in oriented polymer samples from suitable measurements of the intensity of the Raman scattering of polarized light. The measurement of vibrational Raman depolarization ratios has also recently been used to study molecular orientational order in uniaxial nematic and smectic liquid crystal samples.⁸ This paper reports this type of Raman study on hydrostatically extruded isotactic polypropylene samples.

Theoretical Consideration

According to x-ray studies, crystalline isotactic polypropylene contains three monomer units, $-\text{CH}_2-\text{CH}(\text{CH}_3)-$, in one turn in a helical conformation, with a fiber identity period of $6.50 \text{ \AA}$.⁹ The skeletal chain is alternate sequences of trans and gauche conformations. The molecular vibrations of an infinitely extended helical IPP molecule can be analyzed under the factor group of line group which is isomorphous to the point group C_3 . Analysis of this factor group indicates that a total of 77 vibrational modes are distributed among 25 totally symmetric A modes and 26 doubly degenerate E modes. Tadakoro, *et al.*¹⁰ and Schachtschneider¹¹ have calculated the normal modes of IPP. In the Raman spectrum of molten IPP,¹² which is also believed to contain helical chains,¹³ it was found that A modes are polarized and E modes are depolarized, in good agreement with the calculation.

For substances in the liquid and gas phase in which there is no preferred orientational alignment in the sample, Raman scattering intensities are characterized by two invariant quantities α and β , which are defined respectively by

$$\alpha = \frac{1}{3} \text{Tr } \alpha \quad (1)$$

$$\beta^2 = \frac{1}{2} [(\alpha_{11}-\alpha_{12})^2 + (\alpha_{22}-\alpha_{33})^2 + (\alpha_{33}-\alpha_{11})^2 + 6(\alpha_{12}^2 + \alpha_{23}^2 + \alpha_{31}^2)] \quad (2)$$

where α_{ij} are the elements of Raman tensor α .

In this case, for molecules with C_3 symmetry the depolarization ratio for totally symmetric modes is less than $\frac{3}{4}$ and depolarization ratio for E modes is $\frac{3}{4}$. However, in the case of oriented samples the Raman scattering intensities may vary, depending on the scattering geometry used in the experiment.

The experimental geometries to be reported here are schematically illustrated in Fig. 1. We define the space-fixed z axis in the sample as the direction of extrusion. For a given geometry (orientation I or II) and with incident polarization indicated by a first subscript $i = x, y, z$; the spectrally integrated intensities are measured at two polarizations indicated by a second subscript. The primary measurements used in subsequent analysis are the following ratios of integrated intensities:

$$R_1 = \frac{I_{zy}}{I_{zz}}, \quad R_2 = \frac{I_{yz}}{I_{yy}}, \quad R_3 = \frac{I_{xy}}{I_{xz}}$$

We have carried out the calculation of Raman intensities for different orientations using the irreducible spherical tensor algebra for isotactic polypropylene. In terms of irreducible spherical tensors, the Raman polarizability tensor in the space-fixed coordinate system $\alpha_{ij}^{(v)}$ is related to the molecule-fixed coordinate system $\alpha_M^{(v)}(1, m)$ by

$$\alpha_{ij}^{(v)} = \sum_{l, m, q} (-1)^q T_{ij}(1, q) D_{qm}^{(l)}(\Omega) \alpha_M^{(v)}(1, m) \quad (3)$$

For A type vibrational modes in isotactic polypropylene the only non-vanishing Raman tensors are

$$\begin{aligned}\alpha_M^{(A)}(0,0) &= \frac{-1}{\sqrt{3}} (2a + b) \\ \alpha_M^{(A)}(2,0) &= \frac{2}{\sqrt{6}} (b - a)\end{aligned}\quad (4)$$

where a and b are elements of Raman tensor $\alpha_M^{(\nu)}$ given in terms of the point group of the molecule:

$$\alpha_M^{(A)} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \quad (5)$$

$T_{ij}(1,q)$ are defined by the polarization vectors of the incident ($\hat{n}^{(i)}$) and scattered light ($\hat{n}^{(j)}$). For example, for zz scattering, the only non vanishing T_{ij} elements are

$$T_{22}(0,0) = -\frac{1}{\sqrt{3}}, \quad T_{22}(2,0) = \frac{2}{\sqrt{6}} \quad (6)$$

The quantity Ω in the rotation matrix $D_{qm}^{(\ell)}(\Omega)$ denotes the three Euler angles (ϕ, θ, ψ) relating the molecule fixed coordinate system to the space-fixed laboratory coordinate system (chosen to reflect the macroscopic symmetry of the system).

According to Eqs. (3) and (6) the intensity I_{zz} for an A mode is proportional to

$$\langle |\alpha_{zz}^{(A)}|^2 \rangle = \langle \left| \frac{-1}{\sqrt{3}} \alpha_M^{(A)}(0,0) + \frac{2}{\sqrt{6}} D_{00}^{(2)}(\Omega) \alpha_M^{(A)}(2,0) \right|^2 \rangle \quad (7)$$

where the angular brackets indicate average over different orientations. Namely $\langle \cdot \rangle$ is given by

$$\langle \cdot \rangle = \int_0 f(\Omega) d\Omega \quad (8)$$

where $f(\Omega)$ is a distribution function describing the orientational order

of molecules. This orientational distribution function can be expanded in terms of generalized spherical harmonics and order parameters of the system.

Substitution of Eq. (3) into Eq. (7) gives

$$\langle |\alpha_{zz}^{(A)}|^2 \rangle = \alpha^2 + \frac{4}{3} \alpha \beta \langle D_{00}^{(2)}(\Omega) \rangle + \frac{4}{9} \langle D_{00}^{(2)}(\Omega) \rangle \langle D_{00}^{(2)}(\Omega) \rangle \quad (9)$$

The third term on the right-hand side of Eq. (9) may be written in terms of Clebsch-Gordan series as

$$\begin{aligned} \langle D_{00}^{(2)}(\Omega) \rangle \langle D_{00}^{(2)}(\Omega) \rangle &= \sum_j (2j+1) \begin{pmatrix} 2 & 2 & j \\ 0 & 0 & 0 \end{pmatrix} \langle D_{00}^{(j)}(\Omega) \rangle \begin{pmatrix} 2 & 2 & j \\ 0 & 0 & 0 \end{pmatrix} \\ &= \frac{1}{5} + \frac{2}{7} \langle D_{00}^{(2)}(\Omega) \rangle + \frac{18}{35} \langle D_{00}^{(4)}(\Omega) \rangle \end{aligned} \quad (10)$$

Substituting Eq. (10) into Eq. (9), we obtain

$$\langle |\alpha_{zz}^{(A)}|^2 \rangle = \alpha^2 + \frac{4}{45} \beta^2 + \left(\frac{4}{3} \alpha \beta + \frac{8}{63} \beta^2 \right) \langle P_2 \rangle + \frac{8}{35} \beta^2 \langle P_4 \rangle \quad (11)$$

where the order parameters $\langle P_\ell \rangle$ are given by

$$\langle P_\ell \rangle = \langle P_\ell(\cos\theta) \rangle = \langle D_{00}^{(\ell)}(\Omega) \rangle \quad (12)$$

We can also calculate the I_{zy} scattering intensity. For this geometry T_{ij} elements are given by

$$T_{zy}(2, \pm 1) = \frac{i}{2} \quad (13)$$

and using this we can write

$$\begin{aligned} \langle |\alpha_{zy}^{(A)}|^2 \rangle &= \left\{ \frac{1}{4} \langle D_{10}^{(2)}(\Omega) \rangle \langle D_{10}^{(2)}(\Omega) \rangle - \frac{1}{2} \langle D_{10}^{(2)}(\Omega) \rangle \langle D_{-10}^{(2)}(\Omega) \rangle \right. \\ &\quad \left. + \frac{1}{4} \langle D_{-10}^{(2)}(\Omega) \rangle \langle D_{-10}^{(2)}(\Omega) \rangle \right\} |\alpha_M^{(A)}(2, 0)|^2 \end{aligned} \quad (14)$$

For the hydrostatically extruded isotactic polypropylene samples investigated here, we have found that the alignment perpendicular to the direction of extrusion is negligible. Therefore, for simplicity, we assume that the distribution function has a cylindrical symmetry about the c-axis. In this approximation, the probability distribution function $f(\Omega)$ depends only on θ and is independent of ϕ and ψ . As a result, the first and third terms on the right side of Eq. (14) vanish. We may again express the second term on the right-hand side of Eq. (14) in terms of the Clebsch-Gordan series,

$$\begin{aligned} \langle D_{10}^{(2)}(\Omega) D_{-10}^{(2)}(\Omega) \rangle &= \sum_{j=0}^4 (2j+1) \begin{pmatrix} 2 & 2 & j \\ 1 & -1 & 0 \end{pmatrix} \langle D_{00}^{(j)}(\Omega) \rangle \begin{pmatrix} 2 & 2 & j \\ 0 & 0 & 0 \end{pmatrix} \\ &= -\frac{1}{5} - \frac{1}{7} \langle D_{00}^{(2)} \rangle + \frac{12}{35} \langle D_{00}^{(4)} \rangle \end{aligned} \quad (15)$$

Substitution of Eq. (15) into Eq. (14) gives

$$\langle |\alpha_{zy}^{(\Lambda)}|^2 \rangle = \beta^2 \left(\frac{1}{15} + \frac{1}{21} \langle P_2 \rangle - \frac{4}{35} \langle P_4 \rangle \right) \quad (16)$$

We can also calculate the intensities I_{xy} and I_{yy} in a similar manner. The results are

$$\langle |\alpha_{xy}|^2 \rangle = \beta^2 \left\{ \frac{1}{15} - \frac{2}{21} \langle P_2 \rangle + \frac{1}{35} \langle P_4 \rangle \right\} \quad (17)$$

$$\begin{aligned} \langle |\alpha_{yy}|^2 \rangle &= (\alpha^2 + \frac{4}{45} \beta^2) - (\frac{2}{3} \alpha \beta + \frac{4}{63} \beta^2) \langle P_2 \rangle \\ &+ \frac{3}{35} \beta^2 \langle P_4 \rangle \end{aligned} \quad (18)$$

From Eq. (11) and Eqs. (16)-(18) we can calculate three independent intensity ratios R_1 , R_2 and R_3 . For a particular extruded sample these three ratios give rise to three equations linear in two unknowns $\langle P_2 \rangle$, $\langle P_4 \rangle$ with one parameter given by α/β . In addition, we can get a relation for the depolarization ratio measured in the isotropic phase. In the isotropic phase the order para-

meters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ vanish and we obtain the well known result for the depolarization ratio,

$$R_{\text{iso}} = \frac{3\beta^2}{4\beta^2 + 45\alpha^2} \quad (19)$$

For solids with perfect alignment $\langle P_2 \rangle = \langle P_4 \rangle = 1$ and we have

$$\begin{aligned} \langle |\alpha_{zz}^{(A)}|^2 \rangle &= (\alpha + \frac{2}{3}\beta)^2 \\ \langle |\alpha_{yy}^{(A)}|^2 \rangle &= (\alpha - \frac{1}{3}\beta)^2 \\ \langle |\alpha_{zy}^{(A)}|^2 \rangle &= \langle |\alpha_{xy}^{(A)}|^2 \rangle = 0 \end{aligned} \quad (20)$$

which are in agreement with Snyder's calculation for uniaxially aligned polymers of C_3 symmetry.¹³

Experimental

The samples of hydrostatically extruded polypropylene were prepared according to a technique described previously.^{4,5} The high pressure container in the present version consists of an extrusion cylinder which has a 25 mm inner diameter. The dye employed exclusively in this study has a throat of 6.0 mm diameter. The samples studied in this paper were extruded at a temperature of 110°C. The rods of UBE Industries grade J 105 G polypropylene (M.I. = 5) were used as the starting materials. The melting temperature of the original material as measured with Perkin-Elmer model DSC-2 differential scanning calorimeter was 164°C. The density of the original material was 0.9063 gm/cc.

An unextruded sample and samples with the extrusion ratio, R_E , equal to 2.7, 3.0, 4.5 and 6.0 were used for Raman scattering experiment. The extruded samples could be easily cleaved along the axis of extrusion. Cleaved

samples were carefully polished on all sides to minimize surface imperfections which could give rise to polarization scrambling of the Raman scattered light.

The Raman spectra were obtained using a Spex 1401 double grating monochromator coupled to a photon counting system. An argon ion laser tuned to 4880 Å was used for excitation. The slit widths of the spectrometer were adjusted to yield a spectral resolution of the order of 2 cm^{-1} . The experiments were done with approximately 100 mw incident power.

The scattering geometries used in the Raman experiment are given in Fig. 1. As already mentioned, highly polished samples of IPP were used in the scattering experiments. To further reduce the surface scattering the extruded samples were immersed in water.

We also checked the effect of multiple scattering within the sample on the accuracy of the intensity ratios. This was examined by first measuring the intensity ratio of samples by directing the incident light very close to the surface and then by moving the incident light about 1.5 mm away from the surface. For the 1256 cm^{-1} band of IPP, which gives the lowest I_{zy}/I_{zz} intensity ratio, we see no measurable polarization loss due to multiple scattering. However, we were not able to obtain any polarization information on the unextruded sample. The virgin sample is opaque (unlike the extruded samples which are quite clear) and multiple scattering within this sample was too large to give any meaningful polarization data. Since even in the most highly oriented sample that we used in this study the birefringence is quite small,⁵ we have neglected various corrections that must be made to the observed intensities due to this effect.

Results and Discussion

We have measured the intensity ratios of the various internal vibrational modes in the hydrostatically extruded isotactic polypropylene. In this paper we have chosen the 1256 cm^{-1} band to carry out a detailed analysis to obtain the order parameters. The 1256 cm^{-1} band has been assigned by Tadokoro *et al.* to be a CH_2 twisting mode with A symmetry.¹⁰ This band gives the smallest intensity ratio R_1 of all bands present in the Raman spectrum of IPP. Moreover, it is directly related to the backbone motion of the polymer and the order parameters obtained from this band should thus reflect the orientational distribution of the backbone of the polymer chain.

Figure 2 shows the intensity ratios R_1 , R_2 of the 1256 cm^{-1} band of IPP as a function of the extrusion ratio. An extremely small R_1 ratio of 0.023 at the extrusion ratio of 6.0 is observed; this result indicates a high degree of chain orientation in such a sample. At lower extrusion ratios, the R_1 value is larger, thus indicating that molecules are less oriented with respect to the direction of extrusion.

The R_{iso} value for this band can be determined from the depolarization ratio measurement of molten IPP.¹² Using the measured R_{iso} value and Eq. (19), we have determined the quantity α/β to be equal to 0.310 ± 0.023 for the 1256 cm^{-1} band. We have then assumed that this α/β value remains constant as the polymer is solidified. This assumption is justified as the depolarization ratios of a number of Raman bands, including the present one, in the smectic form of IPP (in which disorder in the packing of chains were found to exist) are also found to have the depolarization ratio values similar to that obtained for liquid IPP.¹² In the process of carrying out the calcula-

tion to obtain $\langle P_2 \rangle$ and $\langle P_4 \rangle$, we have found that the obtained values for the order parameters are not sensitive to whether the depolarization ratio for the isotropic liquid or that for the smectic form is used.

Knowing the α/β value and with the help of Eqs. (11), (16) and (18) we have calculated $\langle P_2 \rangle$ and $\langle P_4 \rangle$ from the measured values of R_1 and R_2 . The determined $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are given in Fig. 3 as a function of the extrusion ratio. Both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values are found to increase with increasing R_E , indicating that the degree of chain orientation increases with increasing the extrusion ratio. At $R_E = 6.0$, the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values are close to unity. This indicates that at such an extrusion ratio, nearly 100% chain alignment along the direction of extrusion is obtained.

When a polymer crystallizes into an ordered lattice, the increase in the symmetry of the molecules results in fewer and sharper bands as compared with the spectra in the amorphous phase. Moreover, the coupling of the internal vibrations with the intermolecular vibrations may be different in the crystalline phase as compared with that in the amorphous phase. As a result, the observed Raman bands may arise exclusively from the crystalline, or from the amorphous region or from a mixture of the contributions from both regions. Thus from the origin of a vibrational band, one can obtain information about the orientational statistics of chain alignment in each separate region. This information is invaluable as an individual knowledge of the values of the crystalline and the amorphous orientation function is essential if the state of orientation of a deformed polymer is to be deduced.

The 1256 cm^{-1} band in IPP arises from the mixture of crystalline and amorphous regions.¹⁴ For this reason, the obtained $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values represent average total orientational functions. According to the two phase model, the

total average orientational function F can be expressed in terms of the average orientation function of each phase weighted by the degree of crystallinity β ,¹⁴

$$F = \beta F_c + (1-\beta)F_a \quad (21)$$

where F_c and F_a represent the average orientation functions of the crystalline and amorphous regions, respectively. In Eq. (21), F may be identified with $\langle P_2 \rangle$ or $\langle P_4 \rangle$.

It is useful to compare the $\langle P_2 \rangle$ result obtained from the Raman data with the result obtained from birefringence measurements for IPP. Birefringence also gives a measure of the total average molecular orientation, due to the fact that the difference in the principal refractive index parallel and perpendicular to the direction of extrusion has contributions from the polarizabilities of all of the molecular units in both the crystalline and amorphous regions in the sample. In the two phase model, the measured birefringence Δ for a uniaxially oriented polycrystalline polymer may be defined as¹⁵

$$\Delta = \beta \Delta_c^\circ \langle P_2 \rangle + (1-\beta) \Delta_a^\circ \langle P_2 \rangle \quad (22)$$

where Δ_c° and Δ_a° are the intrinsic birefringence for the perfectly oriented crystalline and amorphous regions, respectively.

For IPP, Δ_c° and Δ_a° have been found to be nearly equal (at room temperature $\Delta_c^\circ = 0.0416$, and $\Delta_a^\circ = 0.0387$).⁵ Thus we may set $\Delta_c^\circ = \Delta_a^\circ = \Delta^\circ$, and Eq. (22) reduces to

$$\Delta = \Delta^\circ [\beta \langle P_2 \rangle_c + (1-\beta) \langle P_2 \rangle_a] = \Delta^\circ \langle P_2 \rangle \quad (23)$$

We plot in Fig. 4, the values of $\langle P_2 \rangle$ obtained from the Raman data versus the measured Δ at all extrusion ratios. The plot indicates that Δ varies linearly with $\langle P_2 \rangle$, thus supporting the reliability of $\langle P_2 \rangle$ data obtained by Raman measurements.

A similar linear relationship between Δ and $\langle P_2 \rangle$ has also been obtained for thin films of poly (ethylene terephthalate).⁷ Since one does not in general expect β to vary significantly with deformation according to Eqs. (21) and (22) a linear relationship may indicate one of two possibilities: 1) $\langle P_2 \rangle_a$ changes in proportion to $\langle P_2 \rangle_c$; 2) Δ_c^0 and Δ_a^0 are approximately equal. For IPP, we have found that the latter is the case. It would be of interest to investigate further the orientational functions for crystalline and amorphous regions in poly (ethylene terephthalate) to determine which of the two possibilities is applicable.

It is well known that x-ray diffraction can provide unambiguously $\langle P_2 \rangle_c$ for the crystalline part of the polycrystalline polymer.¹⁶ Using the x-ray technique, Nakayama and Kanetsuna have recently obtained the $\langle P_2 \rangle_c$ value for hydrostatically extruded IPP.^{4,5} Using the reported values for β and $\langle P_2 \rangle_c$ for IPP, we can determine $\langle P_2 \rangle_a$ from Eq. (21). The results for $\langle P_2 \rangle_a$ for IPP are shown as a function of the extrusion ratio in Fig. 5. The previously determined $\langle P_2 \rangle_a$ for IPP obtained from the birefringence measurement are also included for comparison. The two results are in good agreement, indicating the validity of the two phase model.

We have so far centered the discussion on the orientational order parameters $\langle P_2 \rangle_c$ and $\langle P_2 \rangle_a$. As pointed out above, Raman scattering of oriented polycrystalline polymers can also provide $\langle P_4 \rangle$. In principle, in order to determine the orientational statistics of chain alignment of a polymer, not only

the second moment of the orientational distribution function $\langle P_2 \rangle$, but also $\langle P_4 \rangle$ and higher moments are required. In the past, only $\langle P_2 \rangle$ has been accessible experimentally. In Fig. 2 the results of $\langle P_4 \rangle$ as determined for IPP at various R_E values are given.

The interpretation of $\langle P_4 \rangle$ can be made in the same manner as that of $\langle P_2 \rangle$. That is, the $\langle P_4 \rangle$ value arises from the crystalline as well as from amorphous regions (of Eq. (21)). However, unlike $\langle P_2 \rangle$, there are no other experimental data for $\langle P_4 \rangle$ presently available for comparison, let alone the $\langle P_4 \rangle$ values separately for the crystalline and amorphous regions. The present result represents the first determination of $\langle P_4 \rangle$ for an extruded polymer.

Any theory about the orientational distribution function for chain segments in the solid polymer must therefore be consistent both with the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values determined experimentally.

In the case of stretched polymers the behavior of the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ has been described in terms two different models. One of these is the spherical harmonics expansion based upon the segment orientational distribution function for a stretching cross-linked rubber network. This work presumes an affine transformation of the distances between crosslinking points in the network. The other is the aggregate model in which the polymer is assumed to consist of an aggregate of rotating rigid units embedded in a continuum. The orientational distribution function of the rotating rigid units can then be calculated.

Both of these models are found to give reasonable orientational distributions for stretched polymers. These models may possibly be extended to hydrostatically extruded polymers. However, modifications of the models are necessary, considering the fact that the process of hydrostatic extrusion

leads not only to an increase of chain orientation but also to a better chain packing as well as fibril to fibril adhesion. The experimentally determined orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ would certainly be useful to provide a good test for any theoretical model for the orientation statistics of chain alignment of deformed polymers.

Summary and Conclusion

The study of the intensity of different polarization components of the vibrational Raman spectra of hydrostatically extruded isotactic polypropylene has been made. By investigating the CH_2 twisting mode at 1256 cm^{-1} , we have obtained quantitative results for $\langle P_2 \rangle$ and $\langle P_4 \rangle$ which are the second and fourth moments of the orientational distribution function. The $\langle P_2 \rangle$ values are compared with the birefringence results at various extrusion ratios. The good agreement between the two set of data supports the validity of the two phase model.

Combining the present Raman results with that obtained by x-ray diffraction, we have also obtained the $\langle P_2 \rangle_a$ values in the amorphous region. The $\langle P_4 \rangle$ values have also been obtained for the first time.

Acknowledgement

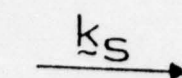
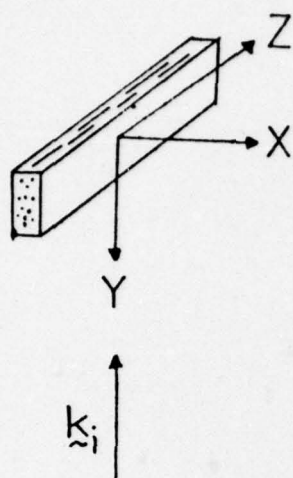
We acknowledge the Office of Naval Research for supporting this work. We also thank Dr. K. Nakayama and Dr. K. Kanetsuna for providing the samples to make such a study possible.

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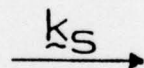
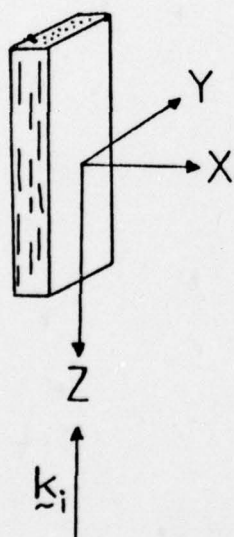
Figure Captions

- Fig. 1 The orientations of extruded polypropylene samples used in the Raman experiment. The cylindrical axis is axis of extrusion which is taken to be the z-axis.
- Fig. 2 Raman Intensity Ratios R_1 and R_2 for 1256 cm^{-1} band of polypropylene as a function of extrusion ratio.
- Fig. 3 Experimental values of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for IPP as a function of extrusion ratio.
- Fig. 4 Variation of $\langle P_2 \rangle$ obtained from Raman scattering with birefringence.
- Fig. 5 The result for $\langle P_2 \rangle_a$ as a function of extrusion ratio. The $\langle P_2 \rangle_a$ data obtained from birefringence measurements are also included for comparison.



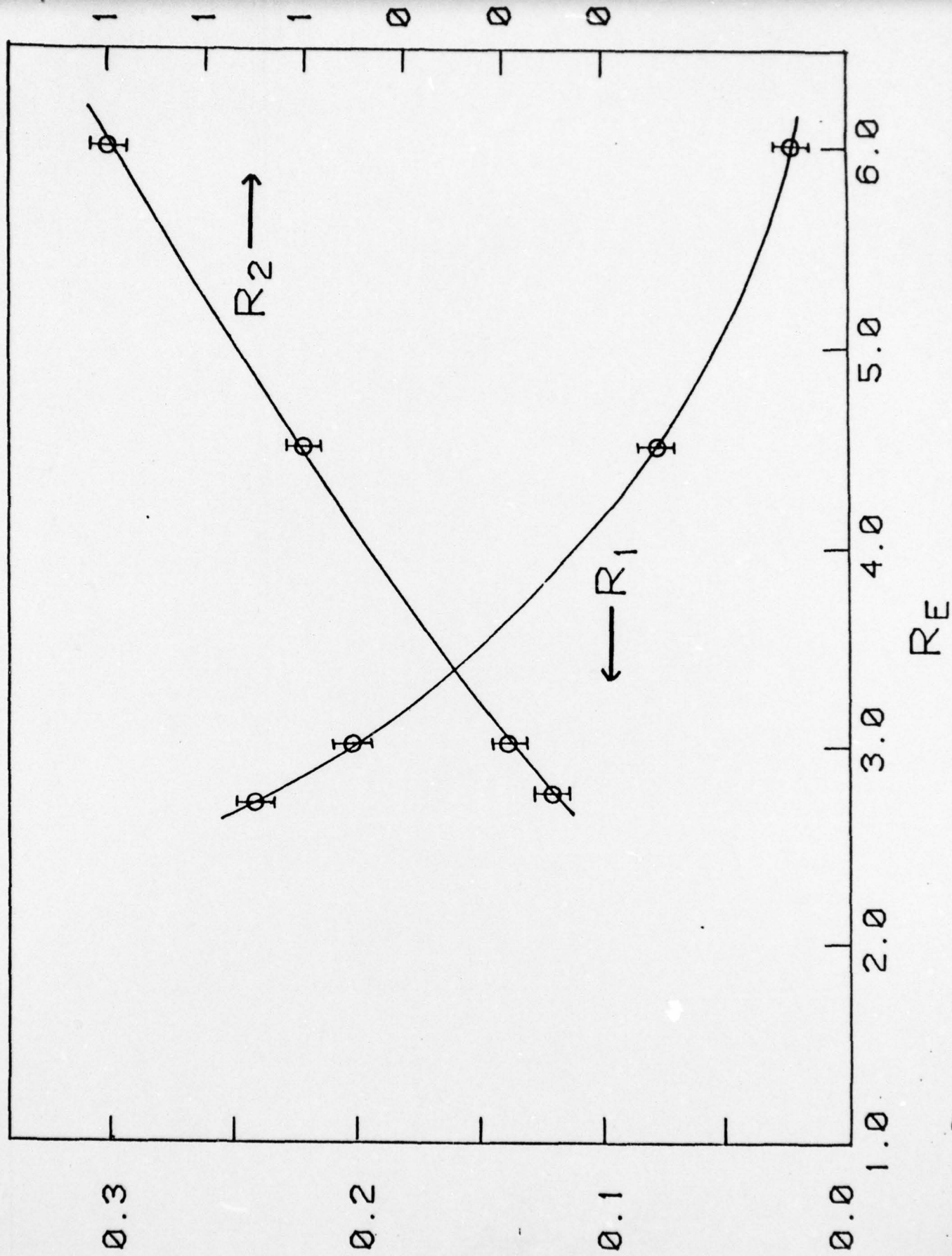
$$\hat{e}_i = \hat{z}, \hat{e}_s = \hat{z} \text{ or } \hat{y}$$

Orientation I



$$\hat{e}_i = \hat{y}, \hat{e}_s = \hat{y} \text{ or } \hat{z}$$

Orientation II



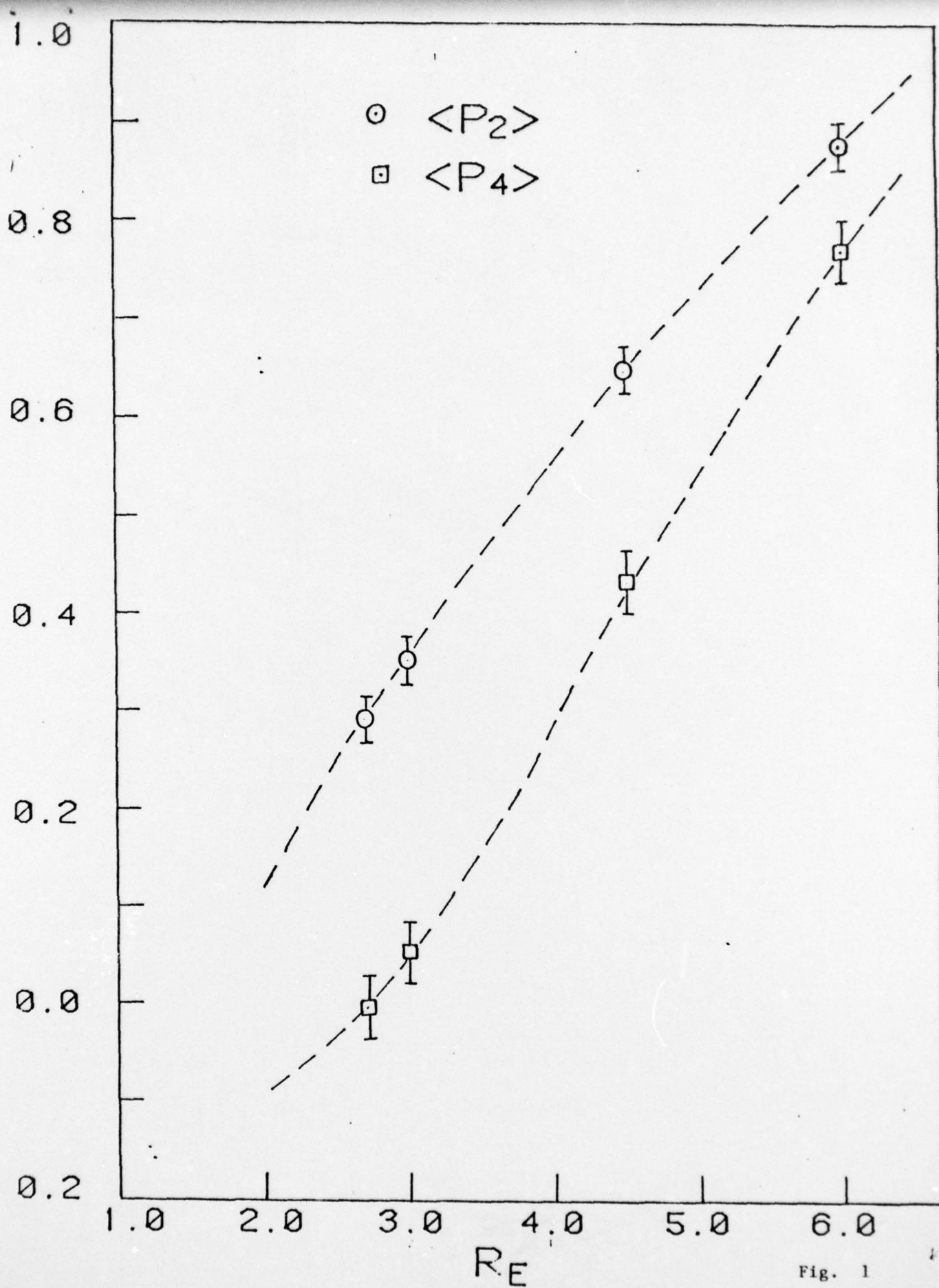
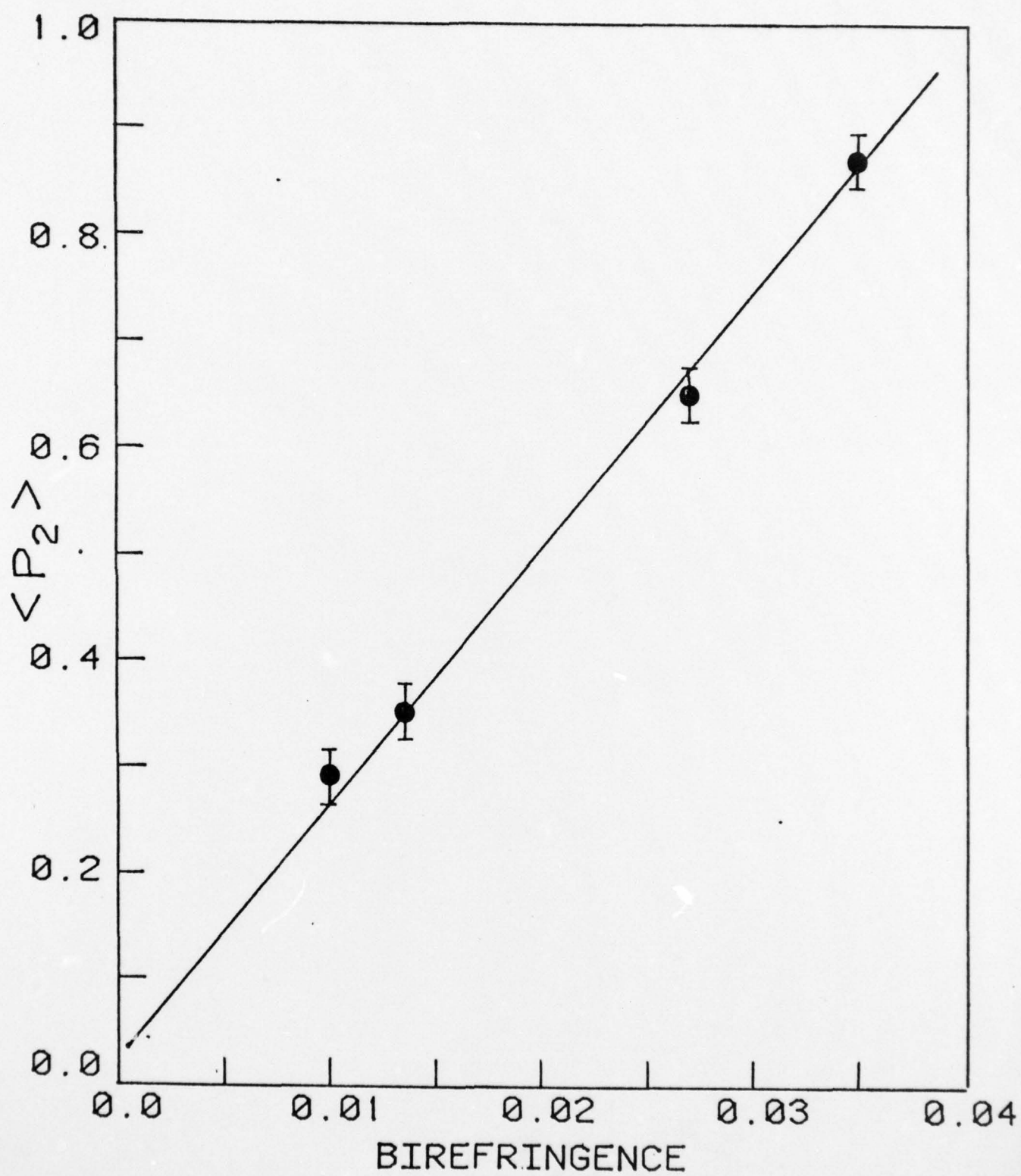
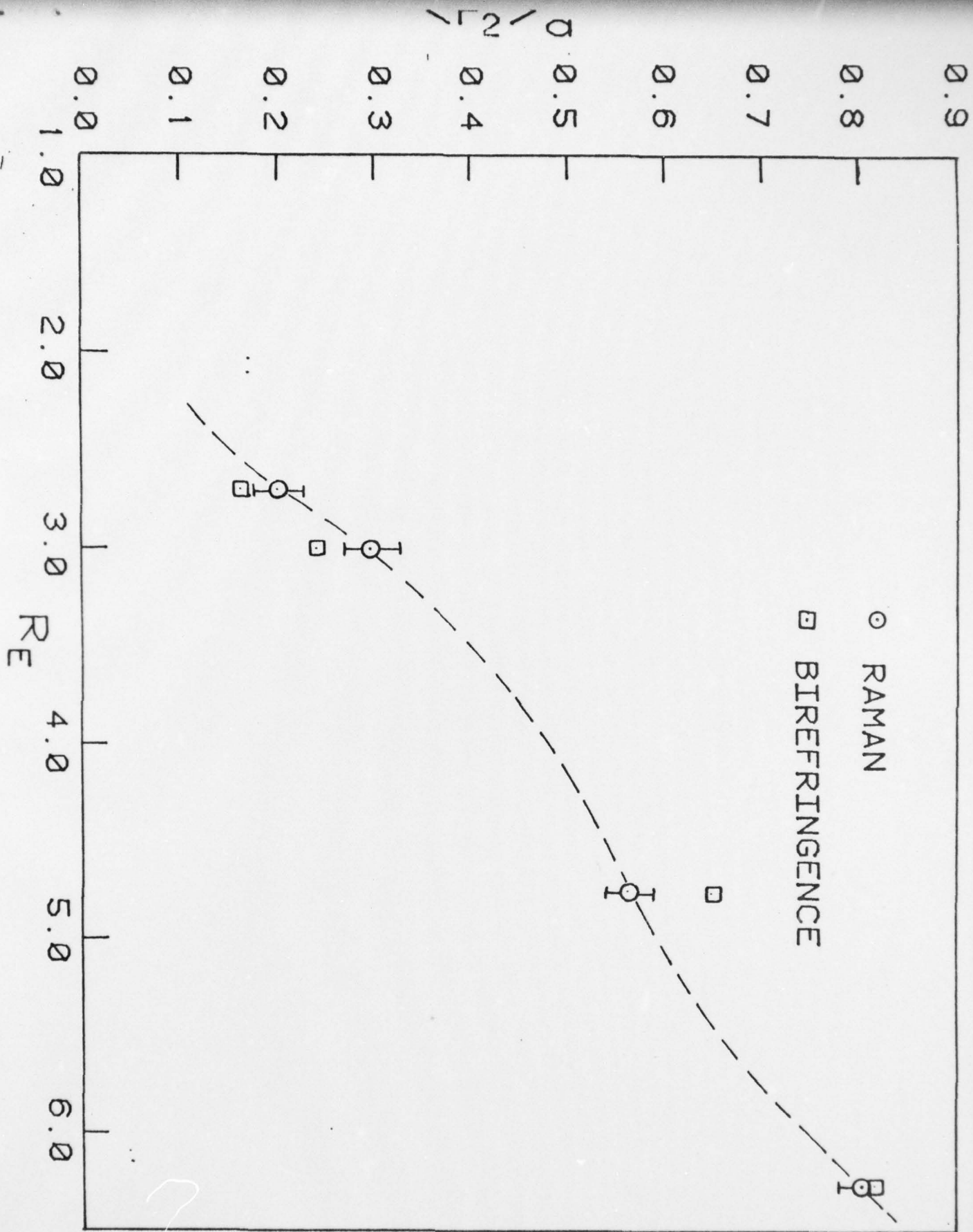


Fig. 1





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