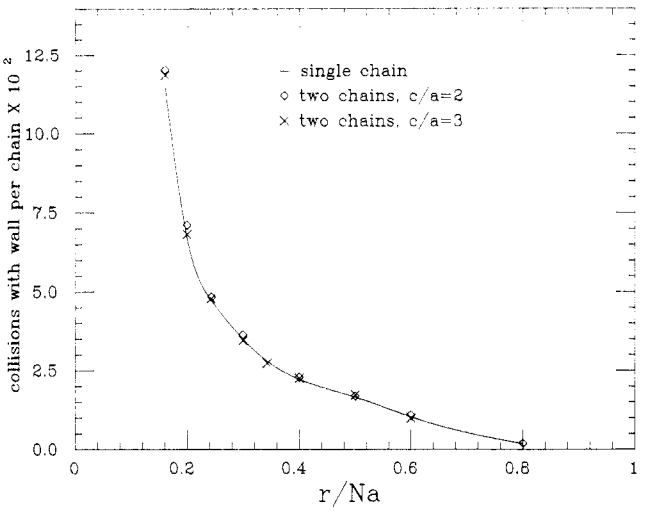


**Figure 8.** Total number of collisions in time period of calculation per tie molecule of the tie molecule atoms with the bounding lamellae. With model parameters representative of a carbon backbone chain, the total period of calculation corresponds to 150 ps.

little effect on the $f$–$r$ relation.

The insensitivity of the $f$–$r$ relation to the interaction between tie molecules extends to other aspects of the process. This is seen in Figure 6, which shows the components $f_p$ and $f_c$, whose sum is $f$, eq 11, in Figure 7, which shows the same quantities for a single chain in a tube, and in Figure 8, which shows the number of collisions per tie molecule of the tie molecule atoms with the bounding lamellae. Note that the number of collisions decreases with increasing extension because of the constraints imposed by the covalent bonds.

## IV. Conclusions

The computer simulation results presented here demonstrate, for the cases treated, that the interaction between a pair of tie molecules has little effect on the force–length relation as found for a single tie molecule. A similar result is found when chain–chain interaction is modeled by enclosing a single tie molecule in a tube which restricts the lateral motions of its atoms.[14]

It is difficult, of course, to generalize with assurance from the results of a limited number of computer simulations. Nevertheless, it appears plausible to conjecture that similar behavior will be found for larger numbers of interacting molecules and for similar types of models. In particular, we expect that the observed features of tensile forces at large separation and compressive forces at small separation with a zero-force intermediate equilibrium configuration[15] will apply as well for further generalizations of models of the amorphous layer.

Numerous questions remain for further study. Among these are the effect of chain length, the behavior of cilia and loops, and the effects of entanglements among tie molecules. We hope to return to these in future work.

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# Temperature-Dependent Studies of the Elastic Constants of Oriented Semicrystalline Polypropylene Films

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ABSTRACT: Longitudinal and transverse hypersonic velocities are determined by Brillouin scattering for isotactic polypropylene films (PP) as a function of stretch ratio at various temperatures ranging from 150 to 330 K. Particular emphasis is placed upon the analysis of the elastic constants $C_{33}$, $C_{11}$, $C_{13}$, and $C_{44}$ for the stretched and unstretched films. The study shows that the effect of temperature is most pronounced on $C_{33}$. Comparison of the Brillouin scattering data with the ultrasonic results shows significant disagreement between the two methods. Theoretical calculations using the reorientation model show good agreement with the Brillouin data. The Voigt affine deformation model of Ward gives a result slightly lower than the Brillouin values for both $C_{11}$ and $C_{33}$.

## Introduction

The study of orientation on polymers by Brillouin scattering leads to information about how the propagation of sound occurs in deformed polymeric solids. For example, it has been shown that when semicrystalline polymers are uniaxially stretched or extruded, the sound velocity propagating along the stretch direction is significantly increased. This anisotropy has been revealed by the in-

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crease in the elastic (stiffness) constant along the stretch direction as the draw ratio is increased. In contrast, the elastic moduli for directions orthogonal to the orientation direction show no increase in magnitude and in some instances even show a decrease as the draw ratio is increased.

Polypropylene is presently considered in the literature as a two-phase solid. Isotactic, syndiotactic, and atactic forms of polypropylene can be obtained by using different polymerization techniques. Isotactic polypropylene consists of helical chains.[1] When a melt of these helical chains is cooled, some of the molecules crystallize into folded-chain lamellae while others do not, thereby forming a two-phase system of crystalline and noncrystalline regions.[2] In semicrystalline polymers, both amorphous and crystalline regions may become oriented by the deformation process. Previous investigations on the effects of deformation on polypropylene have been studied by Wang and Cavanaugh[3,4] using the Brillouin scattering technique. Brillouin scattering is especially convenient since the polymer sample is not perturbed by any external probe, yet fast, accurate measurements with an uncertainty of 1–3% can be made. The Brillouin scattering results of PP extruded rods and stretched films at room temperature have indicated chain extension in the deformation direction is greater in the oriented films.[3] This has been shown by the larger change in magnitude of the elastic constant parallel to the deformation direction for the film samples. An ultrasound study has also been made of the elastic constants of extruded polypropylene rods.[5] A comparison of the ultrasound-derived elastic constants to the Brillouin data at room temperature has shown that considerable discrepancy exists between the two results. Therefore, in order to gain further insight into the nature of the discrepancy and subsequently allow a more detailed comparison between the Brillouin and ultrasound results, we undertook a temperature-dependent study of the elastic constant of oriented semicrystalline polypropylene films by Brillouin scattering.

In this paper, we report Brillouin scattering results of the hypersonic velocities and elastic constants of stretched PP films. We have measured the velocities and elastic constants as a function of temperature both above and below the glass transition region. The elastic constant results at 190 K are then compared to the ultrasound values. In addition, from the elastic constant data at 190 K, we fit the elastic constants to the reorientational model by Wang and Cavanaugh and compare the results to the Voigt model.

## Experimental Section

Isotatic polycrystalline polymer propylene powder beads were purchased from Aldrich. The reported density is 0.85 g/cm$^3$ and $T_g$ = 26 °C. There is no molecular weight information provided, but for high polymer the Brillouin shift is independent of molecular weight. The preparation of polycrystalline polypropylene film samples suitable for Brillouin scattering in the same as that described previously.[3] The preparation method involves melt pressing the polypropylene in powder beads form into films at 270 °C and at 1 metric ton of pressure. The molten polymer films are quenched in ice water to limit the crystallinity. Rectangular pieces of film are drawn with a manually operated puller in a water bath at 80 °C and then cooled gradually to room temperature in the mounting brackets. Besides an unstretched sample, two film specimens of draw ratios 4.0 and 6.8 are also prepared for the temperature-dependent study. A water–methanol mixture is used in the flotation method to determine the density of the film samples. The density of the film is not significantly altered by stretching; a value of 0.899 ± 0.002 g/cm$^3$ at 25 °C was measured for all film samples. This corresponds to 48% crystallinity.

Brillouin spectra are obtained as follows: Single-frequency 4880-Å light from a Spectra Physics Model 165 argon ion laser with an air-spaced etalon is focused on and scattered from the sample. The scattered light is passed through a Burleigh five-pass Fabry–Perot interferometer and detected at 90° to the incident radiation. The output from the photomultiplier tube is fed into a high-speed picoammeter, and the spectra are recorded with an X–Y recorder. The free spectral ranges used are 33.1 and 31.0 GHz. The magnitude of frequency shift of the acoustic phonon is averaged from two adjacent orders to account for nonlinearity of the interferometer. Each data point represents the results of averaging at least two measurements at different times.

Brillouin measurements are made with three separate temperature-control systems. Ambient-temperature measurements are made on a goniometer, and the resulting values are used as a reference for temperatures both below and above ambient temperature. Below ambient temperature, a closed-cycle helium cryostat is used. A specially designed copper film holder is attached to the copper cold tip of the of the cryostat. The film holder is designed to position the film at 45° with respect to the incident beam. A 12.2 × 5.3 mm hole provides an entry–exit port for the light and is beveled on one side to allow the laser light to enter without obstruction. The film sample is mounted to the film holder, and a thin copper sheath about 0.2 mm thick is folded around the film and sandwiched between the copper holder and an outer copper plate, 1.6 mm thick. For Brillouin spectra recorded above room temperature, the film is again surrounded by a thin copper sheath and attached to a rectangular brass frame. The rectangular frame is inserted through a slot between two copper blocks machined with entry–exit ports. Heating tape surrounds the copper block assembly, and the power supplied is controlled by a transformer. Below ambient temperature, Brillouin data are obtained by lowering the temperature of the films; above ambient temperature, the data are obtained by raising the temperature. A check for the presence of thermal hysteresis is also made, and with the exception of the vicinity of the glass transition region, where scatter of the data points is observed, no hysteresis is detected. The temperature readings are recorded with a chromel–constantan thermocouple attached to the copper plate or sheath as close as is feasible to the scattering center. The accuracy of the low-temperature reading is ±0.5 °C; for the high-temperature readings, the accuracy is ±2 °C. The density of the polypropylene film at various temperatures is determined by using the coefficent of thermal expansion, 6.8 × 10$^{-5}$ K$^{-2}$, reported previously.[6] While the expression coefficient is probably not applicable over the entire temperature range studied (150–340 K), this will not make a significant error in the derived elastic constants.

The velocity of an acoustic wave in a solid medium can be calculated from the frequency shift of the scattered light by the equation

$$V_s = \frac{f_B \lambda_i}{2n \sin(\theta/2)} \tag{1}$$

where $f_B$ is the frequency shift (in Hz) of the scattered light, $\lambda_i$ is the wavelength of the incident radiation, $n$ is the refractive index of the medium, and $\theta$ is the scattering angle. When the film is oriented 45° with respect to the incoming beam and the scattering angle is equal to 90°, the velocity becomes independent of the refractive index, and eq 1 assumes a simple form:[7]

$$V_s = f_B \lambda_i / 2^{1/2} \tag{2}$$

Equation 2 is very useful as the refractive index does not enter the equation. Thus, hypersonic velocity $V_s$ can be determined without measuring the refractive index as a function of temperature. The velocity data reported here are determined with eq 2. Uncertainties of the sound velocity as determined with eq 2 may be caused by the birefringence of the film or by slight deviations from the desired alignment; the combined uncertainties from these effects are estimated to be less than 4% in $V_s$.

## Results and Discussion

Brillouin scattering spectra of deformed polymer films show frequency shifts that depend upon the orientation angle, $\alpha$, with $\alpha$ being the angle between the scattering vector, **q**, and the $z$ axis (the $z$ axis being taken parallel to the stretch axis). The shifts result from scattering due

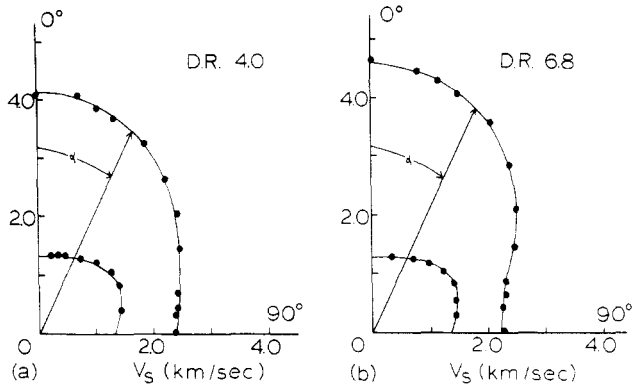


**Figure 1.** Polar plot of the hypersonic velocities of PP films as a function of orientation angle, $\alpha$: (a) DR = 4.0, (b) DR = 6.8.

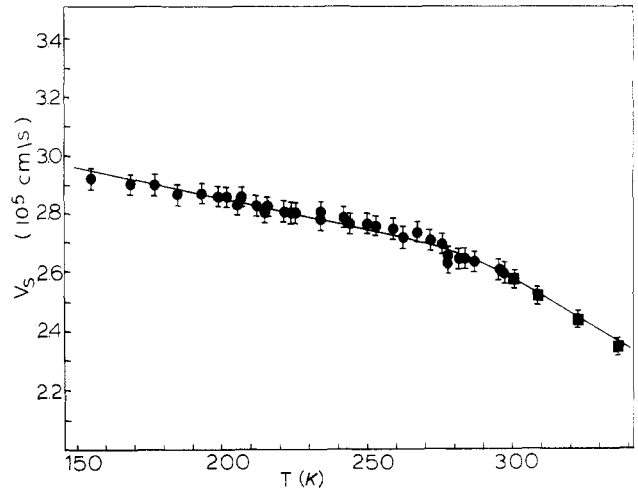


**Figure 2.** Longitudinal phonon velocities as a function of temperature for unstretched film: (●) cooling sample; (■) heating sample.

to longitudinal and transverse sound waves. More precisely, when **q** is parallel ($\alpha$ = 0°) or perpendicular ($\alpha$ = 90°) to the orientation axis, the resultant acoustic waves are purely longitudinal and purely transverse; when $\alpha$ is not 0° or 90°, the waves are mixed and are referred to as quasi-longitudinal and quasi-transverse waves. However, in the following discussion, we will make the distinction between waves as either simply longitudinal or transverse, neglecting the "quasi" prefix. Shown in Figure 1 are polar plots of the hypersonic velocities of the longitudinal and transverse phonons obtained from the Brillouin spectra of polypropylene film samples of draw ratios (DR) 4.0 and 6.8. The polar plots clearly illustrate how the hypersonic velocities change with the orientation angle and depict how the film's anisotropy due to stretching produces the resulting contours. Unstretched films show concentric circles if isotropic conditions exist. It is also evident from Figure 1 that the magnitude of the longitudinal velocity is greater for the more highly stretched film while the transverse velocities are essentially similar in range.

The effect of temperature on the Brillouin frequency shifts is shown in Figure 2. Due to the fact that the Brillouin peak frequency in an amorphous polymer is largely determined by the relaxed part of the bulk modulus (i.e., the adiabatic compressibility contribution), the hypersonic frequency (or velocity) vs. temperature plot will reflect the effect of the glass transition observed in the thermodynamic measurement which is at very low (or zero) frequency. In Figure 2, which shows the longitudinal velocity–temperature results for the unstretched PP sample, the magnitude of the hypersonic velocity increases as the

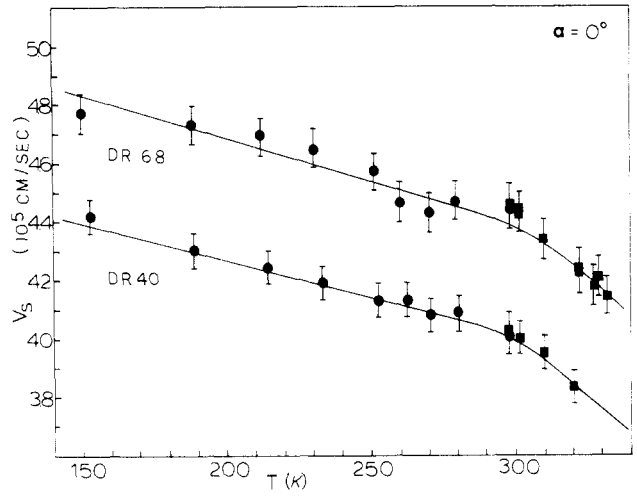


**Figure 3.** Longitudinal phonon velocities as a function of temperature for films with DR = 4.0 and DR = 6.8 ($\alpha$ = 0°). (●) cooling sample; (■) heating sample.

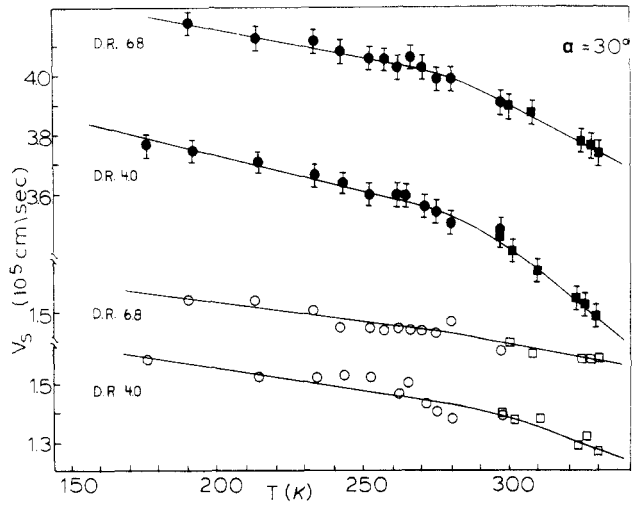


**Figure 4.** Transverse (○) and longitudinal (●) phonon velocities as a function of temperature and draw ratio ($\alpha$ = 30°): (○, ●) cooling sample; (□, ■) heating sample.

temperature decreases, albeit more gradually past the glass transition temperature. A distinctive change in the slope of the $V_s$–T curve is clearly shown around 299 K, consistent with the $T_g$ data (at 26 °C) provided by the supplier.

Microscopically, the glass transition temperature, $T_g$, reflects the point at which the long-range motions of the polymer chain become frozen in, and only short-range, local motions continue to take place. Relaxations of secondary nature from the local motions may also occur below $T_g$ when the amorphous polymer is in the glassy state, but the magnitude is generally much less than the primary $T_g$ relaxation. Similar results were obtained when the PP films were stretched and oriented parallel to the $z$ axis as shown in Figure 3. As has been noted earlier, in this direction the magnitude of the velocity increases with increasing draw ratio, indicative of increasing orientation of the polymer chains along the stretch direction. Noticeable in Figure 3 in comparison with the unstretched sample is the larger slope of the velocity–temperature curve above $T_g$; below $T_g$, however, when the amorphous polymer is in the glassy state, the slopes are very similar.

Additional results of the temperature dependence of phonon velocities were obtained when the PP film was oriented with the **q** vector at 30° and 90° to the $z$ axis ($\alpha$ = 30° and 90°, respectively). The $\alpha$ = 30° results are shown in Figure 4. For the $\alpha$ = 30° orientation, the

transverse peaks become evident and the lower two curves in Figure 4 refer to the transverse phonons. The increase in the velocity gradient of the transverse phonons before and after the glass transition zone is not as large as that for the longitudinal phonons. Again, the slopes of the velocity–temperature curves are similar in magnitude below $T_g$ for both longitudinal and transverse velocities.

Also noticeable in some of the velocity–temperature plots is a gradual variation of data points over a temperature range below 300 K. This may be due to the result of the nonequilibrium nature of the glass transition state. Annealing effects may also occur when the $T_g$ is approached. However, interestingly, measurements of linear thermal expansion and shear modulus and dielectric loss as a function of temperature by Wada et al.[8] have revealed several relaxation processes in isotactic polypropylene. From the exerimental results, Wada et al. have suggested that two groups of amorphous phases exist in polycrystalline PP. They have also provided evidence to show each of these regions to be a separate phase. Thus it is possible that the gradual change in the velocity–temperature curves below the glass transition temperature is an indication of two separate regions with distinct glass transtition temperatures.

The dependence of the hypersonic velocities upon orientation and temperature is a direct result of the change in behavior of the elastic constants of the film. For uniaxially stretched samples of hexagonal symmetry, there are five independent elastic constants while there only two for isotropic samples. To determine these elastic constants, one uses the elastic constant matrix for uniaxially stretched samples given by

$$C_{ij} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{66} \end{bmatrix} \quad (3)$$

where $C_{66} = {}^1/_2(C_{11} - C_{12})$. For isotropic materials, $C_{11} = C_{33}$ and is determined from the longitudinal phonon velocity; $C_{44}$ is determined from the transverse or shear velocity. For anisotropic materials of uniaxial symmetry $C_{66}$ is not determined since the transverse acoustic wave associated with $C_{12}$ is nonactive in Brillouin scattering. To evaluate the elastic constants from the velocity data, the Christoffel equation

$$2\rho V_{\pm}^2 = (C_{11}l_x^2 + C_{33}l_z^2 + C_{44}) \pm \{(C_{11}l_x^2 + C_{33}l_z^2 + C_{44})^2 - 4[(C_{11}l_x^2 + C_{44}l_z^2)(C_{44}l_x^2 + C_{33}l_z^2) - l_x^2l_z^2(C_{13} + C_{44})^2]\}^{1/2} \quad (4)$$

where $l_x = q_x/|\mathbf{q}| = \sin\alpha$ and $l_z = q_z/|\mathbf{q}| = \cos\alpha$ are the direction cosines of the scattering vector in the film, is incorporated into a least-squares fitting routine. The least-squares routine uses a minimization program to best fit initial guesses of the four elastic constants to the Christoffel equation with the corresponding velocity and density data. The accuracy of the fitted elastic constants will increase with increasing $\alpha$.

The elastic constants $C_{33}$ (or $C_{11}$), $C_{44}$, and $C_{13}$ for the undrawn film (DR = 1) as a function of temperature are plotted in Figure 5. The effect of temperature is most pronounced on $C_{33}$, though $C_{44}$ also shows a steady increase as the temperature is decreased. $C_{13}$ remains virtually constant.

Both $C_{44}$ and $C_{13}$ are theoretically calculated elastic constants from the least-squares fit to the Christoffel equation as no transverse wave was observed in the Brillouin spectra of the unoriented film. Calculation of $C_{44}$ and $C_{13}$ is possible since $C_{33}$ is equal to $C_{11}$ in the undrawn film and since one may assume that $C_{13}$ remains constant over the temperature region studied, as was essentially verified in the drawn film samples. The accuracy of the $C_{33}$ data is estimated to be better than 5%.

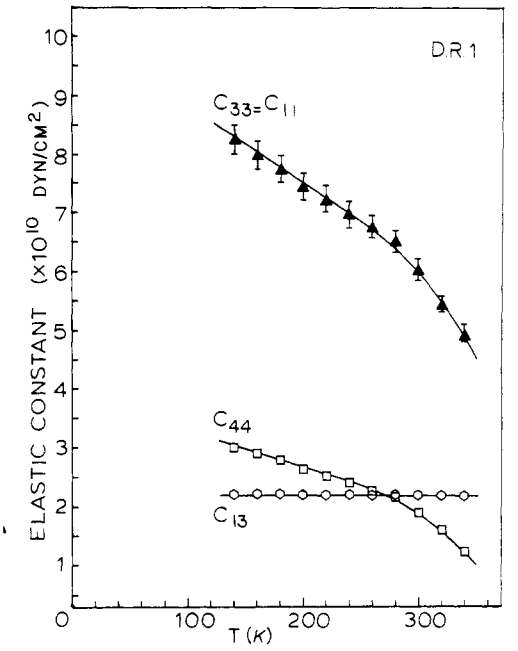


**Figure 5.** Elastic constants as a function of temperature for DR = 1: (▲) $C_{33}$ (=$C_{11}$); (□) $C_{44}$; (○) $C_{13}$. $C_{44}$ and $C_{13}$ are theoretically calculated values.

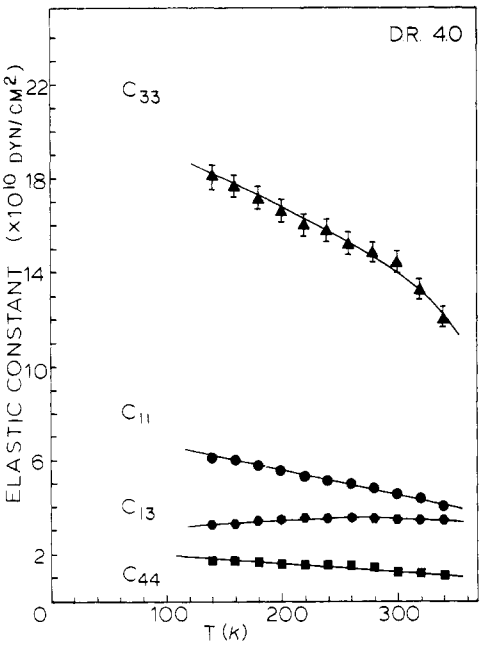


**Figure 6.** Elastic constants as a function of temperature for DR = 4: (▲) $C_{33}$; (●) $C_{11}$; (●) $C_{13}$; (■) $C_{44}$.

The temperature dependence of the elastic constants for an oriented film (DR = 4) is shown in Figure 6. For the oriented film $C_{33}$ and $C_{11}$ are no longer equal, yet the temperature dependence of $C_{33}$ is quite similar to that of the unoriented film. $C_{11}$, however, does not show the same temperature dependence as the unoriented film and increases only gradually with decreasing temperature. It is interesting to note that $C_{44}$ does not increase as the temperature is decreased as it did in the unoriented film. Similar results were obtained with DR = 6.8, as shown in

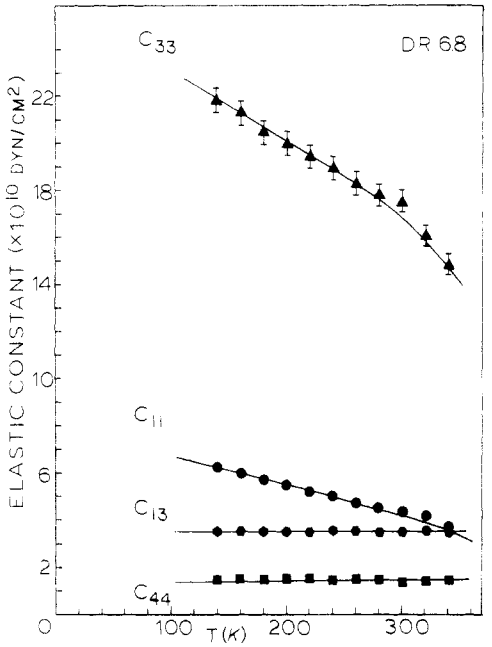


**Figure 7.** Elastic constants as a function of temperature for DR (▲) $C_{33}$; (●) $C_{11}$; (●) $C_{13}$; (—) $C_{44}$.

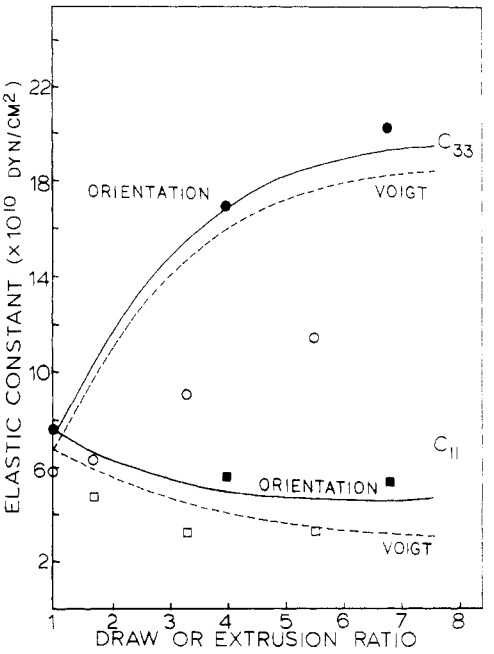


**Figure 8.** Comparison of $C_{33}$ (●) and $C_{11}$ (■) obtained by Brillouin scattering with ultrasonic results (○, □) at 190 K. Also shown are the elastic constants calculated by the orientation and Voigt models.

Figure 7, with the major difference being the larger magnitude of the $C_{33}$ elastic constant. Thus, clearly from the elastic constant data the effect of orientation is most significant on the elastic constants $C_{33}$ and $C_{44}$, while the effect on $C_{11}$ is less pronounced but not negligible. It appears that orienting the amorphous chains of PP along the stretch axis forces the tie molecules into a more strained state, and, as a result, the change of temperature will yield the largest effect on $C_{33}$.

A temperature-dependent study of the elastic constants of drawn PP films has also recently been made by ultrasound techniques at a frequency of 2.5 MHz[10]. A comparison of the hypersonic results from 233 to 330 K with the corresponding ultrasound values shows that elastic constants $C_{33}$ and $C_{11}$ decrease with increasing temperature, with the largest decreases occurring at the glass transition (quoted to be at 333 K at 2.5 MHz). The elastic constant $C_{33}$ shows the largest dependence on temperature and supports the earlier conclusion that orienting PP forces the tie chains in the amorphous region into a more strained state. However, differences in results are also apparent between the two techniques. At approximately 253 K, the ultrasound values for $C_{33}$ and $C_{11}$ at DR = 5.5 begin to appear to reach a plateau (become constant with decreasing temperature) while the corresponding Brillouin values continue to increase even in the glassy state. Since the elastic constant $C_{33}$ is quite sensitive to the change of alignment of the chains in both the crystalline and amorphous regions,[3] the fact that $C_{33}$ obtained by Brillouin scattering continues to increase below the glassy state indicates that the intercrystalline tie molecules play an important role in affecting the behavior of the thermal phonons at low temperatures; it appears that the temperature dependence of the thermal phonons is determined largely by the restoring effect of the intercrystalline tie molecules in the amorphous regions. This result is consistent with the ultrasonic data obtained at DR = 20 (relative to the DR = 5 data), which show a gradual increase in $C_{33}$ moduli as lower temperatures are approached.[10] At such high draw ratios, the only possible changes in chain behavior are in the amorphous regions.

As a means of additional comparison, Figure 8 shows the results we have obtained for $C_{33}$ and $C_{11}$ at 190 K as a function of draw ratio for the oriented polypropylene film and the ultrasonic results of the extruded rods at 190 K reported in ref 5. One notes that there is a fairly large discrepancy between the elastic constants $C_{33}$ and to a lesser extent between the elastic constants $C_{11}$ obtained by two different techniques. The Brillouin scattering values are greater than those obtained by the ultrasonic technique. The results of our previous Brillouin scattering studies show that at room temperature, the value of $C_{33}$ for the stretched polypropylene film is slightly larger than that for the extruded rod, and the value of $C_{11}$ is slightly larger for the extruded samples than that for the drawn films.[3] Thus, if the results of the extruded rods are compared, the difference in the two sets of data would even be greater. Therefore, there is a substantial difference between the Brillouin and ultrasonic data for both $C_{33}$ and $C_{11}$. Also shown in Figure 8 are theoretically calculated curves for $C_{33}$ and $C_{11}$ designated as "Voigt", which are taken from Figure 4a of ref 5. Due to the lack of information on the internal stress–strain distribution in semicrystalline polymers, two commonly used models for understanding the mechanical properties of the semicrystalline polymers are the Voigt model (uniform strain) and the Reuss model (uniform stress), which give the upper and lower bounds, respectively.[11] It has been shown that the elastic constants measured by the ultrasonic method of uniaxially oriented polymers processed by traditional methods tend to follow the Reuss model.[12] However, the Brillouin scattering data are clearly following more closely the Voigt model. It should be pointed out that the Voigt model is similar to the reorientational model of Wang and Cavanaugh,[13,14] in which the ensemble average of orientation of the basic units is formulated in terms of the orientation parameters $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$,[15] whereas in ref 11, the orientation parameters are related to the draw ratio, due to the assumption of the affine deformation model.[11] Ward's calculation has subsequently been modified in terms of the orientation parameters.[12] In reality, the draw ratio is not related to the orientation parameters in a simple way, and the Voigt model of ref 11 is not expected to account correctly for the effect of de-

**Table I**
**Intrinsic Elastic Constants and the Orientation Parameters of Isotactic Polypropylene Films for Those Films with DR = 1.0, 4.0, and 6.8.**

| intrinsic elastic constants[a] | | | | orientation parameters $\langle P_2 \rangle$ | | |
|---|---|---|---|---|---|---|
| $C^\circ_{11}$ | $C^\circ_{33}$ | $C^\circ_{44}$ | $C^\circ_{13}$ | DR = 1 | DR = 4.0 | DR = 6.8 |
| 4.08 | 19.86 | 2.72 | 0.11 | 0.0 | 0.69 | 0.82 |

[a] In units of $10^{10}$ dyn/cm$^2$.

formation on the elastic constants even if the polymer chain undergoes reorientation as it is stretched. The solid curves marked "orientation" use two parameters that relate the intrinsic elastic constants of perfectly oriented samples $C^\circ_{11}$ and $C^\circ_{33}$ to the elastic constants $C_{11}$ and $C_{33}$ at a given orientation. The method also uses the assumption that $C^\circ_{44} = C_{44}$. This assumption yields $\langle P_4(\cos\theta)) \rangle = \langle P_4(\cos\theta) \rangle$. Using a least-squares program and the equations developed in ref 13, it is possible to determine the intrinsic elastic constants, along with the orientation parameter $\langle P_2 \rangle$, from the experimentally determined elastic constants. The determined orientation parameters and intrinsic constants are then used to predict the elastic constants as a function of draw ratio. The solid curves shown in Figure 8 represent the results calculated in this manner. The values of intrinsic elastic constants and $\langle P_2 \rangle$ are given in Table I. One notes that both $C_{33}$ and $C_{11}$ calculated from the orientation model agree quite well with the experimental values at 190 K. The Voigt model prediction gives results slightly lower than the Brillouin values, but it is clearly in disagreement with the ultrasonic values. This comparison thus indicates that either the reorientation model[12-14] or the affine deformation model[11] may be used qualitatively to describe the Brillouin scattering result of oriented polypropylene. However, better agreement of the reorientation model with the experimental results supports the idea that the orientation parameter is not related to the stretch ratio in a simple way described by the affine model.

It should be emphasized that the results of both the Voigt and the reorientation models do not agree with the ultrasonic data. In addition to the discrepancy found in $C_{33}$ and $C_{11}$ obtained by Brillouin scattering and by ultrasonic techniques, there is also a large difference in the $C_{13}$ values obtained by these two techniques. As shown in ref 3, the changes of $C_{13}$ due to external deformation, as determined by Brillouin scattering, are quite similar in both the extruded rod and the oriented film. The present Brillouin $C_{13}$ value at 190 K is found to be equal to $3.4 \times 10$ dyn/cm$^2$ for the DR = 4.0 film. This value is more than a factor of 2 larger than the ultrasonic value of $1.5 \times 10^{10}$ dyn/cm$^2$ at the same draw ratio of 4.0.[5] It is not clear whether the difference in the two results is a manifestation of considerable dispersion in the PP films or whether the ultrasonic data are in error. Further experiments carried out with both ultrasound and Brillouin scattering at different scattering angles are needed to clarify this discrepancy.

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(15) The orientation parameter $\langle P_i(\cos\theta_k) \rangle$ is defined as $\int_0^\pi f(\theta) P_i(\cos\theta) \sin\theta \, d\theta$, where $f(\theta)$ is the orientational distribution function and $\theta$ is the angle between the chain segment and the orientation axis.