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was observed for radioactively tagged heparin in 0.010 N Na_2SO_4 with X between 0.10 and 10.0.[26] Certainly, these data indicate that counterion condensation does take place and that the diffusion coefficient of the polyelectrolyte could be obtained from tracer diffusion studies of condensed or bound counterions. A recent review of counterion binding to polyelectrolytes summarizes the experimental evidence for this phenomena.[6]

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Effect of Chain Alignment on the Brillouin Scattering Spectra of Hydrostatically Extruded Polypropylene

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ABSTRACT: A detailed Brillouin scattering study of hydrostatically extruded polypropylene at room temperature is carried out. The spectra obtained in various scattering configurations are used to determine the hypersonic velocity and elastic constants of the uniaxially deformed polycrystalline polymer. As polypropylene is extruded, C_{33} increases rapidly with increasing extrusion, whereas C_{11} decreases slightly. This result reflects the increasing alignment of the polymer chain segment along the direction of extrusion. The elastic constant C_{13} decreases slightly, but C_{44} does not undergo significant change as the sample is extruded, thus indicating that the shear modulus is insensitive to the orientation of chain segments in semicrystalline polypropylene. Comparison of the Brillouin scattering results with the ultrasonic values indicates that considerable frequency dispersion in the elastic constants is present. Calculation of the orientation parameter using Mosely's theory does not yield correct results. Reasons for the discrepancy are discussed.

Introduction

When a high polymer sample is uniaxially deformed by extrusion it exhibits anisotropic mechanical properties. It has been known for some time that the sound velocity along the draw direction increases progressively with increasing orientation, whereas the sound velocity transverse to the draw direction may decrease or remain unchanged. It is the purpose of this paper to investigate the effect of extrusion on the elastic constants in hydrostatically extruded polypropylene using the Brillouin scattering technique.

Brillouin scattering is very useful in characterizing both the equilibrium and dynamic states of polymeric materials.[1] In Brillouin scattering, light is inelastically scattered from thermal phonons to produce side bands which are shifted from the incident frequency by an amount ν given by

$$\nu = \pm(V/\lambda_0)\{n_i^2 + n_s^2 - 2n_i n_s \cos\theta\}^{1/2} \qquad (1)$$

where θ is the scattering angle, λ_0 is the wavelength of the incident light in vacuo, V is the acoustic phonon velocity, and n_i and n_s are, respectively, indices of refraction of the incident and scattering light waves in their respective directions of propagation.

Most previous Brillouin scattering studies of polymers deal with liquid or clear solid amorphous samples, due to the experimental difficulty associated with a very strong central elastic peak which covers up the much weaker Brillouin side bands.[1,2] As a result, Brillouin scattering has not been used extensively in the study of semicrystalline polymers. However, recent development of high-contrast interferometry has alleviated the experimental difficulty and allows opaque samples to be studied.

In this paper, we report the Brillouin scattering study of hydrostatically extruded isotactic polypropylene using a five-pass Fabry-Perot interferometer system. We have examined the effect of extrusion on the elastic constants of polycrystalline polypropylene in various deformation states. This study should complement the results of polarized Raman scattering studies which we have reported previously.[3]

Experimental Section

The extruded polypropylene samples were kindly provided by Dr. H. Kanetsuna. The technique of preparation has been described previously.[4] An unextruded sample and samples with extrusion ratios (R_e) equal to 2.7, 3.0, 4.5, and 6.3 are used for the Brillouin scattering experiment. The extrusion ratio is defined as the ratio of the cross-sectional area of the original billet to that

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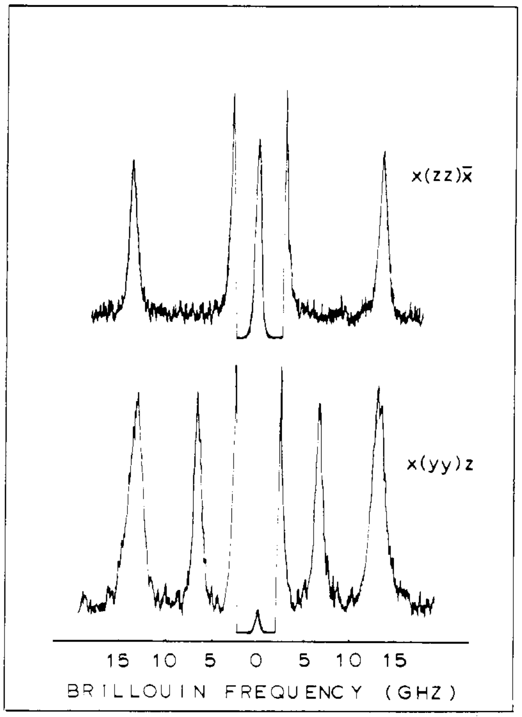

Figure 1. Brillouin spectra of polypropylene obtained in the backscattering, $x(zz)\bar{x}$ and 90° scattering, $x(yy)z$ configurations.

of final extrudate. In each sample, three faces parallel to the extrusion axis are cut at right angles. The faces are carefully polished with jewlers' rouge to minimize surface imperfections which can give rise to polarization scrambling of the scattered light. The sample clarity changes from opaque in the unextruded virgin sample to translucent in the $R_e = 6.3$ extruded sample. A jig which is used to align the polymer rods during cutting and polishing operations is subsequently used to hold the samples at fixed angles in the light scattering experiment.

The sample density is measured by using a density gradient column. No detectable volume changes are observed in the unextruded and extruded samples. The density of all samples is found to be equal to 0.906.[3] The crystal modification of the original material was the monoclinic α form and the orientation of crystallites was hardly detectable. The melting temperature of the unextruded sample was determined to be 164 °C with a Perkin-Elmer Model DSC-2 differential scanning calorimeter. The hydrostatic extrusion was carried out at 110 °C. The index of refraction of the sample is measured from the angle of critical reflectance at the base of a prism. This method gives an index of refraction equal to 1.49 for all samples and is not sensitive enough to detect optical birefringence and the slight change of the index of refraction of polypropylene due to extrusion. Thus, we shall assume that n_i and n_s in eq 1 are equal. As a result, the sound velocity will be accurate only to 3% due to the neglect of birefringence.[5]

The Brillouin spectra are obtained with a Fabry–Perot interferometer operated in five passes. An argon ion laser equipped with an intracavity etalon tuned to a single frequency at about 4880 Å is used for excitation. The free spectral ranges used are 33 and 40 GHz and the overall instrumental finesse is over 60.

The incident laser polarization is selected with or without the use of a half-wave plate which rotates the laser polarization by 90°. The polarization of the scattered light is analyzed with a Gran-Thomson prism polarizer. Both 90° and backscattering ($\simeq$180°) scattering geometries are used to obtain the Brillouin specta.

Results and Discussion

We have obtained Brillouin spectra of hydrostatically extruded isotactic polypropylene in various scattering configurations. Representative Brillouin scattering spectra obtained for the sample with $R_e = 4.5$, using the backscattering geometry in the $x(zz)\bar{x}$ configuration and using 90° geometry in the $x(yy)z$ configuration, are shown in Figure 1. The cylindrical axis is the axis of extrusion, which is taken to be the z axis. The x and y axes are perpendicular to z. Here the Porto notation is used to denote the scattering configuration.[6] In the $x(zz)\bar{x}$ spectrum only one peak is observed while two peaks are present in the $x(yy)z$ spectrum. No detectable difference in the scattering spectrum is observed by rotating the sample about the z axis; thus, the hydrostatically extruded polypropylene exhibits isotropic mechanical properties across the transverse plane.

Table I

Relation of the Change in the Dielectric Tensor to the Strain Tensor in a Uniaxial System

$$\delta\epsilon_{xx} = -\epsilon_{\perp}^2(p_{11}S_{xx} + p_{12}S_{yy} + p_{13}S_{zz})$$
$$\delta\epsilon_{xy} = -\epsilon_{\perp}^2 p_{66}S_{xy}$$
$$\delta\epsilon_{xz} = -\epsilon_{\perp}\epsilon_{\parallel}p_{44}S_{xz}$$
$$\delta\epsilon_{yy} = -\epsilon_{\perp}^2(p_{12}S_{xx} + p_{11}S_{yy} + p_{13}S_{zz})$$
$$\delta\epsilon_{yz} = -\epsilon_{\perp}\epsilon_{\parallel}p_{44}S_{yz}$$
$$\delta\epsilon_{zz} = -\epsilon_{\parallel}^2(p_{13}S_{xx} + p_{13}S_{yy} + p_{33}S_{zz})$$

The intensity of the Brillouin spectrum obtained in the $m(ij)n$ scattering configuration is proportional to the square of $\delta\epsilon_{ij}(\mathbf{q})$, the change of the dielectric tensor, $\epsilon_{ij}(\mathbf{q})$. Here the scattering vector, $\mathbf{q}$, is determined by the propagation directions of the incident and scattering light waves, designated by the indicies m and n, respectively. The changes in the dielectric tensor are linearly related to the strain tensor, S_{kl}, according to the expression (given in the principal axis system)[7]

$$\delta\epsilon_{ij} = -n_i^2 n_j^2 \sum_{k,l} p_{ijkl} S_{kl} \qquad (2)$$

where p_{ijkl} are Pockel's photoelastic constants and both $\delta\epsilon_{ij}$ and S_{kl} are functions of $\mathbf{q}$ but the $\mathbf{q}$ dependence is omitted in eq 2 for brevity in notation.

The $x(zz)y$ spectrum has only one peak and corresponds to scattering from a longitudinal acoustic phonon propagating in the xy plane. According to eq 2, the intensity of this peak is proportional to p_{1133}^2 (or p_{13}^2 in the Voigt notation; the subscripts 1 and 3 refer to both xx and zz as well as the x and z axes, respectively). The spectra obtained in the $\tilde{x}(zz)\tilde{y}$ configurations yield the same information as the $x(zz)y$ spectrum due to the transverse isotropy of the uniaxial system. Here the wavy lines above x and y refer to any direction perpendicular to z; $\tilde{x}$ and $\tilde{y}$ may not be perpendicular to each other.

The two-peak spectrum present in the $x(yy)z$ configuration corresponds to scattering from mixed transverse and longitudinal acoustic phonons. The intensity of the spectrum is determined by p_{12} and p_{13}.

The intensity of the $x(yx)y$ spectrum is weak compared with that of the $x(zz)y$ spectrum, indicating that p_{66} is small compared with p_{13}. Scattering from $x(zx)z$ is associated with p_{44}. In Table I, we summarize the relation of the change in the dielectric tensor to the strain tensor in a uniaxial system.

The hypersonic velocities of the longitudinal and transverse acoustic phonons propagating in various directions are determined from the Brillouin frequency shifts by using eq 1. The results are shown in Figure 2 as a function of extrusion ratio. In Figure 2, the letters L and T indicate longitudinal and transverse modes, respectively. QL and QT are mixed modes, indicating quasi-longitudinal and quasi-transverse modes, respectively. One notes that while the velocity of the longitudinal phonon propagating along the extrusion axis increases with increasing extrusion ratio, the velocity of the longitudinal phonon propagating

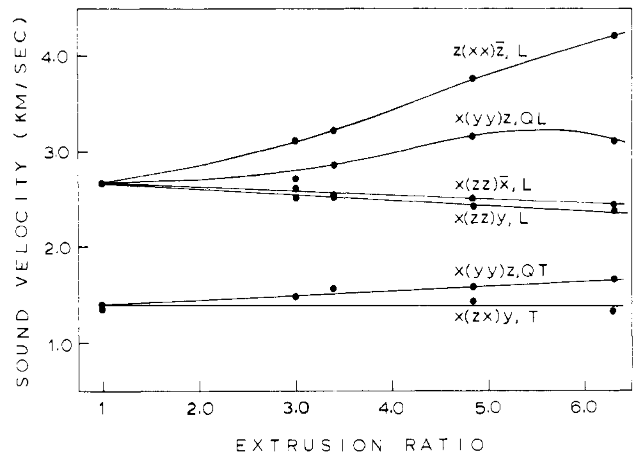

Figure 2. The various hypersonic velocities obtained with different scattering configurations.

in the plane perpendicular to the extrusion axis decreases slightly when the polymer is extruded to about $R_e = 6.4$.

The velocities of the various acoustic phonons propagating in a uniaxially oriented sample are completely described by the elastic constant (stiffness) matrix

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

where $C_{66} = (C_{11} - C_{12})/2$.

The elastic constant matrix relates the stress to strain tensor by

$$T_{ij} = \sum_{k,l} C_{ijkl} S_{kl} \qquad (4)$$

where T_{ij} is the stress tensor; in the absence of dissipation the stress tensor is related to the elastic displacement vector **u** by

$$\rho \frac{\partial^2}{\partial t^2}(u_i) = \sum_j \frac{\partial}{\partial x_j}(T_{ij}) = \sum_{jkl} \frac{\partial}{\partial x_j}(C_{ijkl} S_{kl}) \qquad (5)$$

where $i = x, y, z$.

Equations 4 and 5, together with Table I and the transverse nature of the incident and scattered light waves, complete the description of the Brillouin scattering spectra of a uniaxial system.

The sound velocity curves obtained from the $z(xx)\bar{z}$ and $x(zz)\bar{x}$ scattering configurations are used to determine the elastic constants C_{11} and C_{33} by using the expressions $V(x(zz)\bar{x}) = (C_{11}/\rho)^{1/2}$ and $V(z(xx)\bar{z}) = (C_{33}/\rho)^{1/2}$, respectively. Within the accuracy of the present experiment, the velocity obtained from the $x(zz)y$ scattering configuration agrees with that from $x(zz)\bar{x}$, indicating the consistency of the experimental result with the assumed cylindrical symmetry for the extruded polypropylene. However, a weak high-frequency component also appears in the $x(zz)y$ spectrum (see Figure 3). The frequency of this component increases with extrusion ratio but its intensity depends on scattering angle (it disappears in the $x(zz)\bar{x}$ spectrum; see Figure 1). Since this component is not predicted by the cylindrical symmetry model, it is possible that the appearance of this peak is associated with the inherent structure of semicrystalline polypropylene. The presence of a small concentration of voids may cause the effect; nevertheless, as the polymer is gradually extruded, one expects voids to decrease and hence to observe a decrease in the intensity of the high-frequency component for the high-extrusion sample. This is not observed, however. Thus, this feature is not due to void. Clarification of the nature of this weak component requires a further detailed study.

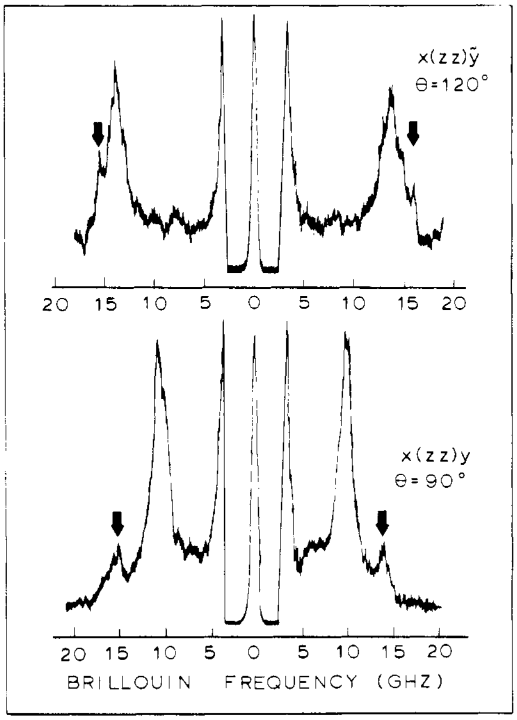

Figure 3. Brillouin scattering spectra obtained in two $x(zz)\tilde{y}$ configurations. Note the presence of extraneous components indicated by arrows.

Elastic constant C_{44} is determined directly from the $x(zx)y$ spectrum, as the velocity associated with the Brillouin peak is equal to $(C_{44}/\rho)^{1/2}$. Knowing C_{11}, C_{33}, and C_{44}, we have determined C_{13} from V_{QL} and V_{QT} obtained from the $x(yy)z$ scattering spectrum, as shown in Figure 2, with the help of the expressions (+ for QL and − for QT)

$$\rho V_{\pm}^2 = [\tfrac{1}{2}(C_{11} + C_{33}) + C_{44}] \pm [\tfrac{1}{4}(C_{11} - C_{33})^2 + (C_{13} + C_{44})^2]^{1/2} \qquad (6)$$

The results for the various elastic constants as a function of the extrusion ratio are given in Figure 4. The elastic constant C_{66} (or C_{12}) is not shown due to the fact that for cylindrical symmetry the acoustic wave associated with the elastic constant C_{66} (or C_{12}) is not active in Brillouin scattering.

One notes that at $R_e = 1$, C_{11} is equal to C_{33}. This result is consistent with the fact that unextruded samples have isotropic mechanical properties. One further notes that the elastic constants associated with the longitudinal wave (C_{11} and C_{33}) are higher than those associated with the transverse wave (C_{13} and C_{44}). This is easily understood from the fact that the intrachain covalent bond is stronger than the interchain van der Waals interaction, and the restoring forces for shear motion are much lower than those for compression. As the sample is extruded, C_{33} increases sharply, and C_{11} decreases gradually. The sharp rise of C_{33} and the accompanying gradual decrease of C_{11} reflect the increasing alignment of the chain segments along the symmetry axis as the sample is extruded. The elastic constant C_{13} decreases slightly, but C_{44} does not undergo significant change as the sample is extruded, thus suggesting that shear modulus is insensitive to the orientation of chain segments. C_{13} does not display the sharp increase

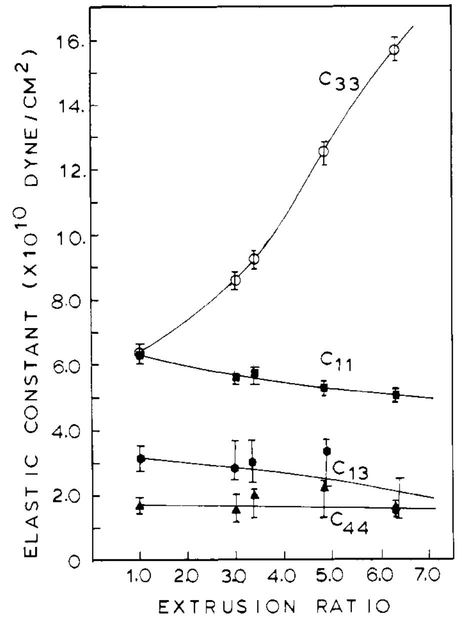

Figure 4. The various elastic constants of polypropylene determined by Brillouin scattering as a function of extrusion ratio.

at R_e = 3.5 as reported in the ultrasonic study.[8]

It is useful to compare the C_{11} and C_{33} values obtained by Brillouin scattering with the corresponding quantities obtained by the ultrasonic technique at 10 MHz.[8] The ultrasonic measurements at 190 K show that C_{11} (or C_{33}) for the unextruded sample is about equal to 5.8 × 10^{10} dyn cm^{-2}. This value is slightly smaller than the Brillouin scattering value ($\simeq$6.2 × 10^{10} dyn cm^{-2}) obtained at room temperature ($\simeq$294 K). At R_e = 6.4, the ultrasonic value at 190 K for C_{33} is 12.4 × 10^{10} dyn cm^{-2} and that for C_{11} is 3.5 × 10^{10} dyn cm^{-2}, in contrast to the room-temperature Brillouin scattering values of 15.8 × 10^{10} dyn cm^{-2} for C_{33} and 5.2 × 10^{10} dyn cm^{-2} for C_{11}. Over the entire R_e = 1–6.4 range, the Brillouin scattering results for C_{11} and C_{33} at room temperature are consistently higher than the ultrasonic values at 190 K. Since the glass transition temperature for polypropylene is about 250 K, the amorphous phase at 190 K is in the glass state and at 294 K it is in the rubber state. The temperature-dependent ultrasonic studies reported in ref 8 show that over the 190–270 K range, the velocity of the longitudinal acoustic wave propagating along the extrusion direction decreases slightly with increasing temperature. This is consistent with the fact that the restoring force decreases with increasing temperature. Thus, in the absence of other mechanisms, the elastic constants at 190 K should be greater than those at 294 K and one should observe larger values for elastic constants at lower temperature, in contrast to the experimental results mentioned above. Hence, that larger elastic constants were observed in Brillouin scattering than in the ultrasonic study is an indication of the effect of dispersion in the frequency range between 10 MHz and 10 GHz. Since Brillouin scattering monitors acoustic phonons at a frequency considerably higher (about 3 orders of magnitude higher) than the ultrasonic one, it appears that in polypropylene the dispersion effect causing the velocity increase outweighs the softening effect due to the temperature increase. For polypropylene, the intercrystalline tie molecules are known to show a greater restoring effect when the amorphous region is in the rubber state.[9,10] That the observed elastic constants are larger in Brillouin scattering than in the ultrasonic study apparently indicates that the average relaxation frequency of the elastic modulus associated with the tie molecules lies lower than 10 GHz. Thus in the hypersonic frequency range the tie molecules respond adiabatically to the external perturbation and polypropylene shows the limiting high-frequency response.

The rise of C_{33} with increasing extrusion as polypropylene is extruded from R_e = 1 to R_e = 6.4 is about a factor of 2.6 in Brillouin scattering, in contrast to a factor of 2.1 in the ultrasonic study. This result is consistent with that obtained previously[5,8] and again indicates that the reinforcing effect of the intercrystalline tie molecules in the amorphous region of polypropylene is more effective in the rubber state than in the glass state.

As mentioned above, the hydrostatic extrusion does not change the density of the extrudate. The sample density, in a two-phase model, corresponds to about 55% crystalline fraction in volume. In general, the elastic constants (or the Young's modulus) are affected by the molecular orientation and the degree of crystallinity. Moreover, the presence of voids may also affect the values of elastic constant; however, as pointed out previously, we do not expect the voids to play a significant role as the polymer is increasingly extruded. The fact that the deformation of polypropylene does not change significantly the degree of crystallinity indicates the increase in C_{33}, as well as the decrease in C_{11}, is affected by the enhanced chain segment orientation.

Since orientation of polymer chain segments can occur in both the crystalline and amorphous regions, deduction of the orientation function in a semicrystalline sample using the sonic data presents some difficulty. Moreover, wide-angle X-ray data indicate that about 90% crystalline orientation has occurred during deformation up to R_e = 4.5; it is clear that the rapid increase in C_{33} with increasing extrusion reflects both crystalline and amorphous orientations. Further increase in C_{33} above R_e = 5 is thus due to the chain segment orientation in the amorphous region.

Moseley has related the sonic velocity of oriented polymers to Hermann's orientation parameter α by the simple expression[11]

$$\alpha = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle = 1 - (V_u/V)^2 = 1 - C_{33}{}^0/C_{33} \qquad (7)$$

where V_u is the longitudinal velocity of an unoriented sample and V is the corresponding velocity of sound propagating along the direction of orientation in an oriented sample. θ is the angle between the polymer chain axis and the direction of sound propagation, which coincides with the direction of alignment. $C_{33}{}^0$ is the elastic constant of the unoriented sample.

While eq 7 has been shown to be useful for obtaining the orientation parameter in the amorphous phase of poly(ethylene terephthalate),[12] it is not expected to have a general applicability, due to drastic approximations introduced in deriving eq 7.[11] Since we have determined C_{33} as a function of extrusion ratio, it is a simple matter to compute the quantity $1 - C_{33}{}^0/C_{33}$. The calculated result is labeled as Brillouin in Figure 5; also shown for comparison is the Hermann orientation function obtained by Raman scattering.

The Hermann function was obtained from the Raman intensity measurements of the band at 1256 cm^{-1}, assigned to be a CH_2 twisting mode with A symmetry. Since the 1256-cm^{-1} band arises from the mixture of crystalline and amorphous regions,[13] the Hermann orientation parameter, labeled as Raman in Figure 5, represents the combined crystalline and amorphous orientations. The Raman result is accurate and is in fact in agreement with the orientation parameter deduced from the birefringence data. The discrepancy between the Brillouin and Raman results

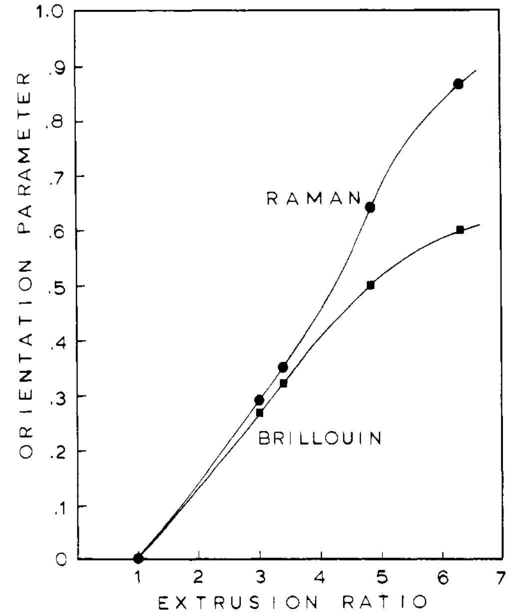

Figure 5. The orientation parameter for polypropylene as a function of extrusion ratio as deduced from Raman (ref 3) and Brillouin scattering (this work). Note the difference at high extrusion ratio.

shown in Figure 5 is believed to be due to invalidity of eq 7 for polypropylene.

Since the Hermann orientation parameter is the average of the local orientation function of polymer chain segments, whereas the sound velocity (or the elastic constant) is a collective property, we do not expect eq 7 to be adequate for approximating the Hermann orientation parameter. Moreover, according to eq 7, the orientation parameter α depends only on the ratio of elastic constants; thus, a material with a given α can have a range of C_{33}. More important, the pair correlation effect which is ignored in Moseley's simple model is expected to present a major drawback in the theory. To illustrate this point, we write, following Born and Huang,[7] the crystalline part of the elastic constant, $C_{33}{}^{c}$, to be

$$C_{33}{}^{c} = \rho \langle \sum_{k,k'} (1/m_k m_{k'})^{1/2} \sum_{n,l} \phi_{zz}{}^{kk'}(n,l) [z\tbinom{n}{k} - z\tbinom{l}{k'}]^2 \rangle \tag{8}$$

where $\phi_{zz}{}^{kk'}(n,l) = \partial^2\phi/\partial[z\tbinom{n}{k} - z\tbinom{l}{k'}]^2|_0$, ϕ being the potential energy the crystal. m_r is the mass of the kth segment in the nth unit cell. ρ is the number density of segments in a unit cell, and the angular brackets represent the ensemble average. $z\tbinom{n}{k}$ is the projection of the segment k in the nth unit cell along the orientation axis. If we represent the orientation angle of $\tbinom{n}{k}$ segment with respect to the orientation axis by θ_{nk} and write $z\tbinom{n}{k} = r_{n,k} \cos \theta_{n,k}$, then eq 8 becomes

$$C_{33}{}^{c} = \rho \langle \sum_{k,k'} (1/m_k m_{k'})^{1/2} \sum_{n,l} \phi_{zz}{}^{kk'}(n,l) \times [r_{n,k}{}^2 \cos^2 \theta_{n,k} + r_{l,k'}{}^2 \cos^2 \theta_{l,k'} - 2r_{n,k} r_{l,k'} \cos \theta_{n,k} \cos \theta_{l,k'}] \rangle \tag{9}$$

In eq 9 the first two terms represent the single-particle orientation functions and the second term represents the pair angular correlation. If the orientation and segment length are statistically independent,[14] we can average the segment length $r_{n,k}$ and orientation angle separately and eq 9 reduces to

$$C_{33}{}^{c} = \rho\{\Delta\langle \cos^2 \theta \rangle - \Delta'\langle \cos \theta_1 \cos \theta_2 \rangle\} \tag{10}$$

where Δ and Δ' result from the average over the segment lengths. The quantities θ_1 and θ_2 represent the orientation angles with respect to the orientation axis. θ_1 and θ_2 are the orientation angles of the two segments which are correlated orientationally. The Δ' is positive, the pair correlation term will decrease $C_{33}{}^{c}$. Clearly, the second term on the right-hand side of eq 10 is expected to make a contribution to the elastic constants on polycrystalline polypropylene; unfortunately, at present, there is no information about the magnitude of its contribution. The wide-angle X-ray diffraction study of polycrystalline polypropylene with different degrees of crystallinity is expected to provide data that can be used to evaluate the single-particle and pair-correlation orientational functions. It is hoped that data of this type will become available in the future.

In the above, we consider only the contribution due to the crystalline portion. To obtain the total elastic constant, the amorphous portion must be added so that the effect of deformation on the elastic constants of a semicrystalline solid can be accounted for. However, the microscopic expression for the elastic constants for the amorphous material has not been developed. Except under a favorable circumstance (such as the case of a bulk amorphous polymer well represented by a random chain statistics) it is evident from eq 9 that Mosley's model, albeit only qualitative, is inadequate. In a general semicrystalline polymer system, the elastic constants depend significantly on the detailed feature of micromorphology in the sample. Not only the local orientation factors of chain segments in the amorphous and crystalline regions are important, but couplings between segments of chains in each region as well as between amorphous and crystalline regions are expected to play an important role. Comparison of the local average orientation factor as obtained by Raman scattering with the present Brillouin results, as shown in Figure 5, clearly demonstrates that even in an ideal system such as polypropylene, the sonic velocities and the elastic constants are not related to the segment orientation factor in a simple way. It is our hope in the future work that a proper microscopic model will be developed such that the hypersonic velocity data will be related to segment orientation and information regarding the micromorphology of amorphous and semicrystalline polymers can be quantitatively obtained by Brillouin scattering.

Summary and Conclusion

We have carried out a detailed Brillouin scattering study of hydrostatically extruded polypropylene at room temperature. The spectra obtained in various scattering configurations are used to determine the hypersonic velocities and elastic constants of the uniaxially deformed semicrystalline polymer. For the unextruded sample, C_{11} and C_{33} are equal, but as the polymer is extruded, the C_{33} increases rapidly, accompanied by a mild decrease of C_{11}, thus reflecting the increasing alignment of the polymer chain segments along the direction of extrusion. The elastic constant C_{13} decreases slightly, but C_{44} does not undergo significant change as the sample is extruded, thereby suggesting that the shear modulus is insensitive to the orientation of chain segment in polypropylene.

Comparison of the Brillouin scattering results with the ultrasonic values indicates that considerable dispersion is present; the average relaxation frequency associated with the dispersion mechanism is slow compared with the hypersonic frequency; thus the elastic constants at the gigahertz frequency represent the high-frequency limiting values. The present Brillouin study supports the earlier result that extrusion has a greater effect on the elastic response of the intercrystalline tie molecules in the rubber state than in the glass state of polypropylene. Comparison

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of the orientation parameter determined by the hypersonic velocity obtained from the Brillouin scattering with that obtained from Raman scattering and birefringence indicates the inadequacy of Moseley's model, which relates the sonic velocity with the orientation parameter. We have discussed the effect of crystallinity and chain segment orientation as well as the effect of pair orientation correlation on the elastic constants. The pair correlation effect is left out in Moseley's model. Further experimental work together with theory is needed to develop a reliable microscopic model for the determination of the orientation parameter from Brillouin scattering for the deformed semicrystalline polymer.

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(14) This may not be a good approximation for systems near the glass transition temperature. Recent experimental studies using light scattering indicate the presence of strong coupling between the segment center of mass and the segment orientation.

End Effects and Asymmetries of the Distribution of Chain Atoms in Polymethylene Chains Perturbed by Attachment to an Impenetrable Interface

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ABSTRACT: Polymethylene chains in which the chain atom at one end is attached to an impenetrable interface have been studied by using a rotational isomeric state model which accurately reproduces configuration-dependent physical properties of the unperturbed chain in free solution. Properties investigated are the mean-square radius of gyration, asymmetry of the distribution of chain atoms, and the probability of observing a particular rotational state at bonds near the site of attachment to the impenetrable interface. Limiting behavior of infinitely long chains was characterized by studying finite chains with up to 1000 bonds. Attachment of the chain to an impenetrable interface produces only a small expansion in the mean-square radius of gyration. The mean-square end-to-end distance, in contrast, increases significantly due to the perturbation produced by the impenetrable interface. Nonidentity of the effect of the interface on the mean-square end-to-end distance and radius of gyration should be kept in mind in any experimental characterization of the thickness of an attached polymer layer. The increase in the mean-square radius of gyration is not isotropic. It serves to change the symmetry of the average distribution of chain atoms about the first two bonds in the chain from spherical to that of a prolate ellipsoid. Individual configurations become, on the average, more asymmetric. The probability for observation of a trans placement is not changed when a long polymethylene chain is attached to an impenetrable interface. End effects on the probability for a particular placement extend only about 20 bonds into the chain. The maximum disturbance of this probability is only slightly greater than that seen with an unperturbed chain in free solution.

If bond lengths and bond angles in the chain molecule are considered to be constant, its configuration becomes a function solely of the rotational state occupied by internal bonds in the chain. One means of characterizing the rotational state occupancy is through p_η, the first-order a priori probability that an internal bond will occupy rotational state η.[1] For an unperturbed simple linear chain (e.g., polymethylene) containing a large number of bonds, p_η should be identical with the a priori probability for occupancy of rotational state η by bond i (denoted $p_{\eta;i}$) for most i. Exceptions are provided only by bonds sufficiently close to either end of the chain so that they are influenced by end effects. A measure of the importance of end effects is therefore given by the dependence of $p_{\eta;i}$ on i. End effects are found to be small in the case of unperturbed polymethylene.[1] If the number of bonds, n, is large, p_η differs significantly from $p_{\eta;i}$ only for i less than five and i greater than $n - 4$. Similar behavior is exhibited by the second-order a priori probabilities, $p_{\xi\eta}$ and $p_{\xi\eta;i}$. Here $p_{\xi\eta;i}$ denotes the a priori probability that bond i is in rotational state η, with bond $i - 1$ simultaneously in rotational state ξ.

In the spirit of first- and second-order a priori probabilities, p_η and $p_{\xi\eta}$, we can also define $(n - 2)$-order a priori probabilities, which equate to the probability for observation of a specified chain configuration. Perturbation of the chain will reduce certain of the $(n - 2)$-order a priori

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