plan to use the (ψ_1,ϕ_2) maps for the study of conformational properties of stereocooligo- and stereocopolypeptides.

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Studies of Elastic Properties of Stretched Films of Polycarbonate by Brillouin Scattering

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ABSTRACT: Results of the Brillouin scattering study of polycarbonate (PC) films stretched at a temperature slightly above T_g are reported. The elastic constants C_{11}, C_{13}, C_{33}, and C_{44} are determined as a function of stretch ratio. By use of the affine orientational model recently developed by Wang and Cavanaugh, the orientation parameter is obtained as a function of stretch ratio. The changes in the elastic constants and the orientation parameter are discussed in terms of chain morphology. The results in PC films are found to be significantly different from those in other polymer films, such as poly(ethylene terephthalate) and isotactic polypropylene, recently investigated in this laboratory. The reason for the difference is discussed.

Introduction

Viscoelastic properties of polymers are affected by externally applied perturbations. The external perturbations, such as stretching or extrusion, induce a preferred orientation of polymer chain segments along the deformation axis. The increased chain orientation occurs in both the crystalline and amorphous regions. In some cases, reorganization of the semicrystalline structure with replacement of lamellae by fibrous elements may also occur. One manifestation of this is an increase in the elastic (stiffness) constant along the axis of stretching, but Young's modulus perpendicular to the stretching axis or shear modulus about the axis may not be significantly affected. However, in polymers, such as poly(ethylene terephthalate),[1] polyethylene,[2] polyamides (Nylon 6-6),[1] and other semicrystalline polymers,[3] an increase in Young's modulus with orientation has been found. These studies are carried out by using low-frequency acoustic or ultrasonic techniques. The results may be due in part to the reorganization of the crystal structure and in part to the stretching of many of the intercrystalline tie molecules. In any case, a full description of the anisotropic elastic property of the solid polymer will require separate specification of the orientation of crystalline and amorphous regions.[4]

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In recent years, Wang and co-workers have used the Raman and Brillouin light-scattering technique to study the effect of chain orientation of hydrostatically extruded rods[5-7] and stretched films.[8-10] Although Brillouin scattering has been used in this laboratory during the past years mainly in the study of high-frequency viscoelasticity in amorphous polymers,[11,12] the development of multipass, high-contrast Fabry-Perot interferometry[13] has prompted the application of the Brillouin scattering technique to study the semicrystalline polymer solids.[14] By use of Brillouin scattering, information about the hypersonic velocity and attenuation coefficient in a polymer medium that remains in thermodynamic equilibrium can be obtained. Moreover, as noted previously,[8] Brillouin scattering has an advantage in the study of solid-state polymers in which the shape and size of the sample are relatively unimportant. This reduces the amount of sample preparation efforts, which are substantial in the previous experiments. Our recent work on polymer films also demonstrates that the hypersonic (both the longitudinal and transverse) behavior across the surface of an extruded rod or an oriented film can be mapped accurately with a relatively simple scattering geometry.[8-10]

In this paper, we report results of the Brillouin scattering study of stretched polycarbonate films. Due to its high impact strength and modulus characteristics, as well as excellent thermal stability and complete transparency, polycarbonate (PC) derived from bisphenol-A is one of the most important polymers suitable for application. A detailed account of the chemical and physical properties of PC can be found in ref 15-17. Brillouin scattering spectra of PC were reported previously by Durvasula and Gammon[18,19] and by Patterson[14] as a function of temperature. By comparing the Brillouin data with the ultrasonic results, Patterson has noticed a considerable dispersion in the longitudinal phonon velocity below the glass transition temperature ($T_g \simeq 150$ °C). Velocity dispersion in the transverse shear wave below T_g was also found by Durvasula and Gammon,[19] but these authors were uncertain about the origin of the dispersion. They even hinted a possibility of an error in the low-frequency shear modulus data, due to a very large (2 order of magnitude) drop of the shear velocity value above T_g, which does not appear in the hypersonic shear velocity result. Another independent ultrasonic study as a function of temperature will be useful to resolve this uncertainty. It is hoped that efforts in this direction will be carried out shortly.

We have studied the hypersonic velocities in PC films stretched slightly above T_g in various directions on the film surface. From the velocity data, we have determined for the first time the elastic constants C_{11}, C_{33}, C_{13}, and C_{44} as a function of stretch ratio. Using the reorientational model recently developed by Wang and Cavanaugh,[6,20] we have also obtained the orientation parameter. The result is then compared with that obtained by using the Moseley model.[21] We have discussed the change in the orientation parameter in terms of chain morphology.

Experimental Section

Polycarbonate resin was purchased from Aldrich Chemical Co. as amorphous clear nuggets ($\bar{M}_w$ = 20 000–25 000; density 1.20; T_m = 267 °C; $T_g \simeq 150$ °C; $n^{20}{}_D$ 1.5850).[22] Preparation of the PC film samples was similar to that described in ref 8. Films were melt cast in a hydraulic press, fitted with polished heated copper plates. The films were melt cast at a temperature of 270 °C and at a pressure of 0.5 metric tons, jointly applied for 2 min. The hot films were then quenched in ice water to maximize optical quality by increasing the content of the amorphous phase. The PC films having a good optical quality, unblemished surface, and uniform thickness were selected for further experimentation.

The films were then uniaxially stretched in a silicone oil bath at a temperature slightly above T_g (152–153 °C) with a manually operated puller. The draw was about 100% per min. In addition to the unstretched film, six specimens with stretch ratios (R_S) of 1.8, 2.9, 4.1, 5.0, 6.1, and 8.1 were prepared for Brillouin scattering.

The densities of the film samples were measured with a flotation method. An aqueous solution of calcium chloride with a density of about 1.22 g/cm^3 was used. The density of the film was found to be unaffected by stretching. At room temperature (22 °C), a value of 1.1983 ± 0.0005 g/cm^3 was measured for all film samples. This result suggests that the presence of partial crystallization, as reported by Patterson,[14] has only a negligible effect on the density, if any.

A five-pass Fabry-Perot interferometer was used to resolve the Brillouin scattering spectra for films of various stretch ratios at several orientation angles. The overall finesse of the optical instrument was about 55. The free spectral range used was about 23 GHz. An argon ion laser (Spectra-Physics 165) with a single-mode operation at about 4880 Å was used to excite the Brillouin scattering spectrum. The optical setup and electronics used in this work were similar to those reported in ref 8–10.

For the angular-dependent measurement to obtain the velocity contour, the scattering geometry as shown in Figure 1 in ref 9 was used. A least-squares fitting program was used to fit the Christoffel equation[23] to the velocity contours to obtain the elastic constants and the orientation parameter as a function of stretch ratio.

Results and Discussion

In an optically isotropic medium, the hypersonic velocity V_B is related to the Brillouin frequency shift f_B (in Hz) by eq 1, where λ_i is the incident wavelength, n is the index

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

of refraction, and θ is the scattering angle. Equation 1 needs to be modified for an anisotropic medium. However, the birefringence in the index of refraction in the oriented PC film is small, $[(n_\parallel - n_\perp)/n_\parallel] < 10^{-3}$, $n_\parallel$ and $n_\perp$ being the indices parallel and perpendicular to the orientation axis; the sound velocity deduced for the shear wave from eq 1 will yield a result with an accruacy not limited by the anisotropy in the index of refraction but by other factors such as the broad width and weak intensity of the spectral peak. Nevertheless, the sound velocity from the longitudinal phonon reported in this work is accurate to better than 1% and that from the transverse phonon to 5%.

It has been shown previously[8,24] that when the scattering geometry is at 90° and the film bisects the angle made by the incident and scattering beams, the hypersonic velocity–frequency relationship given in eq 1 reduces to

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

It should be noted that in this scattering geometry, the index of refraction does not enter eq 2 and for that reason it is a very useful scattering geometry for obtaining the sound velocity by Brillouin scattering from samples whose index of refraction is difficult to measure. All Brillouin spectra reported in this work was obtained by using this scattering geometry.

The Brillouin spectral data in all PC films were obtained by using the Vv configuration. The Vv spectra display clear features due to scattering from longitudinal and transverse acoustic waves. The longitudinal and transverse waves are in general mixed, except for the cases when the scattering vector **q** is parallel or perpendicular to the orientation axis. The scattering vector **q** corresponds to the phonon propagation direction.

Shown in Figure 1 are the hypersonic velocity curves as a function of stretch ratio obtained from the Brillouin spectral lines using eq 2 for various orientation angles α. The orientation angle α is defined as the angle between

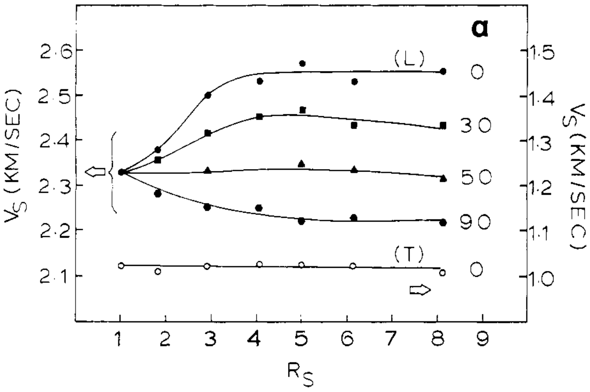

Figure 1. Hypersonic velocities (V_S) of polycarbonate films at room temperature plotted as a function of stretch ratio R_S for the different film angles α (0°, 30°, 50°, 90°). (L) Longitudinal wave; (T) transverse wave.

$\mathbf{q}$ and the direction of the stretching axis. It is important to note that both the longitudinal and transverse acoustic components are observed also in the unstretched PC film at $\alpha = 0°$ and 90°. This result contrasts with those from the other polymer films we have previously studied.[8-10,20] In those films, the transverse components do not appear in the pure mode directions ($\alpha = 0°$ and 90°) under the same laser excitation intensity. They appear only in the directions at which the transverse and longitudinal modes become mixed.

For the film samples, the intensity of the QL and QT Brillouin lines associated with the scattering vector $\mathbf{q}$ in the film face (the xz plane, z being the stretching direction of the film), it can be shown[25] that the scattering factor[26] (proportional to the intensity) for a one-phase medium is given as function of α by

$$\beta_m = (\rho V_{m,\alpha}{}^2)^{-1}[(p_{11}U_x \sin\alpha + p_{13}U_z \cos\alpha)\cos^2\alpha + (p_{33}U_z \cos\alpha + p_{31}U_x \sin\alpha)\sin^2\alpha] \quad (3)$$

when U_x and U_z are the components of the displacement eigenvector for the wave propagating in the xz plane. These are related to the elastic constants and the angle α by

$$(C_{11}\sin^2\alpha + C_{44}\cos^2\alpha - \rho V_{m,\alpha}{}^2)U_x = [(C_{13} + C_{44})\sin\alpha\cos\alpha]U_z \quad (4)$$

where the subscript m refers to the QL or QT wave and $\rho V_{m,\alpha}{}^2$ is determined at each angle. p_{ij}'s are the Pockel photoelastic coefficients.

The ratio of the scattering factors $\rho_\beta = \beta(\mathrm{QT})/\beta(\mathrm{QL})$ has been studied in ref 25 for polypropylene. When this ratio is plotted as a function of α, it reaches a maximum at 45° for each film but decreases to nearly zero at $\alpha = 0°$ and 90°.[25] Shown in Figure 2 is the intensity ratio of ρ_β as a function of α for PC films with different stretch ratios. One notes clearly that the maximum value of ρ_β occurs approximately at $\alpha = 45°$, and the value of maximum of ρ_β increases with the draw ratio, consistent with the result previously found in polypropylene; however, the ρ_β values for PC films at $\alpha = 0°$ and 90° are still substantial in contrast to the result found in polypropylene.

Two possible mechanisms are believed to be responsible for the large intensity of the shear mode in the unoriented film as well as in the oriented films in the pure mode configurations ($\alpha = 0°$ and 90°). One is due to dynamic coupling of the polarizability anisotropy to the shear motion in the amorphous region, similar to the mechanism found to be responsible for the appearance of the transverse shear mode in supercooled liquids and glasses consisting of small optically anisotropic molecules.[27-29] The other is random orientation of crystallites in the PC films due to partial crystallization. The partial crystallinity will enhance scattering of the shear modes. In combination with the above mentioned mechanisms, shear wave is expected to scatter light more strongly in the pure mode directions in a semicrystalline than in an amorphous film sample, despite the fact that the degree of birefringence in PC films is not large enough to affect the values of sound velocity. Durvasula and Gammon[19] have estimated the strain-optical coefficient $(p_{44}/p_{12})^2$ to be about 10^{-2}, which is comparable to the $(p_{44}/p_{12})^2$ value ($\simeq 7 \times 10^{-2}$) found in fused silica[29] and nearly 2 orders of magnitude larger than the value of PMMA.[30] Patterson has attributed this to angular correlation of phenyl groups between neighboring chains in PC.[14] It is not clear that this is a correct mechanism because the phenyl group correlation is also present in polystyrene, but this polymer has a very small strain-optical coefficient. The large $(p_{44}/p_{12})^2$ value found in PC is more likely associated with the chain rigidity due to the incorporation of the phenyl groups in the chain backbone. It would be useful to study the effect of chemical structure on the behavior of the shear mode so that the origin of the large strain-optical coefficient in PC may be clarified.

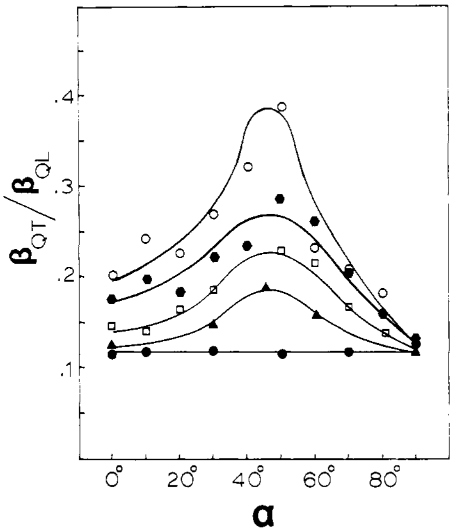

Figure 2. Ratio of scattering factors for the QT and QL modes plotted as a function of α for several stretched films. (○) R_S = 8.1; (⬢) R_S = 5.0; (□) R_S = 2.9; (▲) R_S = 1.9; (●) R_S = 1.0.

One notes in Figure 1 that, at $\alpha = 0°$, the hypersonic velocity increases with increasing R_S, approached a plateau value at $R_S \simeq 5.0$. On the other hand, at $\alpha = 90°$, the velocity decreases with increasing R_S, also approaching a plateau value at $R_S \simeq 5.0$. As noted above, $\alpha = 0°$ and 90° correspond to two pure longitudinal mode directions, despite the fact that scattering from the shear mode also appears in these directions. However, as shown in Figure 1, the transverse wave velocity (observed at $\alpha = 0°$) is insensitive to stretching.

The change of hypersonic velocities with stretching is more clearly illustrated in terms of polar plots of the sound velocity vs. the sound propagation direction. Shown in Figure 3 are the polar plots for an unstretched (R_S = 1.0) and for a stretched (R_S = 5.0) film. The polar plot shows two concentric circles in the unstretched film, indicating a perfect acoustic isotropy for both the longitudinal and transverse waves on the film surface. However, the circles are distorted in the stretched film, as shown in the R_S = 5.0 film. Maximum quasi-longitudinal and quasi-transverse sound velocities are found at $\alpha = 45°$; the velocities at $\alpha = 0°$ are larger than those at $\alpha = 90°$.

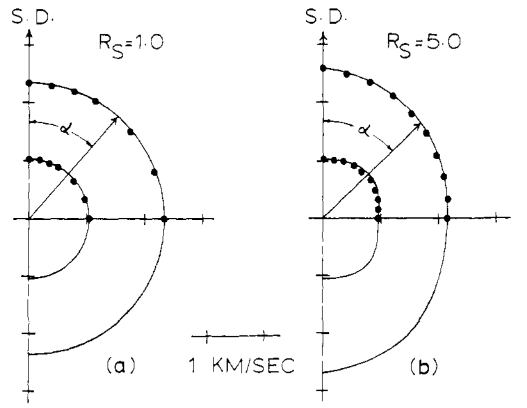

Figure 3. Polar plots of sound velocities in polycarbonate films vs. the sound propagation direction for two films (R_S = 1.0 and 5.0) S.D. is the stretch direction. (●) Experiment data; (—) fit to the Christoffel equation.

Table I
Elastic Constants as a Function of Stretch Ratio R_S for Polycarbonate Films

	C_{11}		C_{33}		C_{44}		C_{13}	
R_S	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
1.00	6.45	6.45	6.48	6.46	1.22	1.22	4.02	4.00
1.80	6.27	6.31	6.81	6.91	1.27	1.22	3.88	3.90
2.92	6.14	6.17	7.37	7.37	1.25	1.22	4.08	3.80
4.06	6.06	6.09	7.69	7.63	1.27	1.22	4.09	3.74
5.00	5.78	5.91	7.95	8.21	1.27	1.22	4.03	3.61
6.14	5.84	5.95	7.81	7.85	1.24	1.22	4.01	3.59
8.14	5.90	5.98	7.34	7.78	1.26	1.22	3.89	3.61

[a] Experimental values, dyn/cm^2 × 10^{10}. [b] Calculative values according to the model reported in ref 20, dyn/cm^2 × 10^{10}.

The shape of those velocity contour maps is associated with the change of elastic constants of the films as a result of stretching. This can be analyzed in terms of the Christoffel equation[23] for the propagation of acoustic waves in an anisotropic medium. The elastic constant matrix for a uniaxial oriented sample is given by

$$C_{ij} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{66} \end{bmatrix} \quad (5)$$

where $C_{66} = {}^1/_2(C_{11} - C_{12})$. The Christoffel equation, which relates the velocities and elastic constants for the acoustic waves propagating on the film surface, is given by[9]

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

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. The quasi-longitudinal (QL) and quasi-transverse (QT) phonons are associated with the plus and the minus roots, respectively. Knowing the density data and the hypersonic velocities as a function of α, one can calculate the elastic constants as a function of R_S using eq 6. We have used a least-squares computer fitting the program to include all experimental data in this calculation. The results for elastic constants C_{11}, C_{33}, C_{13}, and C_{44} obtained from the calculation are shown in Figure 4 and also in Table I. The elastic constant C_{66} (or C_{12}) is not shown, as it cannot be determined by the Brillouin scattering technique.

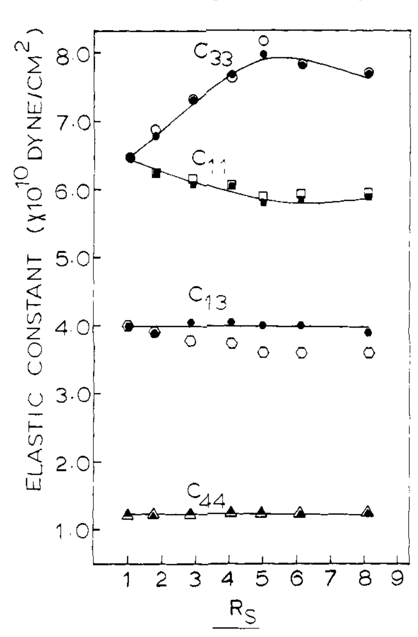

Figure 4. Elastic constants C_{11}, C_{33}, C_{13}, and C_{44} of polycarbonate films plotted vs. the stretch ratio (R_S). The solid points are the measured values; open points are the fit to the theory (see text).

Table II
Orientation Parameter as a Function of Stretch Ratio R_S for Polycarbonate Films

R_S	$\langle P_2\rangle$ [a]	*f* [b]
1.0	0.00	0.00
1.8	0.03	0.05
2.9	0.05	0.12
4.1	0.06	0.13
5.0	0.10	0.19
6.1	0.10	0.17
8.1	0.09	0.16

[a] Values according to ref 20. [b] The values according to Moseley's model.[21]

Although the behavior of the elastic constants in the PC films as the films are stretched is similar to that found in other polymer films,[8,9,20] there are some significant differences. For example, although the C_{33} values for the unstretched poly(ethylene terephthalate) (PET) and polypropylene (PP) films are lower than that for the PC film, as those films are stretched to R_S = 5.0 they become 4–5 times greater than the values of the unstretched films. On the other hand, the C_{33} value for PC only increases 23% from the unstretched value at 6.48 × 10^{10} dyn/cm^2 to the maximum value for the film stretched to R_S = 5.0 at 7.95 × 10^{10} dyn/cm^2. More interestingly, above R_S = 5.0, C_{33} shows a decrease rather than an increase found in other films.

The behavior of the elastic constants in the stretched films is closely associated with the increased chain segment orientation. A simplified model proposed by Moseley has related the sonic velocity of the oriented polymers to the orientation parameter $\langle P_2\rangle$ by[21] eq 7, where $C_{33}{}^{u}$ and ρ^0

$$\langle P_2\rangle \equiv {}^1\!/_2\langle 3\cos^2\theta - 1\rangle = 1 - (C_{33}{}^{u}/C_{33})(\rho/\rho^0) \quad (7)$$

are the elastic constant and density of the unextruded sample, respectively. The orientation parameter calculated according to eq 7 is shown in Figure 4 and also in Table II (designated as f) as a function of stretch ratio.

In order to derive eq 7, Moseley has assumed that acoustic waves propagate in an oriented fiber in a way similar to the current conducted through parallel circuits and that for an oriented sample $C_{33} \gg C_{11}$. However, even though the C_{33} value may be several times larger than the C_{11} value, the effect of C_{33} in the highly oriented state cannot be neglected. Furthermore, the propagation of sound waves cannot be treated in a manner like current flowing in a parallel electronic circuit. Assuming that polymer chains reorient when the films are stretched, i.e., the combined intermolecular effect such as partial crystallization and chain reorientation can be approximated as the rotational transformation of the strain tensor, Wang and Cavanaugh have shown that the elastic constants C_{11}, C_{33}, and C_{13} of an oriented film are rigorously related to the orientation parameter $\langle P_2 \rangle$ by[6,20]

$$C_{11} = (\lambda + 2\mu)(1 - \langle P_2 \rangle) + C_{11}^0 \langle P_2 \rangle \qquad (8)$$

$$C_{33} = (\lambda + 2\mu)(1 - \langle P_2 \rangle) + C_{33}^0 \langle P_2 \rangle \qquad (9)$$

$$C_{13} = \mu(1 - \langle P_2 \rangle) + C_{13}^0 \langle P_2 \rangle \qquad (10)$$

where λ and μ are the two Lame constants for the unoriented isotropic films; C_{11}^0, C_{33}^0, and C_{13}^0 are the elastic constants of the oriented films when $\langle P_2 \rangle = 1$.

One notes in Figure 4 that C_{11} of the stretched film is less than C_{11}^u, where C_{11}^u $(= \lambda + 2\mu)$ is the C_{11} (or C_{33}) value of an unoriented film. On the other hand, as the film is stretched C_{33} becomes greater than $(\lambda + 2\mu)$.

To obtain the orientation parameter from the experimentally determined elastic constants using eq 8 and 9, we need to determine the intrinsic elastic constants C_{11}^0, C_{33}^0, and C_{13}^0 for the perfectly oriented units. To do this, we set $C_{11}^0 = AC_{11}^u$ and $C_{33}^0 = BC_{11}^u$, where A and B are fitting parameters that are less than and greater than unity, respectively. According to ref 20, the C_{13}^0 values are related to C_{11}^0 and C_{33}^0 by eq 11, which is the result

$$C_{13}^0 = (\lambda + 2\mu)(^{15}/_4 - {}^3/_4 B - 2A) - 2\mu \qquad (11)$$

of eq 8–10, together with the assumption that C_{44} remains unchanged as the films are stretched; i.e., $C_{44}^0 = \mu$. This is justified by the present experimental result (see Figure 3). Having obtained eq 11, we then make an initial guess of the values A and B. The A and B values, along with the measured unoriented elastic constants, determine a full set of initial constants for the calculation. The value of $\langle P_2 \rangle$ for each sample can then be calculated according to eq 8–10 and a least-squares program. The calculated C_{11}, C_{33}, and C_{13} values are compared with the experimental results; the process is repeated, varying A and B so that the difference between the experimental results and the calculated values is minimized.

The orientation parameters $\langle P_2 \rangle$ calculated according to this method are shown in Table II and also plotted as a function of stretch ratio (R_S) in Figure 5. One notes that for all stretched films, the $\langle P_2 \rangle$ value calculated by using the method of Wang and Cavanaugh is always less than that obtained by Moseley's model (eq 7). Clearly Moseley has overestimated the value of C_{33}^0 in his theory.

The best values calculated by using eq 8–10 are plotted in Figure 4 as well as tabulated in Table I. Except for a small discrepancy in the C_{13} values at large R_S values, they compare well with the experimental values. The small discrepancy in C_{13} indicates the orientation of PC films is not completely affine. However, in view of the C_{11} and C_{33} results, the agreement between theory and experiment is sound. Not only is the decrease in C_{11} accounted for, but also the increase as well as the subsequent decrease of C_{33} at $R_S \geq 5.0$ are correctly predicted by the theory, thus indicating that the variation of the elastic constants of the stretched PC films is mainly due to the induced orientation of the polymer chains. However, compared with other polymer films such as PET[9] and PP[7,9,10] films, the induced chain orientation in PC is quite small. In the present PC films, at low R_S, $\langle P_2 \rangle$ increases slowly with increasing R_S, reaching a saturated value of about $\langle P_2 \rangle \simeq 0.1$ at $R_S = 5.0$.

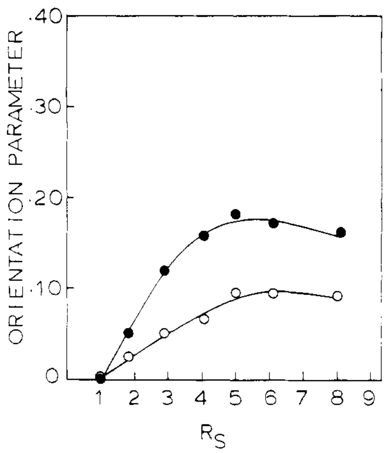

Figure 5. Orientation parameter plotted as a function of stretch ratio (R_S). (●) Total orientation paramer, f, according to the Moseley model; (○) orientation paramer, $\langle P_2 \rangle$, according to the model of Wang and Cavanaugh[6] (see text).

Like the PET films,[31,32] the PC film may be oriented and crystallized by stretching.[16,17] The induced chain orientation of stretched isotactic polypropylene films is well-known,[7] although the stress-induced crystallization is negligible.[33] In PET, Misra and Stein[31] have shown that the films stretched above T_g develop a rodlike superstructure oriented in the direction normal to stretching. However, as noted above in both the PET[6] and the isotactic PP films,[20] the elastic constant C_{33} increases to 4–5 times its unstretched value at $R_S = 5.0$, whereas in the PC film it only increases about 23% of the initial value. This comparison suggests that there is a fundamental difference between the morphology of PC films and that of PET, despite the fact that the phenyl group in PET is also incorporated into the chain backbone. Apparently, the stress-induced chain orientation in semicrystalline polymers depends to a large degree on the tie molecules in the amorphous phase. At low R_S, the stress-induced chain orientation in PET and in PP occurs in the amorphous region with the interlamellae strands or tie molecules connecting the neighboring lamellae in the direction of elongation. Clearly, this does not occur in the stretched PC films. In other words, the stress-induced crystallization in amorphous PC does not result in a superstructure like PET. Crystallization only occurs randomly at a local scale. As a result, no spherulite-like aggregate is present in PC to facilitate the orientation of the interlamella tie molecules. The difficulty in forming the spherulite structure in PC may be due to its rigid-chain backbone.

Finally, one notes that Poisson's ratio (σ) and Young's modulus (E) of the unoriented film can be readily obtained from the present data according to the expressions[23]

$$\sigma = {}^1/_2(C_{11}^u - 2C_{44}^u)/(C_{11}^u - C_{44}^u) \qquad (12)$$

$$E = 2C_{44}^u(1 + \sigma) \qquad (13)$$

The value of σ found in this study is 0.382, which agrees well with that reported in ref 14 and 17. However, Young's modulus E calculated according to eq 13 in the present work is equal to 3.38×10^{10} dyn/cm^2. This is 35% higher than the 2.5×10^{10} dyn/cm^2 value measured at low frequency (reported in ref 17 and 34). This difference suggests that considerable frequency dispersion may be present in the PC film above T_g.

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Registry No. Bisphenol A polycarbonate, 24936-68-3; bisphenol A–carbonic acid copolymer, 25037-45-0.

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Complex Branch Formation in Low-Density Polyethylene

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ABSTRACT: Formation of complex branches, which might arise from two intramolecular rearrangements of the Roedel type, has been investigated in polyethylene. A rotational isomeric state model is used for the polyethylene chain statistics, with inclusion of the effect of a trifunctional branch point on weighting of all configurations. It is assumed that reactive configurations are those in which pertinent carbon atoms are separated by a distance $r^* \pm \Delta r$, there simultaneously being approximate adherence to "three-in-a-line" geometry. This approach has recently been shown to rationalize several characteristics of branching in low-density polyethylene, including the common occurrence of butyl, less frequent presence of amyl, and occassional detection of 1,3-paired diethyl and 2-ethylhexyl branches (Mattice, W. L.; Stehling, F. C. *Macromolecules* **1981**, *14*, 1479). Present calculations successfully rationalize the observation of 1,3-paired ethyl butyl and tetrafunctional butyl branches, but they provide no explanation for the formation of tetrafunctional ethyl branches. They also suggest that 2-butylhexyl is an attractive candidate for unassigned resonances in the ^{13}C NMR spectra of low-density polyethylene.

Free radical initiated polymerization of ethylene at high pressure gives rise to low-density polyethylene. In addition to long branches,[1,2] this material contains short branches which influence morphology and solid-state properties. The number and type of short branches vary from one sample to the next.[3–13] Quantitative characterization of short branches is most easily achieved with ^{13}C NMR.[3–8,10–13] Short branches reported in low-density polyethylene include butyl,[3–8,11–13] ethyl,[3–8,11,13] amyl,[5,6,10–13] 1,3-paired diethyl,[11,13] 2-ethylhexyl,[11,13] 1,3-paired ethyl butyl,[13] tetrafunctional ethyl,[13] tetrafunctional ethyl butyl,[13] and tetrafunctional butyl.[13] Additional resonances, arising from short branches of unknown composition, are also found.

Intramolecular hydrogen atom abstraction via a cyclic intermediate is an attractive mechanism for formation of short branches.[14] Analysis of probabilities for observation of configurations conducive to this abstraction, using a rotational isomeric state model for the chain statistics,[15,16] can successfully rationalize occurrence of several known types of short branches.[17] The rotational isomeric state model can be reasonably parameterized so that a single Roedel-type rearrangement would be most likely to yield a butyl branch, could also give rise to longer branches, but would not produce branches shorter than butyl. Simple extensions of this mechanism have been proposed as a source of 2-ethylhexyl,[18] 1,3-paired diethyl,[18] and tetrafunctional butyl[14] branches. The rotational isomeric state