

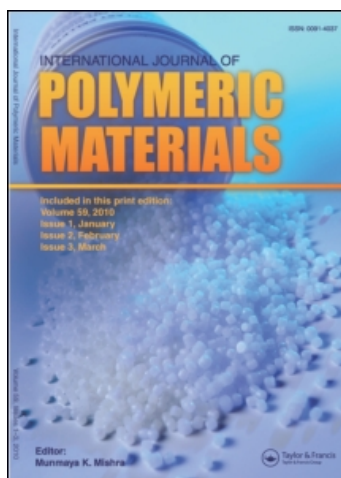
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# Brillouin Spectroscopy of Oriented Polymers

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We give a short overview of how to measure orientation-dependent velocities of hypersound by Brillouin spectroscopy, and what kind of data have been attained by this method. The observations in drawn segmented poly(urethane)-elastomers differ from all others: the sound velocity perpendicular to the chains runs through a minimum. At a draw ratio of  $\sim 3.8$  a sudden step in the sound velocity indicates a strain-induced structural change.

**KEY WORDS** Brillouin scattering, sound velocity, orientation, birefringence, Poisson number, poly(urethane).

## INTRODUCTION

By measuring the Doppler-shift of light scattered by acoustic phonons (the Brillouin–Mandelstam scattering) we are able to determine the direction-dependent sound velocities  $V$  at frequencies of some GHz (Figure 1).

What can we learn from these high frequency (GHz) sound waves in oriented polymers? Their direction dependence in anisotropic samples follows from elasticity theory<sup>1</sup> e.g. for uniaxial samples (hexagonal and higher symmetry):

$$V_{\text{QL,QT}} = \left[ \frac{1}{2\rho} \left( A \pm \sqrt{A^2 - 4(B - C)} \right) \right]^{1/2} \quad (1)$$

$$A = c_{11}\sin^2\theta + c_{33}\cos^2\theta + c_{44}$$

$$B = (c_{11}\sin^2\theta + c_{44}\cos^2\theta)(c_{33}\cos^2\theta + c_{44}\sin^2\theta) \quad (2)$$

$$C = (c_{13} + c_{44})^2\sin^2\theta\cos^2\theta$$

$$V_{\text{T}} = \left[ \frac{1}{\rho} (c_{44}\cos^2\theta + c_{66}\sin^2\theta) \right]^{1/2}, \quad (3)$$

“+” is for the quasi-longitudinal (QL) mode, i.e. mostly longitudinal polarized, “–” is for the quasi-transverse (QT) mode, i.e. mostly transverse polarized. T denotes the pure transverse mode which is always polarized perpendicular to the stretching direction,  $\rho$  is the density,  $c_{ij}$  are the elastic stiffness constants in the Voigt notation,  $\theta$  is the angle between direction of drawing and the scattering wave vector  $\mathbf{q}$  (see Figure 1). Using the above equations we obtain the elastic constants by fitting them simultaneously to the whole data set.<sup>2</sup> In Figure 2 we show elastic constants of LDPE for different draw ratios at room

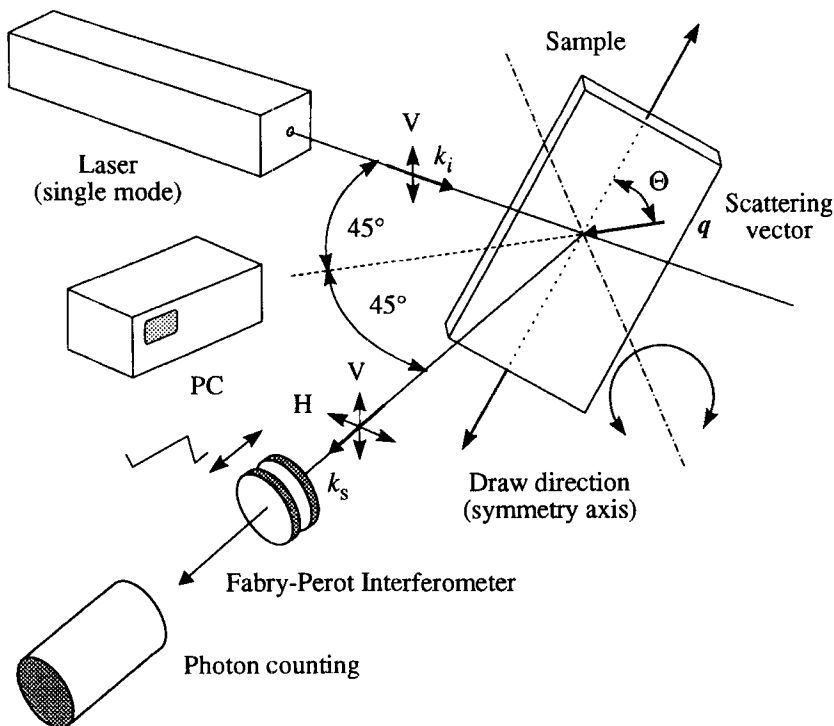


FIGURE 1 Principal arrangement of a Brillouin scattering experiment.

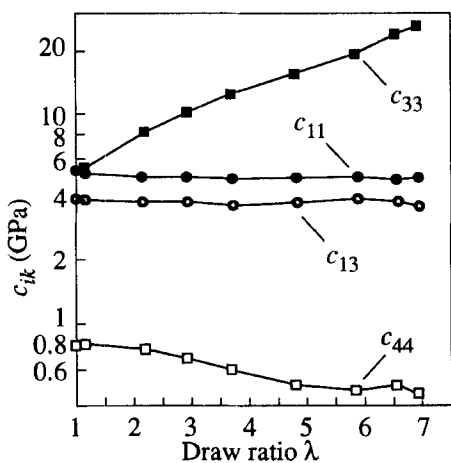


FIGURE 2 Elastic constants of LDPE.<sup>20</sup>

temperature. The most prominent change appears in the chain direction increasing  $c_{33}$ . A general problem is that pure transverse phonons are scarcely to be observed, if at all. Thus the tensor of the elastic stiffness constants cannot be inverted to compliances except for the cases when there is a good guess for  $c_{66}$ .

## ORIENTATIONAL EFFECTS

In describing the properties of oriented polymers the aggregate model is widely used because of its simplicity. The main assumption of this model is the existence of subunits of deformation (see the contribution of H.-G. Kilian at this conference) whose properties are invariant under deformation. This does not imply that the units themselves are invariant in all respects. The macroscopic properties are then calculated as pure orientational averages over these subunits. A general and useful form has been derived by Peetz:<sup>3,4</sup>

$$a = P a_0 \quad (4)$$

$$\begin{aligned} P &= \text{diag}(1, 1, P_2, P_2, P_4) \\ a_v &= T(c_{11}, c_{33}, c_{13}, c_{44}, c_{66}) \\ a_r &= T\left(s_{11}, s_{33}, s_{13}, \frac{1}{4}s_{44}, \frac{1}{4}s_{66}\right) \\ T &= \begin{pmatrix} 8 & 3 & 4 & 8 & 0 \\ 1 & 1 & -2 & 6 & 5 \\ -4 & 3 & 1 & 2 & 0 \\ 1 & 1 & -2 & 3 & -7 \\ 1 & 1 & -2 & -4 & 0 \end{pmatrix}. \end{aligned} \quad (5)$$

$a$  denotes the orientationally averaged elastic properties of the material, and  $a_0$  denotes those of the subunit. Depending on the averaging chosen we use  $a_v$ ,  $a_r$  for the Voigt-(elastic stiffness tensor) and the Reuss-(elastic compliances)-averaging, respectively. The orientation parameters  $P_2$  and  $P_4$ , are averages of the Legendre polynomials with respect to the orientation density distribution.  $P_2$  is often called the 'Hermans' orientation function. Using the proper linear combinations of  $c_{ik}$  produced by the action of the similarity matrix  $T$  (see Reference 4) we can determine the orientation parameters.  $P_2$  is needed generally in describing the effect of orientation on properties at least of the second rank.  $P_4$  is needed when describing tensor properties of the fourth rank. Additionally it serves to characterize the type of orientation function (see the contribution of H.-G. Kilian at this conference) The results obtained so far follow a simple relation:<sup>4,5</sup>

$$P_4 = x P_2 + (1 - x) P_2^2. \quad (6)$$

For PC and PMMA  $x \sim 0.05, 0.06$  respectively has been found being very close to the affine orientation distribution with  $x = 0.061$  at  $P_2 < 0.5$ . This finding does not imply that the relation to the draw ratio and hence the deformation process is affine-like.<sup>5</sup> From the invariants (not shown here) we know that the aggregate model is generally not well fulfilled, which is easily recognized from Figure 2. Astonishingly, it better fits semicrystalline than amorphous polymers when compared at equal average orientation, i.e.  $P_2$ .

If only the velocity in the principal directions can be measured, a crude approximation for low and moderate elastic anisotropies<sup>6</sup> yields

$$P_2 \approx 1 - \frac{c_{11}}{c_{33}} \approx \frac{5}{4} \left(1 - \frac{c_{\text{iso}}}{c_{33}}\right), \quad (7)$$

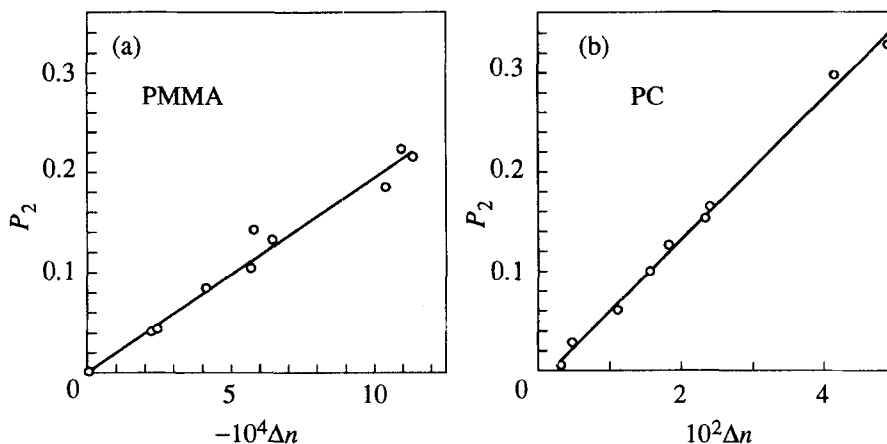


FIGURE 3 Elastic orientation  $P_2$  versus birefringence  $\Delta n$  in PMMA and PC.

which is apart from the factor  $5/4$  the Moseley relation. Examples are shown in Figure 3. This orientation function which is an overall measure of the orientation of force constants (atomic distances, angles, rotations) may be compared to the birefringence relation.

$$P_2 = \frac{\Delta n}{\Delta n_0}. \quad (8)$$

$\Delta n$  is the measured birefringence,  $\Delta n_0$  is that of the subunits. Birefringence is an overall measure of polarizability which is predominantly determined by chemical bond orientation. Thus both properties are intimately related but yet different. Polarizabilities are additive but the birefringence is additionally influenced by the internal field resulting e.g. in a shape contribution of colloidal particles. Elasticity contains no internal field contribution but is dependent on the relative arrangement of force constants and thus on structural aspects. The value of the Brillouin scattering lies in the fact that the acoustic wavelength probing the elastic properties is of the same order as the light wave probing the optical properties ( $\lambda_{\text{sound}} \sim 360$  nm,  $\lambda_{\text{light}} \sim 520$  nm). The wave length determines the length scale of the physical averaging. The experimental averaging is given by the scattering volume, which is larger by about two orders of magnitude.

### UPPER BOUNDS OF $\Delta n_0$

Extrapolation of the plot  $P_2^{\text{elast}}$  versus  $\Delta n$  (Figure 3) to  $P_2^{\text{elast}} = 1$  yields the structural or intrinsic birefringence  $\Delta n_0$ . From the method of determination it is obvious that it is not to be confused with a monomers birefringence. The two may be equal but must not. The local structure may influence the elasticity as well as the birefringence. Examples are given in Table I.

Another possibility to obtain upper bounds of  $\Delta n$  is to use mode ratios.<sup>6</sup>

$$\nu_{1,13} = \frac{c_{11} - 2c_{44}}{2(c_{33} - c_{44})}, \quad \nu_{3,31} = \frac{c_{33} - 2c_{44}}{2(c_{33} - c_{44})}. \quad (9)$$

TABLE I  
Structural birefringence  $\Delta n_0$  determined by extrapolation of mode numbers  $\nu_{3,31}$   
and elastic orientation functions  $P_2^{\text{elast}}$

Polymer	$\nu_{3,31} \rightarrow 0.5$	$P_2^{\text{elast}} \rightarrow 1$	Literature data	References
PMMA	$-5.5 \times 10^{-3}$	$-5.3 \times 10^{-3}$	$-3.2 \dots 6.7 \times 10^{-3}$	10-12
PC	0.204	0.143	0.062 ... 0.23	12-16
PET	0.208	0.205	depends on $\chi_c$ †	17
PVC	$1.1 \times 10^{-2}$	$1.2 \times 10^{-2}$	$5.3 \times 10^{-3}, 8.7 \times 10^{-3}$	12, 18
LDPE	$4.7 \times 10^{-2}$	$5.2 \times 10^{-2}$	$4.9 \times 10^{-2}$ ‡	19

† crystallinity  $\chi_c = 0.27$ , data consistent with  $\Delta n_0^c = 0.22$ ,  $\Delta n_0^a = 0.20$ .

‡ for amorphous-crystalline clusters with  $\chi_c = 0.44$ .

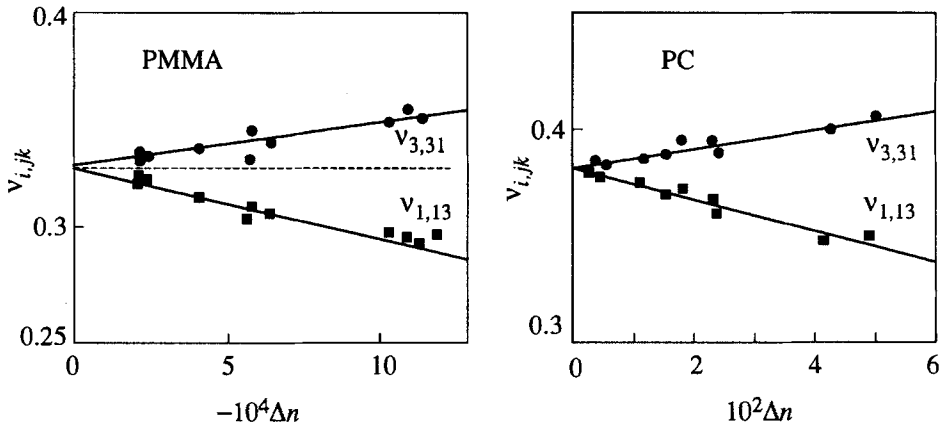


FIGURE 4 Mode numbers  $\nu_{i,j,k}$  of PMMA and PC versus birefringence  $\Delta n$ .

$\nu_{i,j,k}$  means that the longitudinal wave running in  $i$ -direction is compared to the transverse one running in  $j$ -direction being polarized in  $k$ -direction. The range of values is:

$$2V_T \leq V_L : 0 \leq \nu \leq \frac{1}{2}; \quad 2V_T = V_L : \nu = \frac{1}{2}; \quad \frac{V_T}{V_L} = 0 : \nu = 0. \quad (10)$$

In the isotropic case  $c_{11} = c_{33} \Rightarrow \nu_{1,13} = \nu_{3,31} = \nu$  where  $\nu$  is the Poisson number (Table II). In the anisotropic case  $\nu > 0.5$  is possible but  $\nu_{1,13}, \nu_{3,31} < 0.5$  still holds! Thus extrapolating a plot of  $\nu_{3,31}$  versus  $\Delta n$  (Figure 4) to  $\nu_{3,31} = 0.5$  yields another estimate of  $\Delta n_0$ . The results are listed in Table I. Moreover an extrapolation to  $\Delta n = 0$  provides an accurate value of the isotropic Poisson number. Direct measurements of this property are often not possible, because transversely polarized phonons (providing  $c_{44}$ ) are difficult, sometimes impossible, to observe.

A comparison of the structural birefringence determined by both methods yields consistent values for the few polymers investigated so far, with the exception of PC. The reason for this discrepancy is the monomer structure, which has been discussed in some detail in Reference 7.

TABLE II  
Poisson ratios determined by different methods at room temperature

PC	PMMA	PVC	PET	PE	Source
0.309	0.324	0.356	0.390	0.413	Our laboratory Brillouin scattering <sup>21</sup>
0.375	—	—	—	—	Handbook <sup>22</sup> Ultrasound <sup>23</sup>
0.313	—	—	—	—	
	0.34	—	—	0.41	

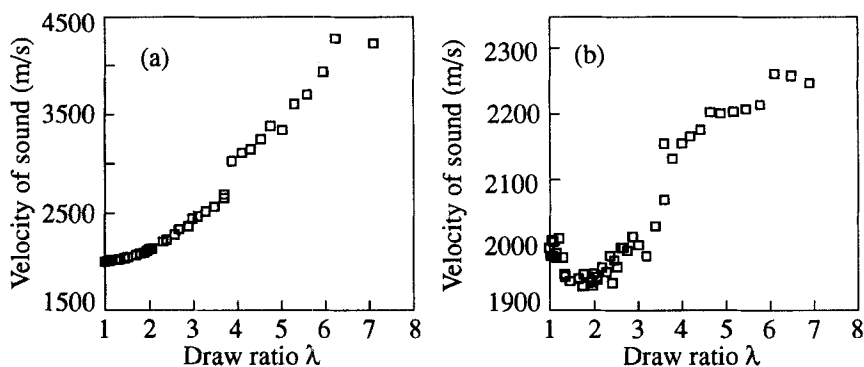


FIGURE 5 Velocity of sound in a segmented PU-elastomer: (a) parallel, (b) perpendicular to the preferred chain orientation.

### UNUSUAL EFFECTS IN PU

The dependences of sound velocity and hence of elastic constants on deformation are relatively simple and similar in stretched polymers.<sup>5,6,8,9</sup> However, rather unexpected features are observed during stretching segmented PU-elastomers with diamide-chain extenders. The structure of a segmented PU-elastomer is that of a network of the so-called soft segments which are cross-linked by domains of hard segments. These domains are built by microphase separation and are stabilized by hydrogen bonds. An important feature of their deformation behavior is an enormous elastic hysteresis accompanied by a mostly linear and reversible birefringence. Despite this simple behavior of the overall orientation indicated by the birefringence, IR-spectroscopy has shown that the orientation of the hard segments may be complicated in detail exhibiting even negative orientation. In our observations a more than twofold increase of the sound velocity in the draw direction is comparable to semicrystalline PET and PE. In rubber networks this increase is very small, just measurable.

The sound velocity perpendicular to the draw direction decreases as usual first but then increases and eventually surpasses the isotropic value. Such a behavior has never been observed before. Most striking is the step in both the velocities at a draw ratio of about 3.8. At higher draw ratios there appear quasi-transverse phonons, i.e. the PU behaves like a solid. If we calculate the orientation parameter according to Equation (7) we find two linear branches.

In the first branch  $F_2$  increases proportionally to birefringence. No signs of any negative orientation are found. The step indicates a transition-like phenomenon which at the

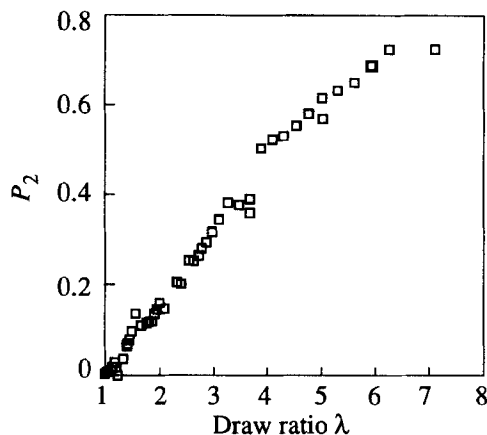


FIGURE 6 The elastic orientation parameter  $P_2$  of the PU-elastomer versus draw ratio.

Brillouin frequencies appears as a “liquid-solid” behavior. It may tentatively be attributed to a cooperative interlocking of hydrogen bonds after the destruction of the original short range order. This enhances the modulus of the oriented polymer resulting in the step of  $P_2$  as well as that of the (hypothetical) isotropic reference state, giving the smaller slope of the second linear branch. An alternative explanation might be the stress-induced crystallization of the soft segments. This could be examined by stretching calorimetry as well as by the Brillouin scattering from elastomers exhibiting stress-crystallization.

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