Polymer Science

Structure and anisotropy in polycarbonate
III. Study of elastic and optical properties of oriented samples
with the method of high resolution Brillouin spectroscopy

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Abstract: High resolution Brillouin spectroscopy (BS) has been used to investigate elastic and optical properties of uniaxially drawn samples of polycarbonate (PC). The results are discussed in the framework of the single phase aggregate model (SPAM) of Ward. According to a recently developed evaluation technique, the SPAM parameters of PC are determined, resulting in the following elastic constants of the structural units: $c_{13} = 33$ GPa, $c_{11} = 7$ GPa, $c_{44} = 9.7$ GPa, $c_{44} = 1.4$ GPa, and $c_{11} = 1$ GPa. A nearly quadratic dependence of the orientation parameter $P_4$ on $P_2$ results, which can be explained by a modified pseudoaffine deformation scheme.

Key words: Polycarbonate, oriented polymers, elastic and optical anisotropy, Brillouin spectroscopy, aggregate model, orientation parameters.

1. Introduction

In the preceding papers of this series about amorphous polycarbonate (PC) [1, 2], it has been shown that orientation of PC does not change the short range order up to 1.5 nm. Therefore, PC seems to be a favourable candidate for the application of the single phase aggregate model (SPAM) of Ward [3]. Though originally formulated for semi-crystalline polymers it is used to describe the oriented state of amorphous polymers as well [4]. A reinvestigation of the SPAM [5] reveals new aspects and proposes an easy test of its applicability and a new way to evaluate the SPAM parameters, if either the Voigt or the Reuss orientation average of the elastic constants holds.

In this paper we present elastic and optical data of oriented PC determined simultaneously by the technique of high resolution Brillouin spectroscopy (BS). These data are used to evaluate the appropriate SPAM parameters.

2. Experimental

For reason of comparison, the investigations presented in this paper have been performed on the same samples used for the previously reported measurements [1, 2]. The plate-like samples had dimensions of about 20 mm x 10 mm with thicknesses between 0.6 and 2.2 mm. As usual for the case of oriented polymers, slight inhomogeneities up to macroscopic dimensions were present in the samples. However, the surface quality and the transparency were sufficient for optical investigations.

A characterisation of the uniaxially oriented PC-samples¹), is given in Table 1 in terms of stretching temperature $T_s$, birefringence $\Delta n'$ (measured with a polarizing microscope at $\lambda = 545$ nm but transformed to $\lambda = 514.5$ nm), and stretch ratio $s$ (for samples 1-7). $s$ was determined from $\Delta n'$ using an experimental curve of $\lambda$ versus $\Delta n'$ at a stretch temperature $T_s = 160^\circ C$²). For more detailed information about the samples, the preceding publications [1, 2] should be consulted.

A convenient way to determine the complete elastic stiffness tensor and the main refractive indices of anisotropic materials with the method of high performance BS has been discussed extensively in a recent publication [7]. In the following, results from this work are used and only briefly reviewed here.

Hypersonic measurements have been performed with a five-pass spectrometer described elsewhere [8]. An argon ion laser was used at a wavelength of $\lambda = 514.5$ nm.

¹) Isotropic sheets of PC with trade name Makrolon 3200 were kindly supplied by Bayer AG, Leverkusen.
²) The samples were prepared by Dr. M. Dettenmaier by the same procedure as used in [6].
Table 1. Characterisation of the PC-samples investigated

<table>
<thead>
<tr>
<th>sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta n')</td>
<td>0.0024</td>
<td>0.0053</td>
<td>0.0102</td>
<td>0.0145</td>
<td>0.0173</td>
<td>0.0226</td>
<td>0.0243</td>
<td>0.0407</td>
<td>0.0461</td>
</tr>
<tr>
<td>(T_s, ^\circ C)</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>25</td>
<td>130</td>
</tr>
<tr>
<td>(\lambda_s)</td>
<td>1.09</td>
<td>1.19</td>
<td>1.41</td>
<td>1.62</td>
<td>1.79</td>
<td>2.12</td>
<td>2.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Elastic and optical properties of the plate-like PC samples were determined using the 90 A- and the 90 R-scattering geometries [7,9].

For the uniaxially oriented PC samples fibre symmetry (transverse isotropy) was assumed and experimentally confirmed. A sample coordinate system \((x_1, x_2, x_3)\) of the plate-like samples is defined with \(x_3\) as the fibre axis and \(x_2\) as the plate normal.

For the 90 A-scattering geometry, the wave vector \(q\) of the scattering sound waves lies orthogonal to the surface normal \((x_2\)-axis\) within the \(x_1x_3\)-plane. If the sample is turned around the \(x_2\)-axis, which in our laboratory is performed by a computer controlled sample holder, the phonon wave vector \(q\) rotates within the \(x_1x_3\)-plane. This allows one to measure a polar diagram of the sound velocity as well of the quasi-longitudinal \((q_l)\) as of the quasi-transverse \((q_t)\) polarized sound waves.

Using the 90 R-scattering geometry the wave vector \(q\) is parallel to \(x_2\).

Within the sample coordinate system the elastic stiffness tensor has the following form if the contracted matrix-notation of Voigt is used:

\[
\mathbf{C} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & \cdots & \cdots \\
C_{12} & C_{11} & C_{13} & \cdots & \cdots \\
C_{13} & C_{13} & C_{33} & \cdots & \cdots \\
\cdots & \cdots & \cdots & C_{44} & \cdots \\
\cdots & \cdots & \cdots & \cdots & C_{66}
\end{bmatrix}
\]

with the relation

\[
c_{12} = c_{11} - 2c_{66}.
\]

Supposed that the density \(\rho\) is known, only four of the five independent elastic stiffness constants \((c_{11}, c_{33}, c_{13}, c_{44})\) can be obtained from the 90 A-measurements.

Using the 90 R-scattering geometry the \(x_2\)-propagating-\(x_1\)-polarized sound waves give rise to a \(VH\)-component of the Brillouin spectra. From this component \(c_{66}\) can be obviously calculated if the main refractive indices \(n_1\) and \(n_3\) and the density \(\rho\) are known. Furthermore the Brillouin lines of the \(x_2\)-propagating-\(x_3\)-polarized sound wave can be detected, giving \(c_{44}\). This can be used for a redundancy test for \(c_{44}\) obtained within the 90 A-scattering geometry.

Using simultaneously all sound velocity data determined with the 90 A- and the 90 R-scattering geometries, all five independent elements of the elastic stiffness tensor can be determined by a least squares fit procedure [7].

The 90 A- and the 90 R-scattering geometries can be also used to determine the main refractive indices \(n_1\) and \(n_3\) of a fibre symmetric material [7], provided that no sound dispersion occurs in the frequency range of interest. As we will show in Section 3, this condition holds within the glassy state of PC at room temperature. Then, from the 90 R-Brillouin frequencies \(f_{90R}(i)(i = 1, 3)\) due to longitudinal \(x_2\)-propagating-\(x_2\)-polarized sound waves with the electric field of the incident laser beam either parallel to \(x_1\) (\(i = 1\)) or parallel to \(x_3\) (\(i = 3\)), respectively, \(n_1\) and \(n_3\) can be determined by comparison with the 90 A-Brillouin frequency \(f_{90A}\) due to \(x_1\)-propagating-\(x_1\)-polarized sound waves according to

\[
n_i = (0.5((f_{90R}(i)/f_{90A})^2 + 1))^{0.5} i = 1, 3
\]

since \(x_1\) and \(x_2\) are equivalent for fibre-symmetric samples. In addition, we were able to measure \(n_1\) and \(n_3\) of some samples directly with an Abbe-refractometer at \(\lambda = 514.5\) nm.

The density \(\rho\) of all PC samples was measured with a flotation method using an aqueous solution of calcium chloride.

3. The model

Macroscopic physical properties of polymers are generally changed by uniaxial drawing. This is due to a reorientational process of molecular segments or larger "structural units" forced by the uniaxial stress field. If these units remain invariant under orientation, it is likely that the SPAM of Ward can be used to relate the macroscopic physical properties to those of the "structural units". We will show that the SPAM holds for the elastic and optical properties of uniaxially oriented PC.

The following discussion is based on a recent reinvestigation of the SPAM [5]. The essential results of this latter work are briefly reviewed. The reported results hold, assuming fibre symmetry, as well on a macroscopic scale as locally for the structural units.

Concerning the elastic properties, the two limiting orientation averages are the Voigt and the Reuss average, assuming boundary conditions of either homogeneous strain or homogeneous stress, respectively. Both orientation averages can be interpreted as linear transformations in appropriate five-dimensional vector spaces of independent elements of either the elastic stiffness of the elastic compliance tensor [5]. The corresponding transformation matrix can be diagonalized by a similarity transformation, showing, that the eigenvalues are the orientation parameters \(P_0 = 1\) (twice), \(P_2\) (twice) and \(P_4\).