JOURNAL OF MATERIALS SCIENCE **30** (1995) 5457–5460

The elastic behaviour of polycarbonate in the glassy state determined by Brillouin scattering

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Measurements of the temperature and hydrostatic pressure dependence of the elastic constants of amorphous polycarbonate in the glassy state using high-resolution Brillouin spectroscopy are reported. It was found that the temperature and the pressure dependence of the longitudinal and the transverse sound velocity are strictly linear, in contrast to the behaviour found in polymethylmethacrylate (PMMA). A simple equation for the behaviour of the elastic constants c_{11} and c_{44}, and the shear, Young's and bulk modulus, can be given, which fits the experimental data well.

1. Introduction

In contrast to most polymers, in polycarbonate (PC), transverse phonon lines are easily observable. Thus this material has generated much interests with respect to Brillouin scattering [1–3]. In the present work, interest focused on the elastic behaviour in the glassy state. Most of the technical applications of polymers are in this range. The glass transition itself is out of the scope of the present work.

Polycarbonate is one of the most important engineering polymers, as it posseses a relatively high impact strength and a high glass transition temperature, T_g, of about 418K (the exact value depends on the sample material used, e.g. with different molecular weight). The melting temperature is about 513 K. Bulk sample of PC may be fully amorphous or partially crystalline. But there is only a noticeable crystallization if it is allowed to occur over weeks at a temperature of about 460 K, and the maximum obtainable crystallization grade is about 17% [4]. Because this treatment was not carried out, we assume a very low or nearly zero crystalline grade in the sample material used here.

It is also well known that different results may be obtained depending on the cooling rate from the melt or anealing the sample for very long periods (e.g. months) at a temperature near T_g (e.g. [1]). This phenomenon does not play a role in our investigations, because our measurements were performed in a temperature and pressure range far away from the glass transition region.

Fig. 1 shows the temperature and pressure range for which Brillouin data for polycarbonate are available. It indicates that our experiments extend the temperature range and especially the pressure range, in to areas in which, as yet, data were lacking. On the other hand, it can be seen that the covered region in the p–T diagram is small.

A further reason to investigate PC was to compare the pressure dependence with that of PMMA, where recently the surprising result of a strong increase in the intensity of the transverse phonon was found [5].

2. Experimental procedure

The Brillouin measurements were performed with a Sandercock 4-pass Fabry-Perot-interferometer. Spectra were taken with different free spectral ranges from 13–15.5 GHz. As a light source the 514.5 nm line of a single-mode argon-ion laser, was used, with maximum power of 100 mW to avoid heating and damage of the sample. The polycarbonate sample of dimensions 5 mm × 5 mm × 5 mm were cut from 5mm thick sheets (Lexan®, General Electric Corp.). The faces were polished to obtain good optical quality and therefore low Rayleigh scattering. To study the temperature dependence of the Brillouin shifts, the samples were mounted in a home-made temperature-controlled (± 0.1 K) liquid-nitrogen cryostat. For the pressure experiments, a three-window optical high-pressure cell [6] was used with synthetic oil (Plexol) as the pressure medium, which additionally serves as an index matching fluid. The sound velocities v_i (i = longitudinal (l) or transverse (t)) using the relation for the Brillouin shifts, $\Delta\nu_i$

$$\Delta\nu_i = \pm\frac{2n}{\lambda_0} v_i \sin\left(\frac{\theta}{2}\right) \tag{1}$$

where n is the index of refraction, λ_0 is the vacuum wavelength of the incident light, and θ the inner scattering angle. The plus sign stands for the Antistokes process, and the minus for the Stokes process. In our experiments two different scattering geometries were used (pressure experiments: 90 °N geometry, temperature experiments: 90 °A geometry [7]) due to the different possibilities for mounting the sample in the pressure cell and the cryostat. Using a 90 °N scattering geometry, Equation 1 becomes

$$\Delta\nu_i = \pm\frac{\sqrt{2}n}{\lambda_0} v_i \tag{2}$$

and for a 90 °A geometry

$$\Delta\nu_i = \pm\frac{\sqrt{2}}{\lambda_0} v_i \tag{3}$$

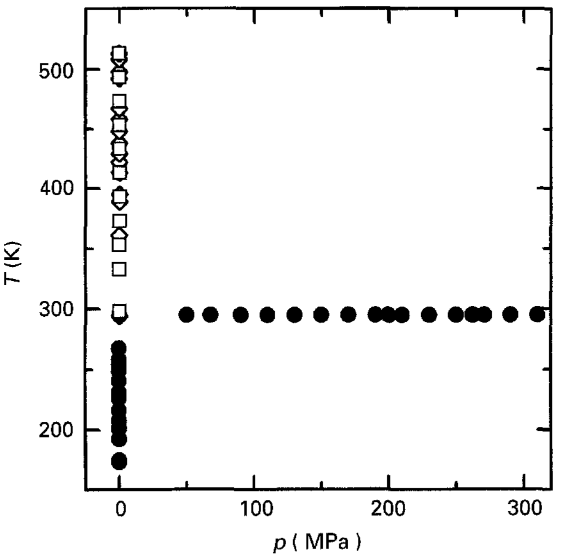

Figure 1 Pressure and temperature range for which Brillouin data of polycarbonate are available: (●) present measurements, (□) [2], (◇) [3].

For an isotropic solid there are only two independent elastic constants, c_{11} and c_{44} [8] which can be calculated knowing the longitudinal and transverse sound velocities and the mass density, ρ

$$c_{11} = v_l^2 \rho \tag{4a}$$

$$c_{44} = v_t^2 \rho \tag{4b}$$

The data for the pressure and temperature dependence of the density were taken from Dollhopf *et al.* [9]. The pressure dependence of the index of refraction was calculated assuming constancy of the specific refraction [10].

3. Results and discussion

Fig. 2 shows typical unpolarized Brillouin spectra at different pressures and temperatures. No experiments were performed to investigate the change in the spectra for different polarization geometries, such as V-H or V-V, because of the depolarizing effect under stress of the sapphire windows of the high-pressure cell. The different intensities can be explained by different accumulation times, different laser powers and the different scattering geometries used. For the 90 °A geometry, the Rayleigh intensity is normally larger than that for 90 °N.

Fig. 3 shows the measured longitudinal and transverse Brillouin shifts versus temperature, compared with those from the literature [1,2]. As mentioned above, the temperature experiments were performed using a 90 °A scattering geometry, whereas the experiments described in the literature used the geometry which we call 90 °N. To compare the data the corresponding shift for the 90 °A geometry was calculated using

$$\Delta v_{90^\circ\mathrm{N}} = n \Delta v_{90^\circ\mathrm{A}} \tag{5}$$

which follows from Equations 2 and 3. Only at room temperature was there a noticable deviation between the literature data and the present results. If the present data are extrapolated to higher temperature, this deviation vanishes. Taking into account that possibly slightly different samples were used, the data are in

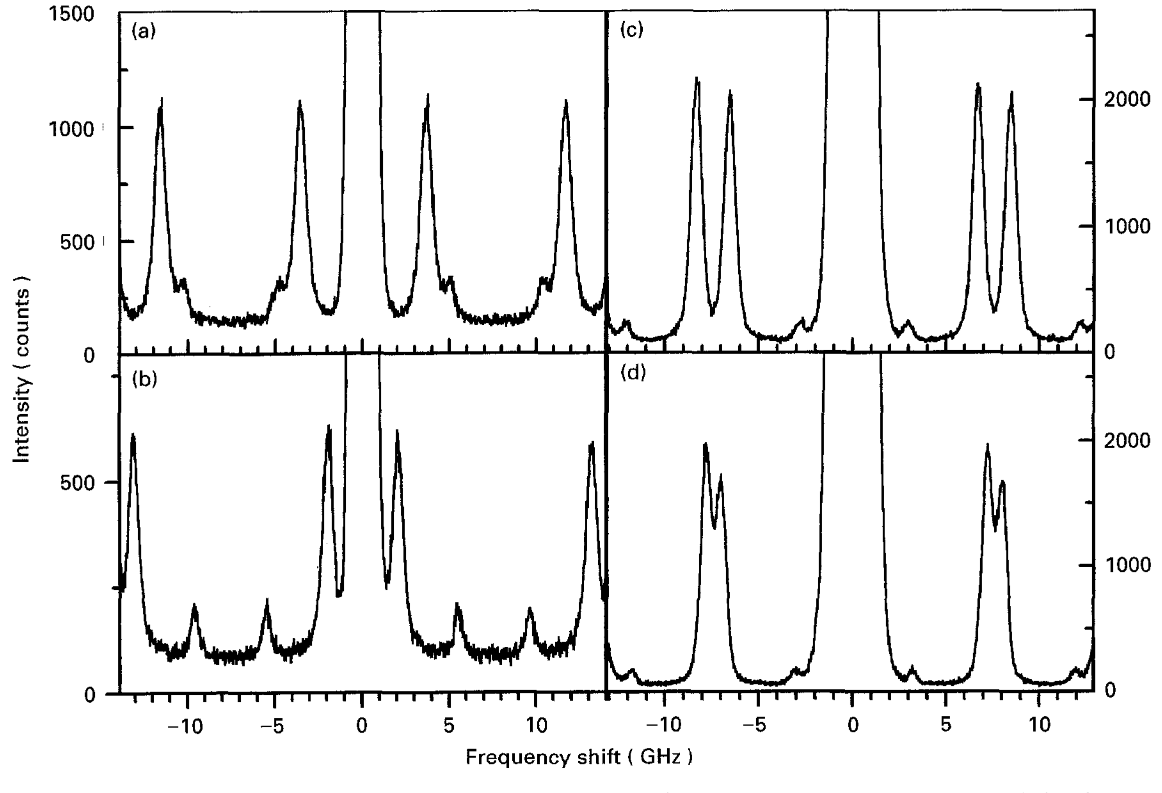

Figure 2 Unpolarized spectra of PC at different pressures and temperatures: (a) $p = 110$ MPa, $T = 294.0$ K, accumulation time $t_a = 38$ min, laser power, P_L, 20 mW; (b) $p = 290$ MPa, $T = 294.0$ K, $t_a = 30$ min, $P_L = 30$ mW; (c) $p = 0.1$ MPa, $T = 288.2$ K, $t_a = 12$ min, $P_L = 70$ mW; (d) $p = 0.1$ MPa, $T = 253.7$ K, $t_a = 12$ min, $P_L = 100$ mW.

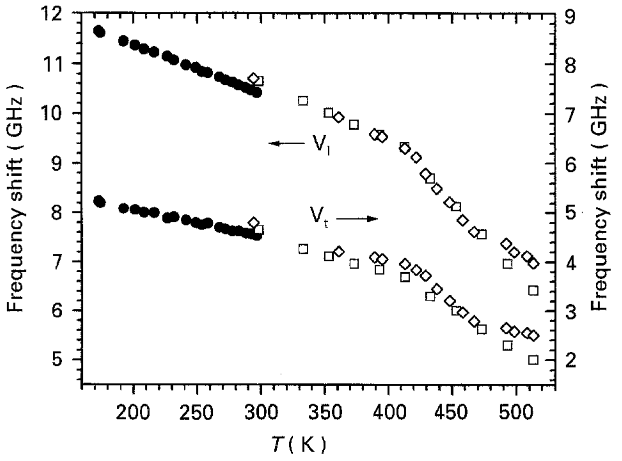

Figure 3 Longitudinal transverse Brillouin shifts versus temperature for polycarbonate (●) present measurements, (□) [1], (◇) [2]).

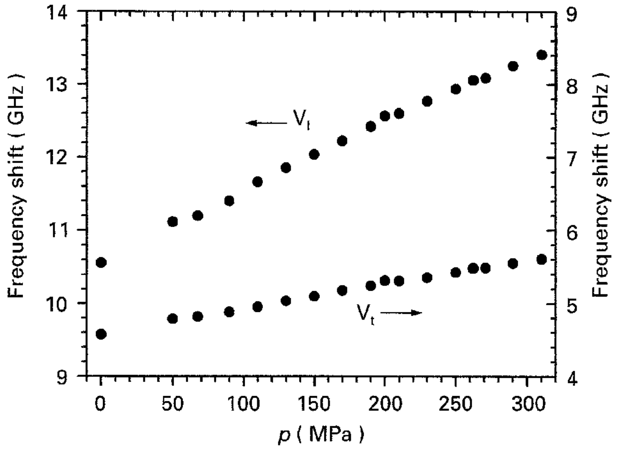

Figure 4 Longitudinal and transverse Brillouin shifts versus pressure for polycarbonate.

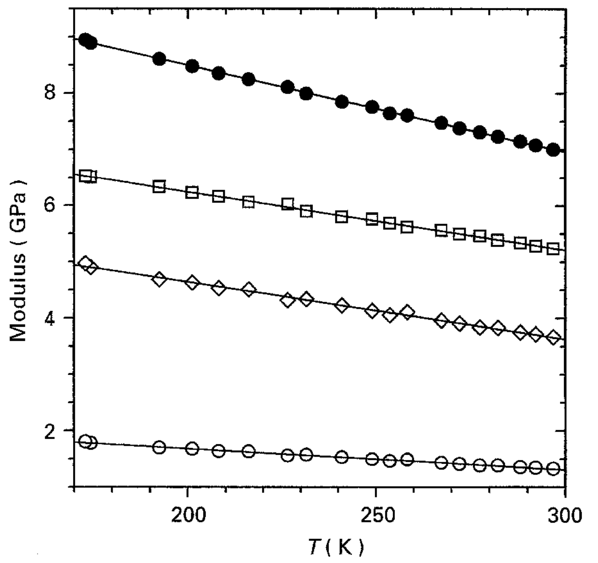

Figure 5 The elastic constants, bulk and Young's modulus versus temperature (●) c_{11}, (○) c_{44}, (□) B, (◇) E. Lines, see text.

good agreement. The longitudinal and transverse Brillouin shifts are plotted versus pressure in Fig. 4.

The linewidth of the Brillouin lines is proportional to the phonon damping. In general, it is hard to give a quantitative value for attentuation, because the measured linewidth is a convolution of the real linewidth of the Brillouin line and the instrumental function, which is very sensitive to the alignment of the Fabry-Perot-interferometer. Therefore, numerical values will not be given, and only the general tendency is described, that with increasing pressure and decreasing temperature the Brillouin lines, and therefore the damping, become smaller. This is exactly as expected.

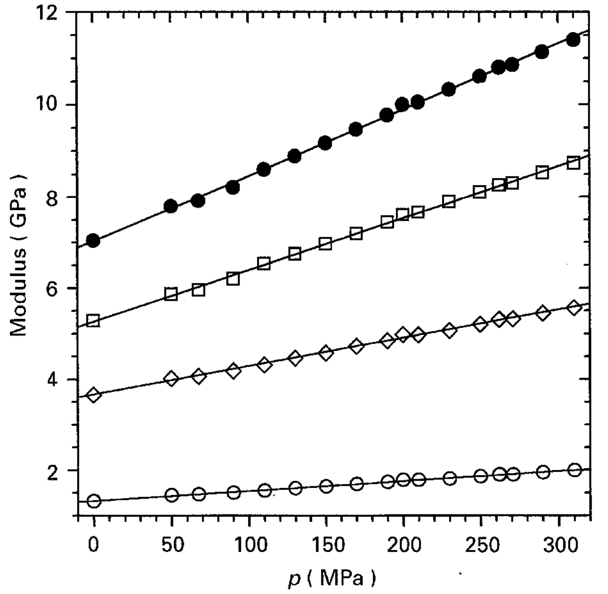

Figure 6 The elastic constants, bulk and Young's modulus versus pressure (●) c_{11}, (○) c_{44}, (□) B, (◇) E. Lines, see text.

Figs 5 and 6 show the temperature and the pressure dependence of elastic constants, the bulk, shear and Young's modulus, respectively. All quantities are strictly linear, with pressure and temperature. We calculated c_{11} and c_{44} from the Brillouin shifts using Equations 2, 3–4. For an isotropic solid the shear modulus, G, the bulk modulus, B, and the Young's modulus, E, are given by [8]

$$G = c_{44} \tag{6}$$

$$B = c_{11} - \frac{4}{3}c_{44} \tag{7}$$

$$E = \frac{c_{44}(3c_{11} - 4c_{44})}{c_{11} - c_{44}} \tag{8}$$

and these equations were used to calculate the moduli from the experimental data.

Because of the linearity of the pressure and temperature dependence of the elastic constants, the following simple empirical functions for c_{11} can be given

$$c_{11} = c_{11}^{0} + \frac{\mathrm{d}c_{11}}{\mathrm{d}p}p + \frac{\mathrm{d}c_{11}}{\mathrm{d}T}T \tag{9}$$

and for c_{44}

$$c_{44} = c_{44}^{0} + \frac{\mathrm{d}c_{44}}{\mathrm{d}p}p + \frac{\mathrm{d}c_{44}}{\mathrm{d}T}T \tag{10}$$

which fit the experimental data very well. The derivatives are all valid at ambient pressure and at room

TABLE I Elastic constants and their derivatives at ambient pressure and temperature ($p = 0.1$ MPa, $T = 295$ K) to be applied in Equations 9 and 10

	c_{ii}^0 (GPa)	dc_{ii}/dp	dc_{ii}/dT (GPa K^{-1})
c_{11}	11.6	14.3	1.54×10^{-2}
c_{44}	2.44	2.19	3.75×10^{-3}

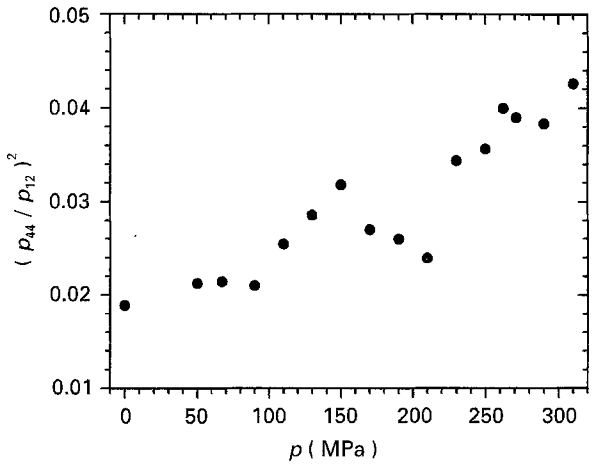

Figure 7 The ratio $(p_{44}/p_{12})^2$ (p_{ij} Pockels coefficients) versus pressure.

temperature ($p = 0.1$ MPa, $T = 295$ K) and are given in Table I.

The theoretical curves for the bulk and Young's moduli, as shown in Figs 5 and 6, were calculated using Equations 7 and 8 with values for c_{11} and c_{44} obtained from the fit function from Equations 9 and 10.

Of course the above functions are only valid in the range covered with our measurements and close to it. The question remains whether pressure and temperature dependences are independent. Experiments are in progress to extend the pressure and temperature range in future.

For an isotropic body, the intensity ratio of the longitudinal and transverse phonon is given by

$$\frac{I_T}{I_L} = \left(\frac{v_L}{v_T}\right)^2 \left|\frac{p_{44}}{p_{12}}\right|^2 \qquad (11)$$

where p_{ij} are Pockels coefficients. Fig. 7 shows the pressure dependence of $(p_{44}/p_{12})^2$. Because the ratio of the longitudinal and transverse sound velocity remains approximately constant, the increase in $(p_{44}/p_{12})^2$ leads to an increase in the intensity ratio of the transverse and longitudinal phonon. This can also be seen in Fig. 2. An increase in the intensity of the transverse phonon with pressure was recently found for PMMA [1], but in a much greater way with a step-like enhancement at about 110 MPa. Unfortunately, there is as yet no satisfactory explanation available for this behaviour, so further investigations on polymeric glasses are necessary.

Acknowledgements

The authors thank H.D. Hochheimer for the opportunity to use his laboratory and for the help with the high-pressure experiments. All measurements were done at the Colorado State University, F. Collins, USA. This work was partially supported by the Deutsche Forschungs Gemeinschaft (DFG) within the SFB 239.

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Received 22 December 1994
and accepted 2 May 1995