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The elastic behaviour under hydrostatic pressure of poly(methyl methacrylate) and its fully deuterated form

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Measurements have been made of the effects of hydrostatic pressure on the velocities of longitudinal and shear ultrasonic waves propagated in a commercial poly(methyl methacrylate) (PMMA) and a fully deuterated PMMA. The experimental results provide a comparison of the bulk and shear moduli and their hydrostatic pressure derivatives for the two polymers. The vibrational anharmonicity of the long wavelength acoustic modes is more pronounced in the deuterated than in the commercial PMMA. $\partial B/\partial P$ is 32% larger in the deuterated form than in the undeuterated polymer, a finding which may be understood by including the isotopic mass difference in a simple vibrational model.

1. Introduction

Although the vibrational spectra of crystalline solids are well understood, this is not the case for polymers. The theoretical difficulties experienced in establishing an understanding of the vibrational anharmonicity of polymers are exacerbated by lack of experimental information on the states and their pressure dependences. To help fill this gap, at least in the long wavelength limit, we have measured the elastic constants and their pressure derivatives of poly(methyl methacrylate) (PMMA) and its fully deuterated form. The elastic constants determine the slope of the dispersion curves at the long wavelength limit. Their pressure dependences provide information on the pressure-induced shift of the vibrational energies of the acoustic modes, thus characterizing the vibrational anharmonicity, that is the non-linearity of the interatomic forces with respect to atomic displacements. Deuteration is a useful tool for studying the molecular dynamics of polymers. Recently, the ultrasonic compressional wave velocity and attenuation have been measured in commercial PMMA and a fully deuterated PMMA [1]. It was found that deuteration leads to a reduction in ultrasonic velocity which can be accounted for completely by the increased density of the deuterated polymer. A larger ultrasonic attenuation observed in the deuterated polymer can be attributed to a reduction in the attempt frequency for barrier hopping of main chain and/or ester methyl groups. The present objective has been to investigate, using the same samples as those in [1], the effects of deuteration on elastic behaviour of PMMA under pressure and hence on vibrational anharmonicity of the long wavelength acoustic modes.

2. Experimental procedure and results

Three cylindrical specimens, each approximately 3 mm long × 10 mm diameter, were employed, two being commercial PMMA, which is predominantly syndiotactic, and the third consisting of fully deuterated PMMA. The measured densities, ρ, were 1.171 ± 0.005 for the commercial and 1.255 ± 0.006 for the deuterated PMMA. The molecular weight of a methylacrylate monomer ($C_2H_2CH_3COOCH_3$) is 100 so that the replacement of eight hydrogen atoms by deuterium increases the density by 8% assuming no change in molecular volume; the density differences between the two polymers confirm this [1].

The velocities of longitudinal (V_l) and shear (V_s) ultrasonic waves were measured at room temperature (292 K) using the pulse-echo overlap technique in the single-ended mode. Ultrasonic pulses at a frequency of 10 MHz were inserted into and received by X- and Y-cut quartz transducers using Dow Resin 276-V9 as the acoustic bond. The adiabatic elastic stiffness constants C^s_{11} $(=\rho_0 V_l^2)$ and C^s_{44} $(=\rho_0 V_s^2)$, the bulk modulus $B^s[=\rho_0(3V_l^2 - 4V_s^2)/3]$, Young's modulus $E^s[=\rho_0 V_s^2(3V_l^2 - 4V_s^2)/(V_l^2 - V_s^2)]$ and Poisson's ratio $\sigma^s[=(V_l^2 - 2V_s^2)/2(V_l^2 - V_s^2)]$ are given in Table I. The differences between the experimental data for the two commercial PMMA specimens are much smaller than with the deuterated specimen. Replacement of hydrogen atoms by deuterium should result in only a small fractional change in elastic moduli compared with the fractional change in density $\Delta\rho/\rho_0$. Hence the corresponding change in velocity $(\Delta V/V)$ is equal to $\frac{1}{2}\Delta\rho/\rho_0$ giving an expected change on deuteration of about −4% [1]; the measured changes $\Delta V_s/V_s$ of −3.6% and $\Delta V_l/V_l$ of −5% are in accord with this.

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The hydrostatic pressure dependences of the ultrasonic wave transit times (T_p) were measured in a piston-and-cylinder apparatus using castor oil as the liquid pressure medium. The hydrostatic pressure was measured from the change in electrical resistivity of a precalibrated manganin wire coil sited within the pressure chamber. To account for pressure-induced changes in crystal dimensions and density, the "natural velocity" $W(=l_0T_p$, where l_0 is the path length at atmospheric pressure) technique [2] was used, the change in ultrasonic wave transit time induced by pressure being converted to change of natural velocity $[(W/W_0) - 1]$. The pressure dependences of the relative changes in natural velocity of the longitudinal and shear-wave velocities were found to be linear up to the maximum pressure applied (0.4×10^8 Pa, Fig. 1) and were rather larger for the deuterated PMMA than for the commercial material. There was no hysteresis as pressure was removed. The hydrostatic pressure derivatives of the elastic stiffness constants, calculated from the hydrostatic pressure dependences of the natural velocity, are given in Table I.

3. Discussion

It is useful to compare the elastic behaviour of these polymers under pressure with that of other amorphous materials. A survey of the elastic properties of a number of glasses can be found in table 4 of Brassington *et al.* [3]. So far as the pressure dependences of elastic constants are concerned, amorphous materials fall into two distinct categories [3,4]. The non-linear elastic properties of a number of oxide glasses including SiO_2 are quite different in kind from those of most materials, in that the pressure derivatives of the bulk and shear moduli are negative [3–5]. However, the elastic behaviour of many glasses, including amorphous arsenic [3], amorphous As_2S_3 [4] and a fluorozirconate glass [6], resemble those of most crystalline solids: they stiffen under pressure. The two polymers studied here are "well-behaved" in the sense that when compressed volumetrically their long wavelength shear and longitudinal acoustic modes stiffen. The bulk and shear moduli are much smaller than those of inorganic glasses: the polymers are much more compressible and have far less resistance to an applied shear stress, even than amorphous selenium ($B_0 = 9.3$ GPa, $\mu = C_{44} = 3.9$ GPa) which can be described as an amorphous molecular solid [7]. They are somewhat less compressible even than the molecular crystal orthorhombic sulphur ($B_0 = 7.74$ GPa) whose S_8 rings are weakly bound by Van der Waals' intermolecular forces [7]. A feature of molecular crystals is that the intermolecular volume is readily compressible; the bulk modulus is small but increases considerably under pressure; thus $\partial B/\partial P$ (= 12) for crystalline sulphur is large [8]. Amorphous selenium also has quite a large $\partial B/\partial P$ (= 8.5) [7]. The polymers show the same features, being readily compressible (small B_0) and having large ($\partial B/\partial P$). This is consistent with their having an intermolecular volume which is much more compressible than that of the molecules themselves. The deuterated polymer is the more compressible and has the larger $\partial B/\partial P$.

The hydrostatic pressure derivatives of the second-order elastic constants are directly related to third-order elastic constants which quantify the coefficients $\partial^3 U(\eta)/\partial\eta_{ab}\partial\eta_{cd}\partial\eta_{ef}$ of the cubic term of the expansion of the strain energy density $U(\eta)$ with respect to the Lagrangian strain η and thus the leading term of the vibrational anharmonicity of the long wavelength modes. Normal practice is to discuss vibrational anharmonicity in terms of mode Grüneisen parameters $\gamma_i\ (= -(\partial \ln \omega_i/\partial \ln V)_{T,P=0})$ where ω_i is the ith mode frequency. For an isotropic solid there are two long wavelength acoustic mode Gruneisen parameters, γ_l and γ_s, which refer to the longitudinal and shear elastic waves, respectively, and are given in Table I together with the mean acoustic mode Grüneisen gamma, $\bar{\gamma}_{el}\ (= (\gamma_l + 2\gamma_s)/3)$. The positive signs of γ_l, γ_s and $\bar{\gamma}_{el}$ show that the long wavelength acoustic mode frequencies increase under pressure. PMMA and the fully deuterated form have quite large mode Grüneisen parameters (more usual values of γ are

TABLE I The elastic properties of PMMA and deuterated PMMA at 292 K

Property	PMMA 1	PMMA 2	Deuterated PMMA
Density (kg m^{-3})	1171	1171	1255
Sample thickness (mm)	3.145	3.032	2.975
Ultrasonic velocities (m sec^{-1}):			
longitudinal V_l	2711	2729	2571
shear V_s	1334	1334	1286
Adiabatic elastic constants:			
Young's modulus, E^s (GPa)	5.58	5.59	5.54
Bulk modulus, B^s (GPa)	5.82	5.94	5.52
Poisson's ratio, σ^s	0.34	0.34	0.33
C_{11}^s (GPa)	8.60	8.72	8.29
C_{44}^s (GPa)	2.08	2.08	2.07
Pressure derivatives:			
$(\partial B^s/\partial P)_{P=0}$	9.96	10.14	13.36
$(\partial C_{44}/\partial P)_{P=0}$	2.53	2.42	2.74
Long wavelength acoustic mode Grüneisen parameters:			
longitudinal, γ_l	4.35	4.38	5.50
shear, γ_s	3.38	3.28	3.48
mean, $\bar{\gamma}_{el}$	3.70	3.65	4.15
thermal, γ^{th}	4.98		

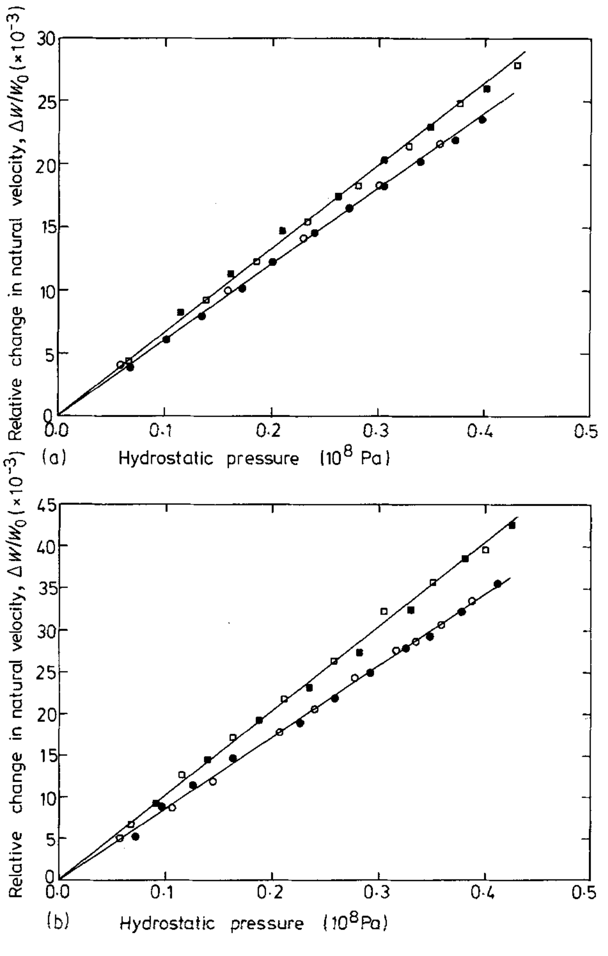

Figure 1 The hydrostatic pressure dependence at 292 K of the natural velocity of (a) longitudinal and (b) shear ultrasonic waves propagated in PMMA, with (●) increasing pressure, (○) decreasing pressure, and fully deuterated PMMA with (■) increasing pressure, (□) decreasing pressure.

about unity) – they show substantial vibrational anharmonicity. Comparison of the acoustic mode Grüneisen gammas shows that the vibrational anharmonicity of the deuterated PMMA, especially that associated with the longitudinal mode, is substantially greater than that of the commercial polymer PMMA.

As well as being responsible for the non-linear acoustic behaviour of a solid under a finite strain, the anharmonicity of lattice vibrations causes thermal expansion which is determined by summation of the anharmonic contributions from all the vibrational states. Thus comparison between the thermal Grüneisen parameter, γ^{th} $(= 3\alpha V B^S/C_p = 3\alpha V B^T/C_v)$, and $\bar{\gamma}_{\text{el}}$ forges a link between the thermal properties and the pressure dependences of the elastic constants. Taking the linear thermal expansion coefficient, α, as $5 \times 10^{-5}\,\text{K}^{-1}$ and the specific heat, C_p, at constant pressure as $1.5\,\text{kJ}\,\text{kg}^{-1}\,\text{K}^{-1}$, gives γ^{th} for PMMA as 4.98. That this is close to the value of 3.7 for $\bar{\gamma}_{\text{el}}$ indicates that either the long wavelength acoustic modes play a central role in the thermal properties of PMMA or that those shorter wavelength excitations which also contribute have similar Grüneisen parameters (~ 4) to those of the acoustic modes. It is likely that both these possibilities apply.

The energies of the C–H and C–D bonds, 3.47 and 3.52 eV, respectively, differ by only 1.4% [9]. It is unlikely that the force constants differ by more than this percentage. Therefore, the 6% reduction of $B(P \to 0)$ on deuteration cannot be understood in terms of force constants, especially when one considers that, if anything, the force constants should increase slightly. The bulk change can be explained as an isotope effect in vibrational behaviour as follows. For simplicity consider a side group or segment of a polymer chain of mass m vibrating with simple harmonic motion in the x direction. The unnormalized spatial wave functions of the stationary states will take the form [10]

$$\psi_n = \text{const.}\ \exp\left(-x^2/2a^2\right) H_n(x) \qquad (1)$$

where the "characteristic length a" is the classical vibrational amplitude for the ground state, and $H_n(x)$, $n = 1, 2, 3, \ldots$, are the Hermite polynomials. Thus a is a measure of the spread of the wave functions and is given by the relation: $ma^2\omega^2/2 = h\omega/2$; hence $a = (h/m\omega)^{0.5}$ and because $\omega = (K/m)^{0.5}$ where K is the force constant for the motion, we have

$$a = h^{0.5}/(mK)^{0.2} \qquad (2)$$

Considering more realistically a three-dimensional motion to a first approximation, one can define a characteristic volume

$$v = a^3 = h^{1.5}/(mK)^{0.75} \qquad (3)$$

this being the volume outside of which the wave function, ψ_n, has fallen to $(1/e)^{0.5}$ of its peak value. As stated earlier, on deuteration the change in K is negligible but m increases substantially. This reduces a and v: thus the wave functions on neighbouring vibrating groups become less spread out. Thus assuming that the molecular volume (i.e. the formula mass/density) remains unchanged (which is the case for our deuterated and undeuterated samples) deuteration increases the free volume of the system and therefore decreases $B(P \to 0)$.

Now turning our attention to the effect of deuteration on $\partial B/\partial P$ it is only necessary to note that because $\partial\psi/\partial x$ increases as a^{-2} for a given x, the pressure gradient of the volume of overlap of neighbouring vibrational wave functions will increase as a decreases, possibly as rapidly as a^{-6}, i.e. $m^{1.5}$. It follows that the pressure derivative of the repulsive forces between the electronic charge clouds of neighbouring groups will increase with m, possibly as rapidly as $m^{1.5}$, explaining why $\partial B/\partial P$ increases on deuteration. For the CH_3 group the replacement of H by D increases m by 20%. Thus $m^{1.5}$ increases by some 30% which is, in fact, in good agreement with the observed 32% enhancement of $\partial B/\partial P$.

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