

The effect of deuteration on the ultrasonic properties of poly(methyl methacrylate)

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Room-temperature ultrasonic compressional wave velocity and attenuation measurements have been carried out on commercial poly-methyl methacrylate (PMMA) and fully deuterated PMMA. Deuteration was found to reduce the velocity by $4.4 \pm 1.2\%$ which can be completely accounted for by the density change of 8.0%, assuming no changes in atomic force constants or molar volume. The attenuation was 17% higher in the deuterated sample. Making reasonable assumptions about the distribution function for the relaxation times of molecular groupings moving in two-well potentials, the attenuation increase is attributed to a reduction in the attempt frequency for barrier hopping of main chain and/or ester methyl groups.

1. Introduction

Recently a growing interest has been expressed in the use of deuteration for the study of the molecular dynamics of polymers [1-3]. Because deuteration affects the mass and moment of inertia of vibrating and rotating groups in the first order, whilst having only a second-order effect on their force constants, the number of variables involved in an isotopic substitution study is relatively small. One important application of the isotope effect is that it presents the most direct proof of the presence of tunnelling states in molecular crystals, which suffer relatively large changes in splitting upon isotopic substitution. These effects have been observed by inelastic neutron scattering [1]. Whilst ultrasonic techniques have been widely used in the investigation of polymer dynamics [4], to our knowledge ultrasonic measurements on deuterated species have not been reported. Definitive data would require ultrasonic measurements to be made over a wide range, including low temperatures if tunnelling phenomena rather than just thermally activated relaxation, are to be observable. However, in this paper we show how useful conclusions can be obtained from simple preliminary measurements at room temperature.

2. General theoretical considerations

The replacement of hydrogen atoms by deuterium in any material should have a straightforward effect on the propagation velocity of ultrasound. Since the fractional change in elastic moduli would be expected to be small compared with the fractional change in density, $\Delta\rho/\rho$, the corresponding change in velocity, c , ought to be given by

$$\frac{\Delta c}{c} = \frac{1}{2} \left(\frac{\Delta\rho}{\rho} \right) \quad (1)$$

In polymers several possible effects on the attenuation

of ultrasound may be envisaged to arise through deuterium substitution; however, with reasonable assumptions the deduction of a simple quantitative relationship is plausible, as is argued below.

Ultrasonic and dielectric relaxation losses in polymeric solids have long been interpreted in terms of the motions of particular side groups or segments of polymer chains [5] in two-well systems. The contribution to the internal friction provided by a two-well system of barrier height, V , and asymmetry (separation of two-well minima) Δ (Fig. 1) is given by [6-10]

$$\frac{nD^2}{4\rho c^2 kT} \operatorname{sech}^2 \left(\frac{\Delta}{2kT} \right) \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (2)$$

where

$$\tau = \tau_0 \exp(V/kT) \operatorname{sech}(\Delta/kT) \quad (3)$$

D is the deformation potential, i.e. the energy shift of the two-well states in a strain field of unit strength, averaged over all well orientations, ω is the angular frequency, k is Boltzmann's constant and T is the absolute temperature, $1/2\tau_0$ is the classical vibration frequency (attempt frequency) for the relaxing element in either well, and V is measured from the mid point between the two-well minima. Some authors refer V to the bottom of the lowest well, in which case

$$\tau = 2\tau_0 \exp(V/kT) [1 + \exp(\Delta/kT)]^{-1}$$

Introducing the distribution functions $n(\Delta)$ and $n(V)$, which satisfy the normalization condition

$$\int_0^\infty \int_0^\infty n(\Delta)n(V) d\Delta dV = n \quad (4)$$

where n is the number of two-well systems per unit volume, the total contribution, to the internal friction arising from n two-well systems having a broad

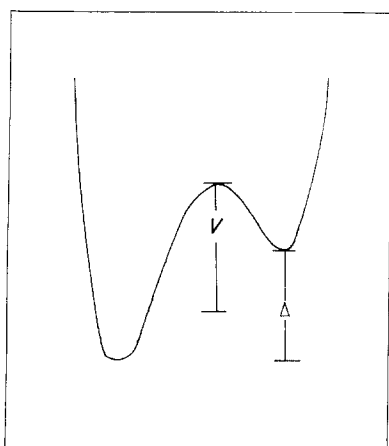


Figure 1 Asymmetric two-well potential of barrier height, V , as defined in the text.

distribution of V and Δ values, is

$$Q^{-1} = \frac{D^2}{4qc^2kT} \times \int_0^\infty \int_0^\infty \frac{\omega\tau}{1 + \omega^2\tau^2} \operatorname{sech}^2(\Delta/kT)n(\Delta)n(V) d\Delta dV \quad (5)$$

The range of integration for Δ is taken from 0 to ∞ , on the assumption that D is averaged over all well orientations thus allowing for positive and negative Δ values. Assuming that $n(\Delta) = n_0$, a constant, for $T < T_g$, the transformation temperature [7]

$$Q^{-1} = \frac{D^2 2n_0\pi}{4qc^2} \int_0^\infty \frac{\omega\tau n(V) dV}{(1 + \omega^2\tau^2)^{1/2} [1 + (1 + \omega^2\tau^2)^{1/2}]} \quad (6)$$

where now

$$\tau = \tau_0 \exp(V/kT) \quad (7)$$

follows an Arrhenius law-type dependence.

Assuming a distribution function of the form

$$n(V) = \frac{1}{V_p} \exp(-V/V_p) \quad (8)$$

where V_p is a constant, Equation 5 becomes, because $\omega\tau_0 \ll 1$

$$Q^{-1} = \frac{\pi D^2 n_0 kT}{4qc^2 V_p} (\omega\tau_0)^{(kT/V_p)} \quad (9)$$

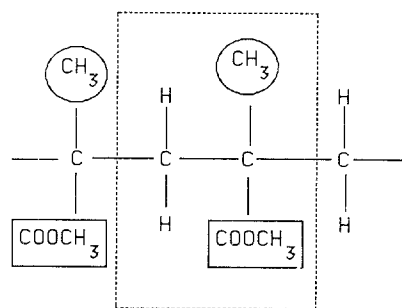
This function is useful in describing the general shape of the frequency and temperature dependence of broad loss peaks in amorphous materials for $T < 300$ K. On the above model, V_p is the arithmetical mean activation energy, i.e.

$$\bar{V} = \frac{\int_0^\infty Vn(V) dV}{\int_0^\infty n(V) dV} = V_p \quad (10)$$

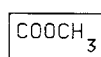
However, V_p , has the further physical significance that the peaks in the $Q^{-1}-T$ plots (ω constant) given by Equation 8, follow the Arrhenius law

$$\omega\tau_0 \exp(V_p/kT) = 1 \quad (11)$$

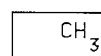
Gilroy and Philips [7] suggested that V_p was related to the transformation temperature.



Alpha -Methyl group



Oxy carbonyl group



Ester methyl group

Figure 2 Structural groupings in PMMA.

Using Equation 8 with Equation 4 for normalization

$$n_0 = \frac{n}{V_p} \quad (12)$$

so that Equation 9 becomes

$$Q^{-1} = \frac{\pi D^2 nkT}{4qc^2 V_p^2} (\omega\tau_0)^{(kT/V_p)} \quad (13)$$

We shall now apply Equation 13 to determine the likely effect of deuterium substitution on Q^{-1} . Bridge and Patel suggested that

$$D = \frac{q}{2} N \left(\frac{\delta y}{\delta x} \right) \quad (14)$$

where q is the appropriate elastic modulus, n is the number of two-well systems per unit volume, δy is the separation of two-well minima and δx is the extremal dimension of the double well. The effect of deuteration on δx and δy will be negligible and of course n will remain unchanged. The C-D bond energy is less than 1% greater than that of the C-H bond. Since to a first approximation, the bond force constants are proportional to bond energies, the changes in force constants caused by deuteration will be very small. Correspondingly, the change in q will be small. Now the two-well systems of interest in PMMA are probably associated with the hindered rotation of the oxy-carbonyl (COOCH_3) side group about a C-C bond to which the rotation of the methyl (CH_3) group (which in principle has three-fold or higher fold symmetry) may contribute (Fig. 2). So the two-well barrier heights will be proportional to the torsional force constant for the C-C bond. Thus following previous arguments, V_p will change very little, probably by less than 1% due to the replacement of all H atoms by D atoms. We have now discussed every material variable on the right-hand side of Equation 8, except τ_0 , and suggested that their dependence on deuteration is small. However, as will be apparent subsequently, the

effect of deuteration on τ_0 is significant. Thus denoting normal and deuterated PMMA by subscripts H and D, respectively, we can write (taking $(V_p)_H \sim (V_p)_D$ and dropping subscripts)

$$\frac{Q_H^{-1}}{Q_D^{-1}} = \left[\frac{(\tau_0)_H}{(\tau_0)_D} \right]^{(kT/V_p)} \quad (15)$$

If only a single barrier height is present rather than a distribution the application of the arguments of the preceding paragraph will yield

$$\frac{Q_H^{-1}}{Q_D^{-1}} = \left[\frac{(\tau_0)_H}{(\tau_0)_D} \right] \left[\frac{1 + \omega^2(\tau_0)_D^2 \exp(2V_p/kT)}{1 + \omega^2(\tau_0)_H^2 \exp(2V_p/kT)} \right] \quad (16)$$

Thus one can define two simple limiting cases

$$\frac{Q_H^{-1}}{Q_D^{-1}} = \left[\frac{(\tau_0)_H}{(\tau_0)_D} \right] \quad (17)$$

for $\omega^2(\tau_0)^2 \exp(2V_p/kT) \ll 1$ or $= 1$

$$\frac{Q_H^{-1}}{Q_D^{-1}} = \left[\frac{(\tau_0)_D}{(\tau_0)_H} \right] \quad (18)$$

for $\omega^2(\tau_0)^2 \exp(2V_p/kT) \gg 1$

3. Experimental details

For simplicity, commercial "mounted" transducers, backed to produce broad band pulses under shock excitation, were employed. These were Ultrasonics 10 mm diameter and Panametrics 8 mm diameter, for 5 and 10 MHz operation, respectively. In each case contact with the specimen is through a thin durable polymer coating on the front face of the transducer and the side entry of the coaxial connector into the transducer casing allowed a constant coupling pressure to be maintained by means of placing a weight on the rear of the case or by clamping. For attenuation measurements moderately narrow band pulses were generated by means of resonant excitation using Matec model 6600 instrumentation. For velocity measurements, broad band pulses (in which the first quarter cycle of each pulse was readily identifiable) were generated using shock excitation by a conventional ultrasonic flaw detector and a broad amplifier (Arenberg model no. WA-600-E; 1 to 60 MHz). Echoes were displayed on a broad band oscilloscope (Tektronix model no. 2245; 150 MHz) and transit times were measured using a precision digital delay generator (Berkeley Nucleonics 7030) with a time jitter of less than 100 psec. Three cylindrical samples, approximately 10 mm long \times 10 mm diameter were employed, two being commercial PMMA which is predominantly syndiotactic and a third consisting of fully deuterated PMMA. Nominally parallel end faces were fine milled and then polished until the attenuation differences between successive pulse echoes were minimized and made as equal as possible, after appropriate bond adjustments. The high attenuation restricted the number of echoes on which measurements could be made to a maximum of four. Time and attenuation data on individual echoes, for five independent bonds and tuning adjustments, are presented in Tables I and II, together with the averaged data and standard deviations.

The measured density values for the samples were 1.255 ± 0.006 and 1.171 ± 0.005 gcm⁻³ for the deuterated PMMA and the commercial PMMA, respectively. Thus allowing for the above standard deviations, the density of the deuterated sample is greater by some 6.3 to 8.0%.

4. Results and discussion

From inspection of Table I it is very clear that velocities are systematically higher at 10 MHz when probe B is used than at 5 MHz when probe A was used. This could be a real effect due to sample dispersion, or due to different systematic errors (from geometrical dispersion or phase angle on reflection effects) with the two probes, or a combination of both causes. In any event velocity changes between samples will be obtained to a greater precision by calculating $\langle \Delta c/c \rangle$ rather than $\Delta \langle c \rangle / \langle c \rangle$. The attenuation data have been treated in the same way; i.e. we have calculated $\langle \alpha_D / \alpha_H \rangle$ rather than $\langle \alpha_D \rangle / \langle \alpha_H \rangle$. The molecular weight of a methacrylate monomer (C₂H₂CH₃COOCH₃) is 100 so that the replacement of eight hydrogen atoms by deuterium increases the density by 8% assuming no change in molecular volume, in good agreement with the experimental density data quoted earlier. Correspondingly, from Equation 1 the expected velocity change on deuteration is -4.0% , in excellent agreement with the observed change of $-4.4\% \pm 1.2$.

To interpret the attenuation data it is important to note that our analysis leading to Equations 15 to 19 will be valid only when a contribution from a single relaxing structural element is dominant. Ordinarily this assumption will be valid over a restricted temperature range and even then the structural element involved will depend on the measurement frequency. In plots of the temperature dependence of mechanical damping the first loss peak to occur below the glass transition temperature is known as the β maximum. At low frequencies, ~ 1 Hz, the β maximum of ordinary PMMA occurs at about 280 K [11], has a mean activation energy (V_p) of 70 kJ mol⁻¹, and is generally agreed to be due to the hindered rotation of the COOCH₃ group about the C-C bond linking it to the main chain [11, 12]. However, at 13 MHz the loss maximum near 280 K at 13 MHz has an activation energy of 28 kJ mol⁻¹ [10, 13]. The attribution of this relaxation peak to the rotation of a methyl group attached to a main chain seems reasonable given that a molecular mechanics calculation by Heijboer *et al.* [11] gave a value of 28 kJ mol⁻¹ as the barrier to rotation of α -methyl group attached to a quaternary carbon atom. Independent measurements by neutron scattering and nuclear magnetic resonance have given barrier heights ranging from 23 to 28 kJ mol⁻¹ [2, 15, 16]. In all cases, pure or almost pure syndiotactic PMMA was used. In view of the frequency range employed in our room-temperature measurements it seems reasonable to assume a dominant attenuation contribution from the relaxation of the α -methyl group. Although this rotation can be well described in terms of a three-fold potential due to the methyl group symmetry, the coupling of the α -methyl group to the

TABLE I Velocity measurements. Sample dimensions: deuterated PMMA, diameter 10 mm, thickness 9.32 mm; PMMA 1 (Perspex), diameter 10 mm, thickness 10.0 mm; PMMA 2 (Perspex), diameter 10 mm, thickness 9.31 mm
(a) Probe: Ultrason, Frequency 5 MHz, diameter 10 mm

Time measurements between successive echoes (μsec)											
Deuterated PMMA				PMMA 1				PMMA 2			
1	2	3	4	1	2	3	4	1	2	3	4
6.256	13.500	20.782	28.046	6.370	13.71	20.849	28.224	5.995	12.936	19.966	27.014
6.279	13.517	20.729	27.981	6.434	13.798	21.210	28.356	6.014	12.958	20.019	27.068
6.284	13.530	20.879	28.165	6.471	13.917	21.307	28.673	5.983	12.921	19.984	27.076
6.287	13.556	20.893	28.253	6.465	13.765	21.088	28.424	6.011	12.954	20.011	27.044
6.279	13.520	20.869	28.253	6.465	13.782	21.315	28.520	6.005	12.952	19.972	27.032
$\Delta t(\text{mean})$		7270.21				7341.71				7011.85	
σ_t		71.79				99.85				54.14	
Vel. (m sec^{-1})		2563.88 \pm 0.25				2724.16 \pm 0.20				2655.50 \pm 0.34	
$\Delta c/c$ (%)						-5.88				-3.45	

(b) Probe: Panametrics, Frequency 10 MHz, Diameter 8 mm

Time measurements between successive echoes (μsec)											
Deuterated PMMA				PMMA 1				PMMA 2			
i	2	3	4	1	2	3	4	1	2	3	4
6.310	13.513	20.750	27.764	6.448	13.797	21.165	28.333	6.009	12.918	19.865	26.828
6.318	13.530	20.757	27.772	6.441	13.772	20.949	28.292	6.006	12.915	19.861	26.821
6.315	13.515	20.757	27.771	6.442	13.777	20.946	28.299	6.008	12.915	19.862	26.825
6.309	13.518	20.751	27.784	6.442	13.775	20.947	28.295	6.002	12.911	19.859	28.819
6.310	13.512	21.760	27.779	6.439	13.782	20.955	28.312	6.005	12.913	19.865	26.825
$\Delta t(\text{mean})$		7163.50				7283.00				6937.50	
σ_t		92.63				83.36				22.84	
Vel. (m sec^{-1})		2602.07 \pm 0.20				2746.12 \pm 0.23				2683.96 \pm 0.81	
$\Delta C/C$ (%)						-5.24				-3.00	

Mean value of $\Delta C/C$: $-4.4 \pm 1.2\%$.

Mean velocity (deuterated sample) $2583 \pm 19 \text{ m sec}^{-1}$, PMMA $2702 \pm 35 \text{ m sec}^{-1}$.

TABLE II Attenuation measurements. All readings refer to the setting (dB) of the attenuator at the receiver input required to bring all echoes to the same reference height.

(a) Probe: Ultrason, frequency 5 MHz, diameter 10 mm

	Deuterated PMMA: Echo				PMMA 1: Echo				PMMA 2: Echo			
	1	2	3	4	1	2	3	4	1	2	3	4
	45.5	29.5	14.5	0.0	39.0	26.0	13.0	0.0	74.0	62.5	51.0	39.0
	45.0	31.0	16.0	2.0	38.5	26.0	13.0	1.0	74.5	63.0	51.0	38.5
	40.5	27.0	14.5	0.0	38.5	25.5	13.0	1.0	75.0	63.0	52.0	39.0
	43.0	28.5	14.0	1.5	39.0	26.0	13.5	1.5	74.0	62.5	51.0	39.0
	44.5	29.5	14.5	0.0	39.0	26.0	13.0	1.0	74.0	63.0	51.5	38.5
$x(\text{mean})$		14.32				12.67				11.75		
σ_x		0.93				0.40				0.49		
$z(\text{mm})$		1.53 \pm 0.09				1.26 \pm 0.04				1.26 \pm 0.05		
σ_D/σ_H						1.21				1.21		

(b) Probe: Panametric, frequency 10 MHz, diameter 8 mm

	Deuterated PMMA: Echo			PMMA 1: Echo			PMMA 2: Echo		
	1	2	3	1	2	3	1	2	3
	31.5	16.0	0.0	36.0	21.0	6.0	31.0	18.5	5.0
	35.0	18.0	4.0	34.5	20.0	5.5	32.5	19.5	5.0
	32.5	17.0	0.0	35.0	20.5	6.0	32.0	19.0	4.0
	35.0	19.5	6.5	35.5	21.0	6.0	32.0	19.0	5.0
	33.5	18.5	3.0	35.5	20.5	6.5	32.0	19.0	4.5
$x(\text{mean})$		15.44			14.77			13.50	
σ_x		1.11			0.24			0.78	
$z(\text{mm})$		1.65 \pm 0.11			1.47 \pm 0.02			1.45 \pm 0.08	
α_D/α_H					1.12			1.14	

Mean value of α_D/α_H : 1.17 ± 0.04 .

main chain which undergoes fast picosecond fluctuations [14], may result in an apparent two-well potential hindering its rotation. Correspondingly, if we assume that the replacement of H atoms by D increases the moment of inertia of the CH₃ by a factor of 2, then the attempt frequency for the rotation barrier is changed according to the relation

$$(\tau_0)_D = 2^{1/2}(\tau_0) \quad (19)$$

Substitution of this condition and $V_p = 23 - 28 \text{ kJ mol}^{-1}$ in Equation 15 gives, for $T = 293 \text{ K}$

$$\frac{\alpha_D}{\alpha_H} = 1.03 \text{ to } 1.04 \quad (20)$$

which should be valid if a broad distribution of barrier heights (as defined by Equation 8) and asymmetries, are present. On the other hand, if a single barrier height is assumed, then taking $\tau \sim 10^{-12} \text{ sec}$ (a reasonable assumption) one finds that $\omega^2(\tau_0)^2 \exp 2V_p/kT \ll 1$, for $V_p = 28 \text{ kJ mol}^{-1}$ and $T = 293 \text{ K}$, in which case (from Equation 17)

$$\frac{\alpha_D}{\alpha_H} = 1.414 \quad (21)$$

Our experimental value (Table I) averaged over data from three samples and two measurement frequencies, is

$$\frac{\alpha_D}{\alpha_H} = 1.17 \pm 0.4 \quad (22)$$

Since this lies between the two preceding bounds, if the attribution of the loss to the α -methyl grouping was accepted, the result would imply a spread of barrier heights somewhat less than that prescribed by Equation 8.

As an alternative calculation, in which a broad spread of barrier heights is accepted, if the experimental range of α_D/α_H values (Equation 22) is substituted into Equation 15, with $T = 293 \text{ K}$, and $(\tau_0)_D = 2(\tau_0)_H$ one obtains

$$4.4 \leq V_p \leq 6.9 \text{ kJ mol}^{-1} \quad (23)$$

This result is in rather good agreement with the range of barrier heights reported for the rotation of the ester methyl group (to which, of course, the condition $(\tau_0)_D = 2(\tau_0)_H$ would still apply). Values quoted for this motion range from 1 to 10 kJ [10].

It is apparent that our experimental data are also consistent with the presence of both types of methyl rotation. It is very important to note that if there is a contribution to the experimental loss from motion of

the COOCH₃ group, the change in the moment of inertia on deuteration is much smaller than for the methyl group case. Therefore, the increase in α on deuteration must still be attributed to methyl groups. In fact the presence of a background attenuation from COOCH₃ motion would mean that the true ratio of α_D/α_H for the methyl groups would be greater than that given by Equation 22. Correspondingly, one must assume a narrower range of barrier heights for α -methyl rotation, or an even lower range of V_p values using the broad distribution of barriers model (Equation 23) and consistent with ester methyl rotation.

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