

Ultrasonic studies of solid poly(alkyl methacrylates)

Alastair M. North, Richard A. Pethrick and David W. Phillips

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK
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The attenuation and velocity of ultrasonic longitudinal waves of frequencies 5–35 MHz in poly(methyl methacrylate), poly(ethyl methacrylate), poly(n-butyl methacrylate) and poly(isobutyl methacrylate) between 233 and 363K are reported. The methyl and ethyl polymers showed evidence of a single relaxation process (associated with cooperative main chain and ester group motions), but the butyl polymers showed also a second relaxation at about 200–230K. This is associated with conformational rearrangement of the alkyl group, and the acoustic energetics are in line with theoretical predications for this process.

The velocity data show the expected decreases due to the main glass transition (and cooperative processes) and to reduction of the intermolecular interaction force constant with increasing size of the alkyl group. Attempts to calculate an acoustic low temperature specific heat yielded values lower than expected from calorimetric observations, showing that the acoustic modes are capable of greater energy storage than is involved in the longitudinal perturbation, and/or that calculation based on a Debye T^3 law are invalid for these glassy polymers.

INTRODUCTION

The transmission of ultrasonic waves through a solid sample can be used to study the dynamic mechanical relaxation in the frequency region of 10^6 – 10^8 Hz. This is approximately 10^6 higher than the range encountered in conventional dynamic mechanical equipment, and so a means is provided for observing molecular relaxation behaviour over an extended frequency/temperature region. Alternatively those molecular processes responsible for a low temperature 'transition' when examined by a low frequency technique, can be observed as higher temperature relaxations.

Low temperature mechanical^{1,2} and dielectric³ measurements of alkyl methacrylate polymers have established the existence of a specific relaxation feature associated with the ester alkyl side chain. This is designated the γ -process, since in a temperature scan it is evidenced as a loss peak below the α -(main chain glass-rubber) and β -(main chain libration and ester carbonyl rotation) transitions. In poly(ethyl methacrylate) this peak occurs at about 50K, 1 kHz [below the postulated δ -(α -methyl rotation) transition] rising to (typical) 100K, 1 Hz (above the α -methyl relaxation) in the longer chain alkyl methacrylates. The molecular motions responsible for these low temperature 'transitions' are important in a number of ways, not least in determining the specific heat and thermal phonon spectrum of the solid.

The objectives of this work were to measure the velocity and attenuation of ultrasonic longitudinal waves in the temperature–frequency region associated with this γ -process, and so to elucidate further the characteristics of the molecular motion involved.

EXPERIMENTAL

The polymers were commercial materials supplied by Du Pont de Nemours and Co. Samples were fabricated as discs, thickness 2mm, by compression moulding for 12 h at $T_g + 40$ K under a pressure of 14 MN/m².

Glass transition temperatures (*Table 1*) were determined using a Perkin–Elmer DSC–1 at a heating rate of 8 K/sec.

Densities (*Table 1*) were measured to $\pm 0.2\%$ by a liquid immersion method.

Polymer tacticities (*Table 1*) were determined from the relative intensities of the methine resonances in 100 MHz ¹H n.m.r. spectroscopy at room temperature in CDCl₃ as solvent. Structures conformed closely to those reported in the literature⁴.

Molecular weights (*Table 1*) were determined using gel permeation chromatography. The molecular weight distributions were uncorrected for the finite resolving power of the columns⁵, and so are likely to be rather narrower than quoted.

The attenuation (α_L) and velocity (C_L) of the ultrasonic longitudinal waves were obtained over a frequency range of 5 to 35 MHz using an immersion technique similar to that described by Waterman⁶. The attenuation measurements have an estimated error of $\pm 5\%$, and uncertainty in the velocity was $\pm 1\%$.

Table 1 Polymer characteristics

Polymer	M_n $\times 10^3$	\bar{M}_w/M_n	Density (kg/m ³)	T_g (K)	Tacticity (% triads)
Poly(methyl methacrylate) (PMMA)	145	3.59	1200	376	s: 60 h: 36 i: 4
Poly(ethyl methacrylate) (PEMA)	110	2.72	1110	340	—
Poly(isobutyl methacrylate) (PIBMA)	101	2.78	1090	324	s: 48 h: 52 i: 0
Poly(n-butyl methacrylate) (PNBMA)	71.3	2.49	1070	293	—

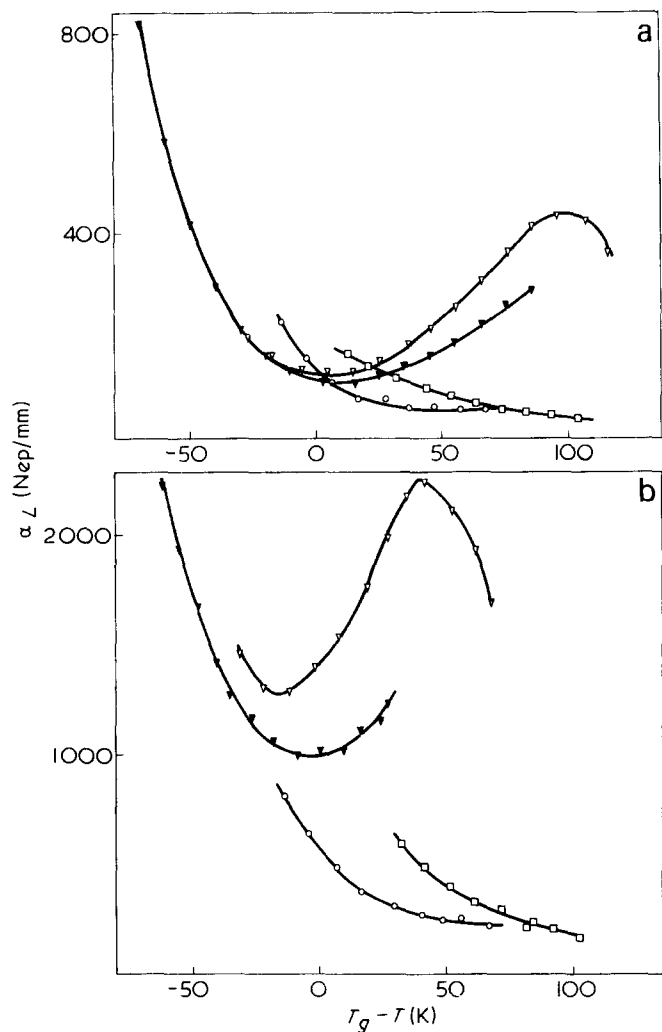


Figure 1 Plots of the acoustic attenuation measured at (a) 5 and (b) 25 MHz versus reduced temperature for the poly(alkyl methacrylates): ∇ , PNBMA; ∇ , PIBMA; \circ , PEMA; \square , PMMA

RESULTS AND DISCUSSION

Ultrasonic attenuation

Isochronal attenuation coefficients for the four polymers, measured at 5 and 25 MHz, are displayed against a reduced temperature, $T_g - T$, in Figure 1. The plots at 15 and 35 MHz are essentially the same except for appropriate changes in position and amplitude of the relaxation features. The methyl and ethyl polymers show only a single loss process within 100K of the glass transition (measured at a low effective frequency). The isothermal frequency dependent attenuation coefficients confirm this analysis, which is in good agreement with observations made at 3 MHz^{7,8}.

The butyl polymers show two relaxation processes. The loss occurring at higher temperatures is known from dielectric^{3,9,10} and mechanical^{1,2,11} measurements to correspond to cooperative backbone and ester group movements (the high frequency/temperature combined $\alpha\beta$ process). The lower temperature phenomenon recorded here can be attributed to the alkyl group relaxation – the γ -process.

A composite Arrhenius plot of the acoustic, and low temperature dielectric and mechanical data (Figure 2) yields an activation energy of 27 kJ/mol for the alkyl group rotation in poly(isobutyl methacrylate). Theoretical calculations of the potential energy profile for internal rotation of the side chain³ indicate that the energy difference between states

should be of the order of 4.0 kJ/mol with an interconversion activation energy of about 21 kJ/mol. The calculations also suggest that there is an energy difference between higher energy forms only of the order of 0.2 kJ/mol. Thus the system may be assumed to approximate to a two state conformational equilibrium, explaining the observation of an acoustic loss peak.

Ultrasonic wave velocity

The 5 MHz longitudinal wave velocities, plotted against the reduced temperature ($T_g - T$) show similar behaviour in all polymers (Figure 3). The main glass transition (or $\alpha\beta$ -

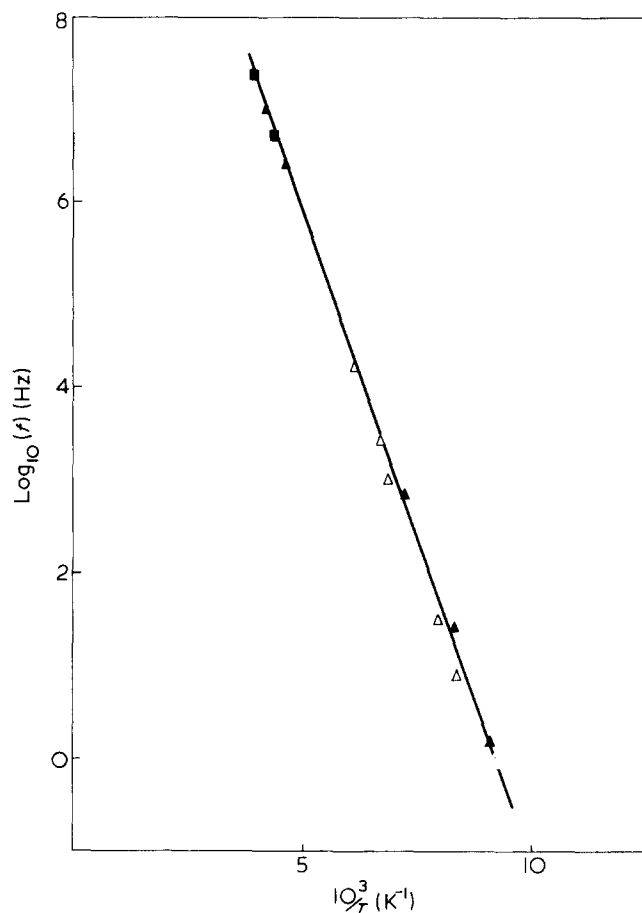


Figure 2 Arrhenius plot for poly(isobutyl methacrylate): Δ , dielectric studies³; \blacktriangle , mechanical/ultrasonic^{7,8,11}; \blacksquare , this work

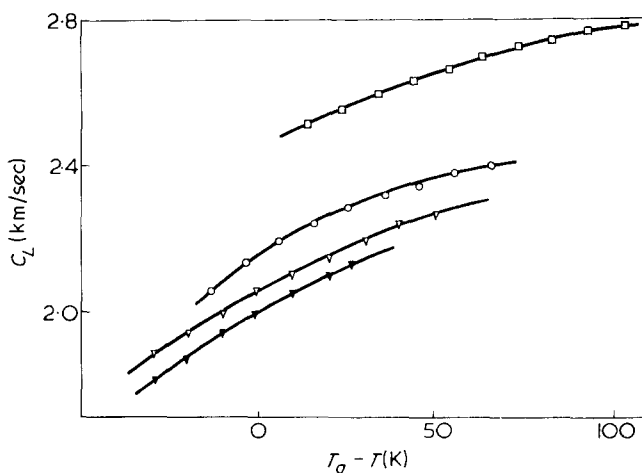


Figure 3 Variation of longitudinal velocity versus reduced temperature for the poly(alkyl methacrylates): ∇ , PNBMA; ∇ , PIBMA; \circ , PEMA; \square , PMMA

Table 2 Velocity and low temperature specific heat ($T \sim 1\text{K}$)

Polymer	Density (kg/m^3)	C_L (m/sec)	$C_V/T^3 \times 10^3$ (J/kgK^{-4})
PMMA	1200	2850	25.6
PEMA	1110	2400	45.6
PIBMA	1090	2350	50.1
PNBMA	1070	2300	53.9

process in the higher alkyl methacrylates) is marked by the expected drop in the longitudinal velocity. The fact that neither of the butyl methacrylates show a marked change of slope in the region of the γ -relaxation indicates that the associated modulus, and molar volume, change is negligible.

The variation in velocity with chemical composition reflects the decrease in the intermolecular interaction force constant as the alkyl side chain length is increased. However it is not possible to calculate these inter- and intra-molecular force constants without further knowledge of the low temperature libration and energy storage mechanisms, requiring full understanding of the low temperature specific heat of these glassy materials.

An approximate value for the low temperature longitudinal wave velocity may be obtained (to about $\pm 6\%$) by extrapolation of unrelaxed values of C_L using Rao's rule¹². If, in addition, it is assumed (often without justification) that the longitudinal wave velocity is double the transverse wave velocity for glassy polymers, it is possible to calculate thermo-acoustic parameters in the manner of Kwan¹³ and Reese¹⁴. When this is done, low temperature values of C_V/T^3 can be estimated for the four polymers (Table 2). Because the velocities measured in this work are still in the relaxation region, the extrapolation, and derived C_V/T^3 values are imprecise, with an estimated uncertainty of $\pm 35\%$ in C_V/T^3 . These are in accord with the observations^{15,16} for polystyrene and PMMA that the acoustic specific heat so obtained is approximately half the value observed by precise calorimetry. Since calorimetry also shows that the Debye T^3 law does not hold^{17,19}, even as low as 1K, the use of ultrasonic data

for the calculation of thermodynamic parameters must be attended with great caution. However, even allowing for failure of the T^3 law the acoustic modes do seem to be capable of greater energy storage than is involved in the longitudinal perturbation.

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