

Acoustic Determination of Polymer Molecular Weights and Rotation Times

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ABSTRACT: An acoustic waveguide device was shown to be sensitive to the molecular weight of poly(ethylene glycol) in solution over a molecular weight range determined by the operating frequency of the device. The acoustic device used generates a shear wave with displacement in the plane of the device surface and normal to the direction of propagation. Liquid over the device exhibits viscous coupling to the oscillating surface, affecting propagation of the acoustic wave. The propagation loss was shown to be directly proportional to the weight percentage of the solute. For a given weight percent of polymer in solution, the loss increased with increasing molecular weight until a maximum loss value was reached; this may be due to the fact that rotational times for polymer molecules increase with molecular weight until they reach a point at which the rotation is limited by the oscillation time on the device surface. The molecular weight at which the maximum loss value was attained was 10,000 g/mol for a device operating at 104 MHz and 3350 g/mol for a device operating at 331 MHz, implying a rotational time of 1 ns for each 2200 increase in molecular weight. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 40: 1490–1495, 2002

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INTRODUCTION

Acoustic sensors can operate effectively in liquids, in which they are suitable for the detection of mass deposited on the sensor surface¹ or for the determination of solution viscosity.^{2–4} The use of acoustic sensors is being extended to biological applications,^{5,6} which often involve the detection of high molecular weight solutes such as proteins or DNA. The work described here was intended to characterize the response of the acoustic waveguide device with respect to increasing sol-

ute molecular weight, looking at the case in which the solute is not adsorbed to the device surface.

The acoustic wave devices used in the experiments reported here are fabricated on quartz with interdigitated gold transducers (IDTs) at each end (Fig. 1) and a surface layer of poly(methyl methacrylate) (PMMA) acting as a waveguide to enhance surface sensitivity. This sort of acoustic device is known as a Love wave device and has been described elsewhere in more detail.^{7,8} A potential can be applied across the IDTs at one end of the device so that there is a difference in potential between one contact pad and the attached gold fingers and the other contact pad with its attached fingers. This will generate a deformation on the underlying quartz via the piezoelectric effect. If an alternating current is applied at an

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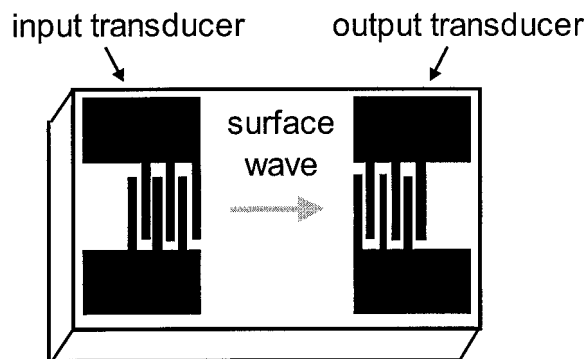


Figure 1. Schematic representation of the acoustic wave device, showing IDTs on a quartz substrate. The bars on the IDTs are not drawn to scale.

appropriate frequency, then an oscillating deformation or acoustic wave can be produced on the quartz. The acoustic wave will travel outward from the region of the IDTs; on reaching the IDTs at the other end of the device, the acoustic wave can be converted back into an electric signal, again via the piezoelectric effect. The phase and amplitude of the input and output electrical signals can be compared to obtain information about the medium adjacent to the device surface in the region between the IDTs, because changes in this region will affect the transmission of the acoustic wave, thereby affecting the output electric signal.

The wavelength of the acoustic wave will be determined by the repeat distance between the fingers of the IDTs. The operating frequency of the device is determined by the wavelength and by the speed of transmission of sound in the medium through which the acoustic wave is traveling, which is in this case quartz and PMMA because the wave travels at the interface between the waveguide and the substrate.

The cut of quartz in the underlying substrate results in a shear wave being produced, so that the oscillating deformation is in the plane of the device surface. This means that the application of liquid to the device surface does not damp the wave excessively. Liquid in contact with the device will exhibit viscous coupling to the oscillating surface, with the oscillations being carried out into the liquid to a penetration depth determined by the viscosity and density of the liquid and by the frequency of the oscillation. The thickness δ of the entrained fluid layer is given by $\delta = (2\eta/\rho\omega)^{1/2}$, where η is the solution viscosity, ρ is the density, and ω is the oscillation frequency.

The amplitude of oscillation within the liquid will be greatest adjacent to the device surface and will decrease to zero in the bulk of the solution. This will produce a velocity gradient within the entrained fluid layer, as shown in Figure 2. Solute molecules within the entrained fluid layer will, therefore, be situated across a velocity gradient and will be subjected to torque about an axis parallel to the direction of propagation of the acoustic wave (Fig. 2). Because the lateral displacement on the device surface reverses direction with each oscillation, the torque on the solute molecules will also reverse direction. Solute molecules that are larger will have a greater rotational time in solution. This would be expected to affect the insertion loss measured in acoustic experiments using different molecular weight fractions of a given polymer if the molecular weight increases to the point that the rotational time for the polymer in solution approaches the oscillation time on the device surface. This was investigated with a series of different molecular weight frac-

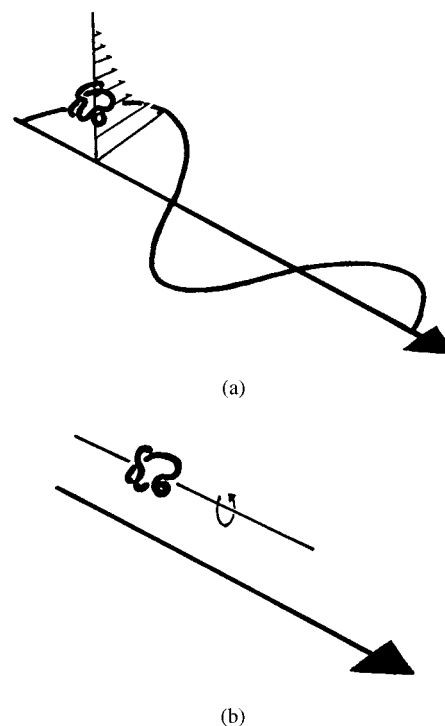


Figure 2. (a) Polymer molecules within the entrained fluid layer will be situated across a velocity gradient created by shear movement on the surface of the acoustic device. (b) The velocity gradient places a torque on the polymer molecules and, therefore, causes rotation about an axis parallel to the direction of propagation of the acoustic wave.

tions of poly(ethylene glycol), (PEG) with devices that operated at 104 or 331 MHz.

EXPERIMENTAL

The acoustic devices were prepared by photolithography with single-crystal, Y-cut, z-propagating 0.5-mm-thick quartz. The 104-MHz device was prepared at the Southampton Electronics Centre (Southampton, United Kingdom) with a 200-nm gold overlayer and a 10-nm chromium adhesion layer. The 331-MHz measurements were made at the third harmonic of a 110-MHz device prepared by us at Nottingham Trent University using a 15-nm gold layer and a 35-nm titanium adhesion layer.

The PMMA waveguide was deposited by the spin coating of the devices with a solution of medium molecular weight PMMA (Aldrich) in 2-ethoxyethyl acetate (Aldrich) for 40 s at 4000 rpm. A 22% (w/w) solution of PMMA was used to coat the 104-MHz device, and a 3.3% (w/w) solution was used to coat the harmonic device to obtain measurements at 331 MHz. The PMMA-covered devices were heated to 195°C for 2 h to facilitate solvent evaporation and improve film adhesion.

A Hewlett-Packard 4195A network analyzer was used to measure the amplitude (insertion loss) of the output electrical signal with respect to a reference signal. A perspex flow cell and silicone rubber gasket were used to hold the solutions in place over the region of the device between the IDTs. A continuous flow of solution was pumped over the device at a flow rate of 0.083 mL/min with a peristaltic pump. During the acquisition of data as a function of time for the experiments described here, a 3-MHz range of the frequency spectrum around the optimum operating frequency was scanned every 43 s to monitor the signal. Data was collected at a fixed frequency, so that one data point was collected every 43 s.

Solutions of PEG were made up in 18 M Ω water from a USF Elga Maxima deionizer at a weight percentage defined as grams of PEG per 100 g of water. PEG 300, 400, 600, 1000, 1500, 2000, and 10000 were obtained from Aldrich; PEG 3350 and 8000 were obtained from Sigma; PEG 6000 was obtained from Fluka and PEG 20000 was obtained from BDH. Values used for the molecular weights were those provided by the manufacturers. Glycerol was obtained from Sigma.

RESULTS AND DISCUSSION

Signal Loss as a Function of the Solute Weight Percentage

Figure 3 illustrates a typical experimental sequence: the insertion loss of the 104-MHz acoustic device was measured while water and PEG solutions were alternately pumped over the device surface. The initial baseline signal with the device in water is approximately -33.35 dB; this changes rapidly when the water is replaced by a 5% solution of PEG 20000. When water is once again pumped over the device surface, the signal returns to its initial value, indicating that the PEG is readily rinsed off. The change in signal amplitude due to the presence of solute was determined, as shown in Figure 3, and is the loss L in subsequent figures.

Initial experiments were carried out with a series of glycerol solutions to determine the relationship between signal loss and solute concentration. Signal loss was plotted as a function of glycerol weight percentage over a 1–11% range, with the weight percentage given as grams of glycerol per 100 g of water (Fig. 4). A correlation coefficient of 0.9999 was obtained for this graph, indicating that signal loss was directly propor-

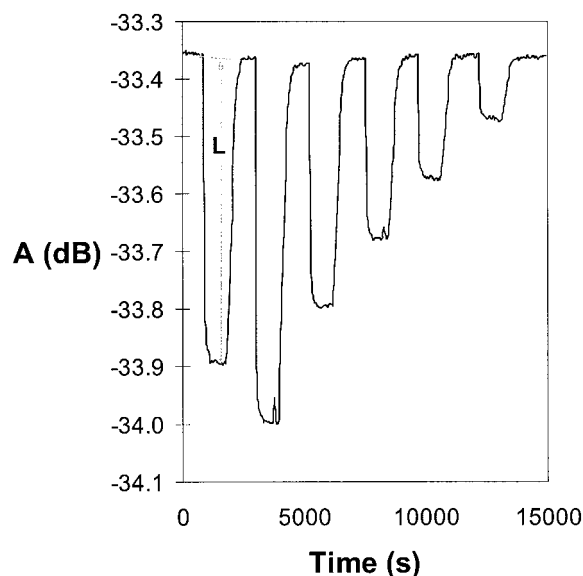


Figure 3. Acoustic response as solutions of PEG 20000 are applied to and rinsed off the surface of a 104-MHz device. Solutions of different weight percentages were applied in the following order: 5, 6, 4, 3, 2, and 1%. The loss L occurring on the addition of solute was calculated as indicated.

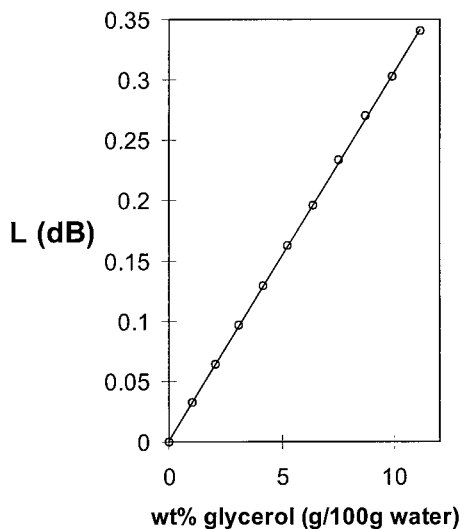


Figure 4. Additional acoustic loss due to the presence of glycerol in solution, measured with a 104-MHz device.

tional to the weight percentage of solute. It should be noted that this applies only to a series of solutions made up in the same solvent.

The data shown in Figure 4 were also plotted as $L/(\rho)^{1/2}$ against $(\eta)^{1/2}$, where ρ is the solution density and η is the viscosity. Values for solution viscosity were obtained from literature values of viscosity for known weight percentage of glycerol solutions.⁹ The relationship between $L/(\rho)^{1/2}$ and $(\eta)^{1/2}$ has been predicted and demonstrated² to be linear for a range of solution viscosities for measurements made with an acoustic plate mode device, another device operating in a shear mode. Although a relatively good linear relationship was demonstrated for the data obtained here, with a correlation coefficient of 0.9987, it did not improve on the fit demonstrated in Figure 4. Signal loss was, therefore, considered in terms of the weight percentage of solute.

The PEG solutions also showed a linear relationship between the signal loss L and the weight percentage of solute, with both the 104-MHz and 331-MHz devices. Results are shown in Figure 5 for measurements made with the 331-MHz device. These data were used to select the weight percentage of PEG for measurements with the molecular weight of PEG varied; 5% was chosen to optimize the signal loss but remain within the demonstrated linear range. The data in Figures 3 and 5 imply that measurements are being made on PEG in solution rather than in an adsorbed layer: Figure 5 shows a linear response rather

than the shape typically associated with a polymer adsorption isotherm, and Figure 3 shows no sign of the PEG being specifically adsorbed to the device surface.

Acoustic Signal Response as a Function of the Molecular Weight

The viscosities of polymer solutions at concentrations of 5–10% can be used as empirical measures of the molecular weight.¹⁰ An analogous approach is used here, with the incremental change in signal amplitude on the addition of a 5% polymer solution plotted as a function of the PEG molecular weight for a molecular weight range of 300–20,000. Although there are many treatments relating viscosity to polymer molecular weight and shape, most of these consider molecules rotating at a constant angular velocity, which is not the case here.

The response obtained with a 104-MHz device is shown in Figure 6, along with the response obtained with a 331-MHz device. As can be seen, for a fixed weight percentage of polymer, the change in signal amplitude increases with increasing molecular weight until a maximum is reached. The maximum value is attained at a

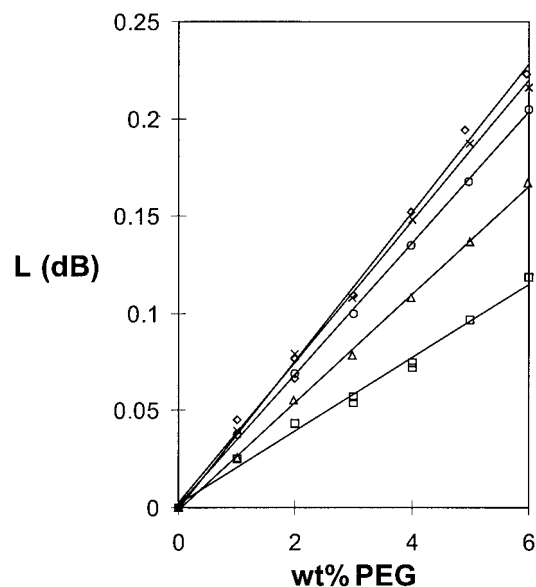


Figure 5. Additional acoustic loss due to PEG in solution, measured with a 331-MHz device. Data are shown as a function of the weight percentage of PEG for PEG of the following molecular weights: PEG 300 (\square), PEG 600 (Δ), PEG 3350 (\circ), PEG 8000 (\diamond), and PEG 20000 (\times).

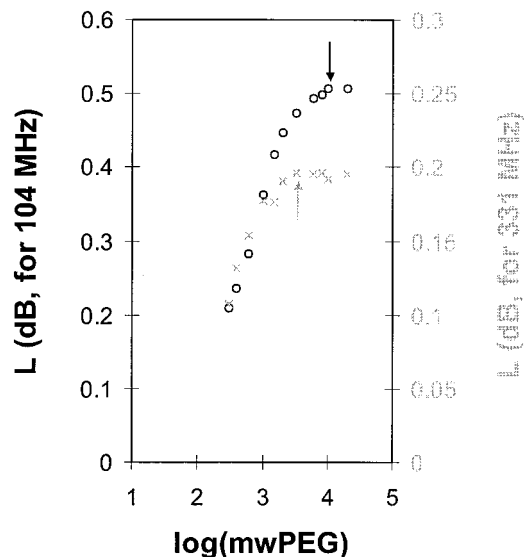


Figure 6. Acoustic response as a function of PEG molecular weight measured at 104 MHz (○, left-hand axis) and 331 MHz (×, right-hand axis). The arrows indicate the data points associated with the lowest molecular weight polymer fraction giving the maximum signal change.

molecular weight of 3350 for the higher frequency device and at 10,000 for the lower frequency device. An increase in the amount of PEG 20000 will cause an additional change in the signal, indicating that the saturation in response is not due to instrumental limitations but is, in fact, due to the high molecular weight of the solute. The absolute values of the changes on the two devices should not be compared because the waveguide thickness was selected to minimize insertion loss rather than to maximize the device sensitivity.

As the molecular weight of the polymer increases, the rotational time of molecules in solution will also increase, eventually reaching a point at which the rotation is limited by the oscillation time of the device. The 104-MHz device will have an oscillation period of 9.6 ns, with a given point on the device surface moving in one direction and then back in the opposite direction during one complete oscillation. If the time in each direction, or half the oscillation time, is equated directly with the rotational time of the polymer at the limiting molecular weight for which the change in signal ceases to increase with molecular weight, this gives a value of 4.8 ns for the rotational time of PEG 10000 from the 104-MHz device and 1.5 ns for PEG 3350 from the 331-MHz device. This gives an average value of 1 ns for every 2200 increase in molecular weight.

A rotational correlation time τ_c can be estimated for a spherical solute molecule with the equation $\tau_c = V_h \eta / kT$, where V_h is the hydrated volume of the solute molecule and η is the viscosity of the solvent, k is Boltzmann's constant, and T is absolute temperature.¹¹ The PEG will have a hydrated specific volume intermediate between that for water at 1 cm³/g and dry PEG at 0.83 cm³/g, so that a τ_c value of 1 ns will correspond to PEG with molecular weights between 2400 and 3000 g/mol. This is in relatively good agreement with the value obtained here.

For both devices used here, proteins will be in a molecular weight range in which the measured loss L does not increase with increasing solute molecular weight. If proteins were freely rotating in solution above the device surface, the acoustic response would be expected to be sensitive only to the weight percentage of the protein in solution. If the acoustic response were considered in terms of molar concentration, then doubling the molecular weight and thereby halving the molar concentration at a fixed weight percentage solution would be expected to halve the response.

The detection of analytes will generally involve the specific adsorption of the analyte of interest to the device surface, which will hinder the rotation. The degree of hindrance will be dependent on the mode of adsorption: attachment to a single flexible tether would permit some rotation, but adsorption through multiple bonds would not. The mode of binding would, therefore, be expected to affect the acoustic response. It has been previously noted¹² that a mass response is insufficient to explain the acoustic response with respect to the binding of a series of biological molecules to a thickness shear mode acoustic wave device.

CONCLUSION

Acoustic devices operating in a shear mode can be used to determine the molecular weight of oligomers or polymers that do not adsorb to the device surface. The molecular weight range that can be studied is dependent on the operating frequency of the device; lower frequency devices are useful for solutes with a greater molecular weight range. The oscillation time on the device surface will limit the rotation of polymer molecules in solution. This can be used to obtain information about molecular rotation times.

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