Contents lists available at ScienceDirect

Ultrasonics

Anomalous temperature dependence of speed of sound of bulk poly(N-isopropylacrylamide) hydrogels near the phase transition

Ezekiel Walker [a,*], Delfino Reyes [b], Arkadii Krokhin [a], Arup Neogi [a]

[a] University of North Texas, Department of Physics, Denton, TX 76201, USA
[b] Universidad Autónoma del Estado de México, Toluca 50120, Mexico

ABSTRACT

Bulk Poly(N-isopropylacrylamide) (PNIPAm) hydrogels are thermally responsive polymers that undergo a sharp volumetric phase transition around its *lower critical solution temperature* of 33 °C. The physical characteristics of bulk, micro-, and nano-form PNIPAm hydrogel have been well-studied, and have applications ranging from biomedical devices to mechanical actuators. An important physical characteristics which reveals lack of available information is speed of sound. Prior studies have utilized Brillouin scattering, multi-echo reflection ultrasound spectroscopy, the sing-around method, and others in measuring the speed of sound. We use a planar resonant cavity with *bulk* PNIPAm hydrogel in aqueous solution to determine the temperature dependent speed of sound around the lower critical solution temperature. The results show sharp nonmonotonic behavior of the sound velocity in vicinity of the phase transition.

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1. Introduction

Poly(N-isopropylacrylamide) (PNIPAm) polymer hydrogels are interesting materials because of their mechanical properties that are stimuli sensitive. Applications for the hydrogel range from artificial muscle [1], to actuators [2], to drug delivery systems [3], and continue to grow as their properties are explored. Thermal stimulation of PNIPAm hydrogel in aqueous solution results in a sharp volumetric phase transition around 33 °C, called the lower critical solution temperature (LCST) [4,5]. Below the LCST, bonding between polymer chains and water is thermodynamically preferable, the cross-linked network of polymer chains is swollen, and the hydrogel is hydrophilic [6]. Above the LCST, bonding amongst the polymer chains becomes thermodynamically preferable, the polymer chain network collapses, some portion of water is expelled from the network, and the gel becomes hydrophobic, precipitating out of the aqueous solution [7]. The elastic bulk modulus, mass density, and viscosity of the gel determine the speed of sound and attenuation. A volumetric phase change in a material will affect each of the properties, resulting in a net change in the speed of sound and attenuation. Thus, for PNIPAm thermal stimulation should significantly affect the acoustic properties of the hydrogel. Here we report the anomalous temperature behavior of the speed of sound caused by the phase transition in the gel.

Ultrasonic spectroscopy is an invaluable tool used to investigate the mechanical properties of a material [8–10]. In particular, it has been used extensively to study the chemical reactions during polymerization of some acrylamide based gels [5,11,12], and the thermal influence on the mechanical properties of a variety of other polymers [5,13,11]. Issues arise when trying to translate the behaviors of other polymer systems to PNIPAm because the cross-linking and gel form will impact the elastic properties [14].

Literature concerning the temperature dependent speed of sound and attenuation coefficient is sparse [13,15,14]. Hirotsu et al. performed a Brillouin scattering study of PNIPAm to examine the hypersonic elastic behavior including the speed of sound and attenuation [13]. In their study, the speed of sound increased from a relatively stable ~1550 m/s below the LCST to ~2250 m/s above it. The attenuation did not maintain the same stable behavior, but was relatively low below the LCST before a sharp increase above it.

In some materials, particularly low viscosity liquids, the hypersonic characteristics of a material can be used as an accurate depiction of the ultrasonic characteristics [8,16]. However, polymers are generally highly viscoelastic materials, and may have polymer chains or cross-linked networks that are comparable with the wavelength of ultrasonic or hypersonic waves [17]. Experimental studies of the ultrasonic behavior within the frequency region 200–800 kHz confirmed a difference, specifically in the speed of sound.

For this work, we investigated the temperature dependent speed of sound of bulk PNIPAm hydrogel in aqueous solution using a planar–planar resonance cavity around the LCST (19–35 °C).

* Corresponding author.
   E-mail address: EzekielWalker@my.unt.edu (E. Walker).

2. Background and theory

Many different techniques have been used in ultrasonic spectroscopy to determine the acoustic characteristics of a material [11,9,16,13,8]. The substantial majority of these techniques are based on analyzing pulse/time-delay characteristics, for example, Brillouin scattering, and/or resonant cavities. Each has advantages and disadvantages based on the amount, thickness, and type of material, the equipment, and frequency range. This work utilizes a planar–planar resonant cavity for measuring the speed of sound [18,19].

For a planar–planar oscillator, the frequency shift between the Fabry–Pérot peaks is related to the speed of sound through the material filling the cavity and the length of the cavity. The cavity used is formed by the placement of two ultrasonic transducers as the cavity boundaries. One transducer operates as the emitter; the source for propagating longitudinal waves in the cavity. The other transducer operates as the detector; the receiver for the cavity.

A general form for the pressure plane wave from the source transducer is written as

$$p_e(x, t) = p_0 e^{i(kx - \omega t) - \alpha x} \approx p_0 e^{i(kx - \omega t)}(1 - \alpha x), \qquad (1)$$

where α is a linear attenuation constant and weak damping is assumed, $\alpha x \ll 1$.

Upon interaction with the receiver, some portion of the wave is absorbed and detected, but some other portion cannot be detected because of the impedance mismatch between the surface of the transducer and the material. For each surface, we denote a reflectivity: r_e, is the reflectivity of the emitting antenna and r_d is the reflectivity of the receiving antenna. For a separation, d, the pressure at the detecting transducer takes the form

$$p_d(d, t) = p_0 e^{-i\omega t} \frac{1 - \alpha d - (1 + \alpha d) r_e r_d e^{2ikd}}{\left(r_e r_d e^{2ikd} - 1\right)^2}. \qquad (2)$$

The attenuation coefficient does not affect the frequency of the resonances as seen in Eq. (2). Neglecting its affects, the equation simplifies, and the detected power is proportional to the square modulus of pressure, is written in the form

$$P(d) \propto |p(d)|^2 = \frac{p_0^2}{1 + (r_e r_d)^2 - 2r_e r_d \cos(2kd)}. \qquad (3)$$

The transmitted field oscillates with frequency $\omega = 2\pi f = kc$, where c is the velocity of a propagating wave through that medium, exhibiting Fabry–Pérot resonances. Two neighboring peaks are separated by frequency interval $\Delta f = c/2d$, i.e. the speed of sound is independent of the reflectivities of the antennas and it is given by the well-known formula

$$c = 2d\Delta f. \qquad (4)$$

Equipment limitations impede our ability experimentally determine the first resonant frequency f_1 to calibrate the cell. However, assuming that c is constant within the frequency range of interest we can use *any* two resonance peaks to determine the speed of sound.

3. Experimental setup

3.1. Materials and Equipment setup

Bulk poly(N-isopropylacrylamide) were made using the free radical polymerization technique as described in Refs. [7,20]. N-Isopropylacrylamide monomer (NIPA, TCI Chemicals), N, N′-methylene-bisacrylamide crosslinker (BIS, Polysciences Inc.), and DI water were mixed together in a ratio of 0.10 (wt): 0.02 (mol NIPA):

0.84 (wt) to make a monomer solution. The solution was then set in an ice bath and pumped with N_2 for 30+ min to remove oxygen from the solution. Ammonium persulfate (98+%, Sigma–Aldrich) initiator and N,N,N′,N′-tetramethyl-ethylenediamine (99%, Sigma Aldrich, TEMED) accelerator were added for final polymerization. The PNIPAm was cut into a disk shape with a thickness and diameter large enough such that the cavity remained completely filled before and after the volumetric phase transition at the LCST.

Two Panametrics V301, unfocused, planar, immersion transducers centered at 0.5 MHz were used as the source, receiver, and boundaries of the resonant cell (Fig. 1). The transducers were aligned so that the faces were parallel to within <0.1°, and the distance between them measured to within <0.1 mm after setup was secured. The transducers were placed in the center of a tank filled with deionized water. The source transducer was driven in continuous mode by a Leader 1300S Function Generator, and dually connected to a Tektronix TDS 2024B oscilloscope. The receiver was connected to an HP3585A Spectrum Analyzer, and dually to a separate channel on the same oscilloscope. The function generator was swept over the range 2–802 kHz at a constant power, and the maximum corresponding signal at each frequency was recorded on the HP3585A.

3.2. Measurement

Calibration of the cell was done using water at room temperature (20 °C). To ensure that the cavity remained filled throughout the experiment, the gel was placed in an aqueous solution above 38 °C, then placed between the transducers. The setup was secured, the separation of the transducers measured, and the gel was allowed to cool to room temperature. For this experiment, transducers were set to be 12.0 mm apart, and the swollen gel diameter was 28 mm, giving a total cell volume of 6080 mm³. The 5.34×10^8 mm³ water bath was then heated at the rate 1.0 °C/h. and data recorded every 2 °C using an in-house k-type thermocouple. The temperature over the sample was measured with accuracy of 0.1 °C during the experiment.

Resonant frequencies from the resulting data were examined to determine the speed of sound using Eq. (4). The Fabry–Pérot resonances for water can clearly be seen in the transmission spectrum in Fig. 2a, and the resonant peaks for PNIPAm at 19–35 °C in Fig. 2b. For water, the spacing between the transducers, which also operate as the cavity walls, is 42 mm. The temperature dependent sound velocity of water, as calculated using the frequency separation of the resonant peaks and Eq. (5), is shown in Fig. 3. The sound velocity agrees well with results available in literature [16,21].

In summation the measurement and subsequent sound velocity calculations are as follows: the transmission spectrum of a material is measured from 2 to 802 kHz, the frequencies of the resulting Fabry–Pérot resonant peaks are recorded, the nearest-neighbor frequency differences are calculated, and Eq. (5) is used to calculate the sound velocity.

4. Results and discussion

Cai and Suo show in their work that mechanically constraining the gel affects the measured sound velocity [22]. Our method to fill the cavity consisted of inducing the phase change in the gel before setting the cavity wall, or transducer, separation. This was done to ensure that the cavity was always filled with the PNIPAm whether or not it was in the hydrophilic or hydrophobic state. Since the phase change is volumetric in nature, there should be some measure of mechanical constraint due to the cavity walls as the gel swells in its hydrophilic state. However, the gel is not contained in any direction other than those of the walls.
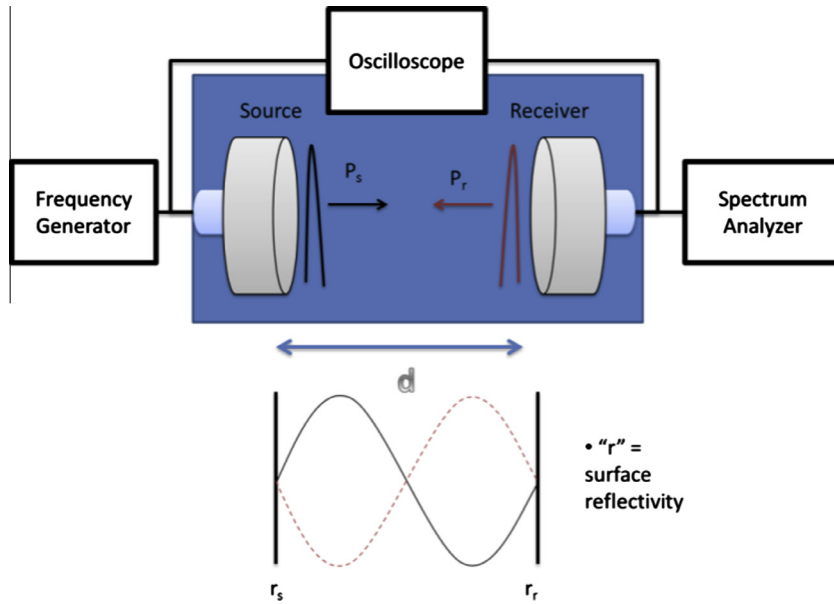
Fig. 1. Example setup for Fabry Pérot resonant cavity.
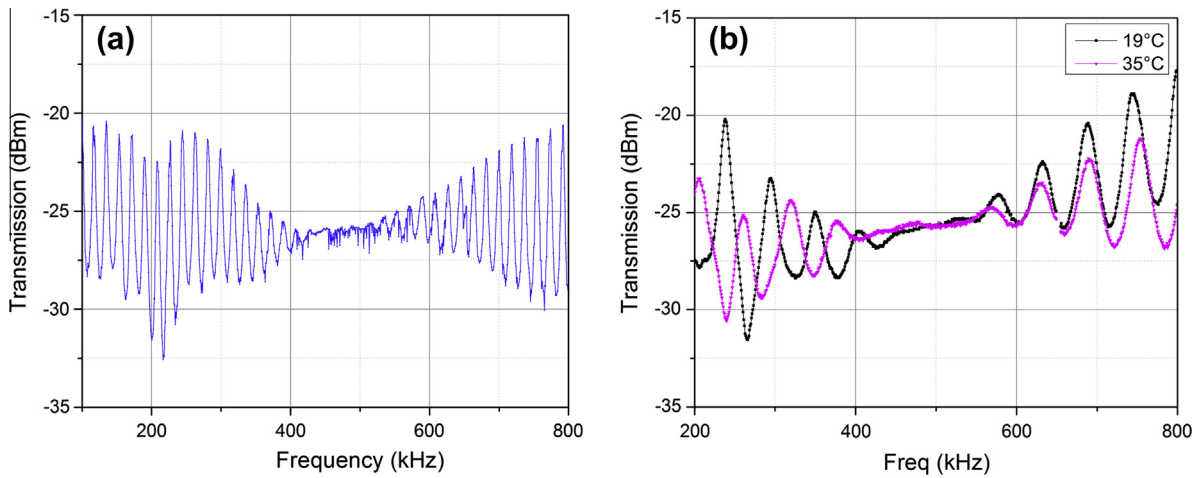

Fig. 2. (a) Left: transmission spectrum of deionized water at 27 °C. The transducers, which make the boundaries of the cavity, are separated by 42 mm. Fabry–Pérot resonance peaks can be clearly seen. (b) Right: transmission spectrum of PNIPAm at 19–35 °C. Sample is between transducers spaced 12 mm apart. As with water, resonant peaks can be clearly seen.

Subsequent measurements were performed at room temperature (20 °C) to determine the effect on the measured sound velocity of our method. In the "unconstrained" measurements, the gel was not heated to induce the volumetric phase transition, and the cavity walls were set for the swollen gel. In the "constrained" measurements, the gel was set as was performed in the experiment. The resulting sound velocities from the measurements were as follows: for unconstrained gel $c = 1352 \pm 13$ m/s and for constrained gel $c = 1358 \pm 13$ m/s. So, for our measurements the mechanical constraint produced by phase transition does not have a significant effect on the measured sound velocity.

We investigated further to verify the effects of mechanical constraint on the hydrogels. For this experiment, we compressed the gel from a volume of $V \approx 4360$ mm^3 to $V' \approx 3010$ mm^3 (a reduction of about 31%) to ensure that constraints that artificially compress the gel would affect the measured sound velocity. The measured sound velocity for the compressed gel was $c' = 1114 \pm 22$ m/s, i.e. the relative change is about 18%. Compression leads to an increase of the mass density of gel which becomes $\rho' = \rho(V/V')$. Since

$$c = \sqrt{K/\rho}, \tag{5}$$

where K is the elastic bulk modulus, the relative change of sound velocity can be estimated through the change of the volume to V'

$$(c - c')/c = 1 - \sqrt{(V'/V)} \approx 0.17. \tag{6}$$

This calculated value is in good agreement with the measured result $(c - c')/c = (1358 - 1114)/1358 = 18\%$ for velocity. This agreement suggests that the elastic modulus K remains independent of internal strain, i.e. the gel follows linear Hook's law even for as large volume deformations as 31%.

The phase transition for PNIPAm begins at 27 °C, but volumetric and viscoelastic properties change slowly until a sharp, significant transition occurs at 33 °C [5,22]. Measured speed of sound in Fig. 3 follows the same behavior. It decreases slightly for $T > 27$ °C, before increasing sharply at 33 °C. The speed of sound from 19 °C to 25 °C slightly fluctuates about the average value of 1344 m/s. The velocity drops to a low of 1315 m/s at 29 °C, before increasing sharply to 1389 m/s near the phase transition temperature of 33 °C. There is a
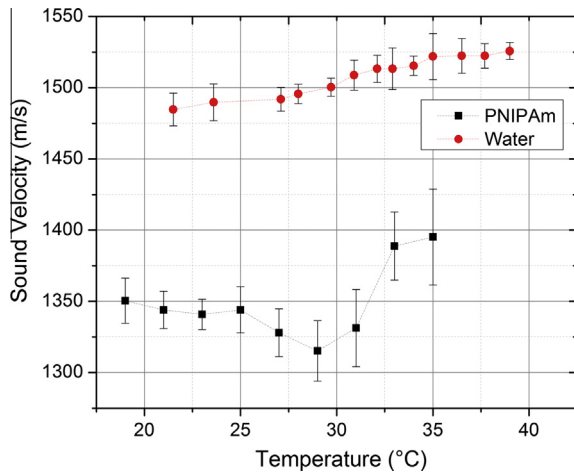
Fig. 3. Measured speed of sound of PNIPAm (squares) and water (dots) vs. temperature.

75 m/s difference between the speed of sound above and below the phase transition, see Fig. 3.

While bulk gel consists mostly of water, the speed of sound in Fig. 3 is systematically lower than 1480 m/s, the standard value for pure water. There are several reasons for the lower sound velocity. Hydrated hydrogel sinks rather quickly when placed in water which would indicate a higher density. Tagit et al. measured the bulk modulus K of PNIPAm microgels in their swollen and collapsed state [23]. Bulk modulus values for the swollen state were lower than pure water, and increased above the phase transition. Though microgels and bulk gels differ in the size of the cross-linked polymer networks by definition, the lowered bulk modulus values found in the paper for microgels could qualitatively cause the same effects in bulk gels. The lower bulk modulus combined with the potentially higher density would result in a lower sound velocity. In the same paper, the measured bulk modulus for microgels increases above the phase transition which agrees well with the behavior of the sound velocity increasing above the phase transition as measured using the Fabry–Pérot resonances. One more reason for lower sound velocity is related with presence of gas which may be accumulated during preparation of the bulk gel. As it was calculated in Ref. [24] even very small percentage of gas considerably reduces speed of sound in fluids.

Within the interval of the phase transition, the measurement uncertainty increases. The differential Fabry–Pérot resonance technique is limited by the assumption that the material under measurement has a frequency independent speed of sound in the range of resonances. The increasing uncertainty with temperature, and especially during the phase change, may be an indication of some frequency dispersion of the speed of sound in the frequency range of this work. Prior work has shown strong frequency dependence in the speed of sound of PNIPAm microgels, but the variation

was over significantly larger range of higher frequencies in the 2+MHz region [11].

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