Sensors and Actuators B 144 (2010) 318–322

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Molecular weight influence study of aqueous poly(ethylene glycol) solutions with a microfluidic Love wave sensor

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ARTICLE INFO

Article history:
Received 15 August 2008
Received in revised form 9 September 2009
Accepted 29 October 2009
Available online 6 November 2009

Keywords:
Acoustic Love wave sensor
Complex fluids
Micro-rheology
Poly(ethylene glycol)

ABSTRACT

Love wave acoustic sensors have shown through the years a great potentiality regarding measurements in liquid environments, especially in the field of biosensors. Their high sensitivity to surface perturbations make them also good candidates for micro-rheology. In this paper, we demonstrate that a Love wave sensor response is also very sensitive to the molecular structure of polymers by investigating its behavior to aqueous poly(ethylene glycol) solutions of various molecular weights. We also report the ability of this type of sensor to determine the critical molecular weight between entanglements (M_c).

1. Introduction

In material science, the study of complex fluids like polymers is particularly challenging because of the large time spectrum covered by relaxation mechanisms. While a lot of methods are available for low frequency rheology ($< 10^2$ Hz), per example rotational rheometers, methods for high frequency rheology ($> 10^6$ Hz) can be difficult to apply. Nevertheless, high frequency measurements can provide very useful informations on the microstructure of a complex fluid, like the backbone strength of a polymer or the solvent–polymer interactions [1].

During our previous studies, we focused on fluids of increasing complexity using a Love wave acoustic sensor combined with a microfluidic chip, from the relatively simple case of aqueous glycerol solutions [2] to more complex polymer fluids like poly(dimethylsiloxane)s [3]. Measurements made on the latter proved that our platform was able to perform measurements in highly viscous environments. While there is a significant bibliography in viscosity study with Love wave sensors [4–6], other physical parameters like molecular weight are usually less considered. Compared to the classical measurement tools used in rheology, acoustic wave based sensors implies smaller displacements and higher frequencies, leading to a good sensitivity to the considered fluid microstructure [7,8]. This has been illustrated by the determination of molecules rotation times for aqueous solutions of poly(ethylene glycol) in the earlier works of Melzak et al. [9]. In this paper we pursue this microstructure investigation of PEG solutions with our microfluidic Love wave platform with two ideas in mind: a study of the sensor response to PEG solutions of identical Newtonian viscosity but formulated with different molecular weights, followed by an observation of entanglements influence.

2. Microfluidic Love wave sensor : experimental apparatus

A Love wave sensor is based on the perturbation of a guided shear horizontal surface acoustic wave. This particular polarization limits energy losses while the wave propagates along with a liquid environment, making this type of acoustic sensor the most suitable for applications in liquid [4,10,11]. The Love wave acoustic energy is mostly confined in the guiding layer, leading to a high surface density energy and therefore a high sensitivity to surface perturbations.

The Love wave sensor used in this study consists of a dual delay line deposited on a AT cut quartz substrate (Euler angles: 0°, 121.5°, and 90°) used as the piezoelectric material. Interdigital Transducers (IDTs) are made by sputtering 70 nm of gold on a 30 nm titanium layer to achieve a good surface adhesion. Each IDT is composed of 44 splitted pairs of electrodes with a 40 μm periodicity which defines the wavelength λ. Each electrode is 5 μm wide with an aperture W of 40 λ, while the center to center path length between electroacoustic transducers (L_{cc}) is equal to 209 λ. A 4 μm plasma enhanced chemical vapor deposited (PECVD) SiO_2 layer is used as the guiding layer. These characteristics lead to a 117 MHz synchronous frequency f_0. This dual delay line set-up allows differ-

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doi:10.1016/j.snb.2009.10.070

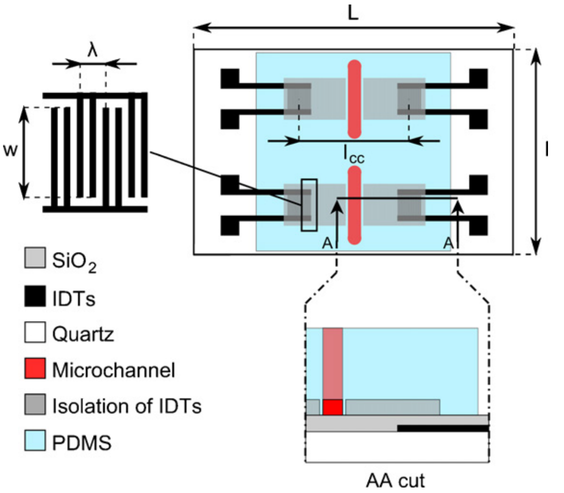

Fig. 1. Love wave dual delay line acoustic sensor combined with a poly(dimethylsiloxane) microfluidic chip (dimensions: $L = 25$ mm, $l = 16$ mm, $\lambda = 40\,\mu$m, $W = 40\lambda$, $L_{cc} = 209\,\lambda$).

ential measurements with a reference, improving the robustness of the platform when the environmental conditions vary during measurements. Working with liquid environments implies some drawbacks while using a Love wave sensor: important insertion losses, especially for viscous liquids, and influence of dielectric properties by the liquid medium can be considered as limitation factors for a micro-rheometer application. These shortcomings can be avoided by a proper isolation of the IDTs from the liquid and a limitation of the surface perturbation. The proposed solution is to bond a specific microfluidic chip on top of the guiding layer. This chip is made out of poly(dimethylsiloxane) using a standard soft lithography process [12]. The liquid is confined to a fraction of the acoustic path, while IDTs are encapsulated in air. Fig. 1 illustrates the geometry of the PDMS chip bonded on the dual delay line.

A covalent bond between the SiO_2 guiding layer and the PDMS chip is obtained by a UV–ozone treatment, ensuring a good sealing of the microchannel. This point is essential especially with highly viscous fluids that generate high pressure strains. Both encapsulation of the IDTs and microchannel are 50 μm high, while the microchannel width in contact with the active area of the acoustic path is set to 2000 μm, corresponding to a surface coverage of 30.5%. Considering these dimensions, the microchannel volume is about 0.2 μL. The microchannel width is taylored for the application, as it influences directly the sensitivity to viscosity variations. For highly viscous fluid, a thinner microchannel can be more adapted in order to limit insertion losses, while for lower viscosities a wider microchannel adds sensitivity to the microsensor. The height of the microchannel can be decreased in order to minimize the volume of liquid, as long as it is greater than the penetration depth of the acoustic wave, defined as $\delta = \sqrt{2\eta/\rho\omega}$ [13]. The geometry of this PDMS chip hardly perturbs the transmission scattering parameter S_{21}, as described in Fig. 2. Moreover, the acoustic reflexions on a naked delay line are eliminated thanks to the acoustic absorbent properties of PDMS, leading to a proper frequency lobe.

The sensor is inserted in an oscillation loop to provide a real time measurement of the frequency and the attenuation. Frequency shifts are measured with a Agilent 53131A frequency counter, while insertion losses are measured with a Agilent E4419B power meter associated with two Agilent E9301A power meter sensors connected to the oscillation loop by Macom CH-132 20 dB directional couplers. Although this set-up is sufficient for large insertion losses variations, the resolution is not sufficient to measure small variations with high precision due to a small signal/noise ratio. In this case, an Agilent 8648B synthesized signal generator is used to apply a sinusoidal signal at the synchronous frequency f_0 and a 0 dBm power level to the input IDT of the delay line, while the output IDT is directly connected to the power meter sensor. This set-up gives a better accuracy on the ΔIL measurement.

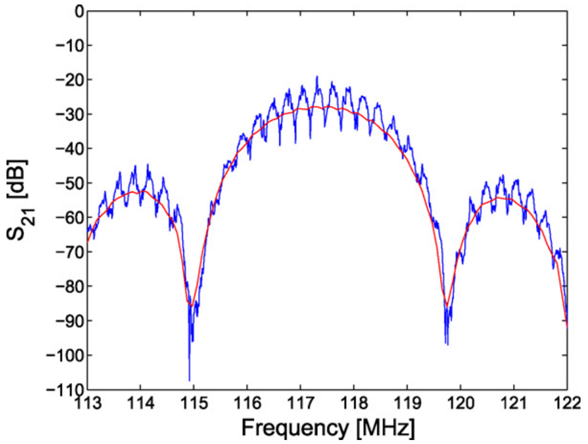

Fig. 2. S_{21} [dB] parameter (insertion loss) as a function of frequency measured with a network analyzer for a delay line with and without a microfluidic PDMS chip. Acoustic reflexions are absorbed by the PDMS bonded around the acoustic path.

Two Bioseb BS-8000 syringe pumps inject the liquid through an electro valve to the microfluidic port of the PDMS chip via Hamilton glass syringes and PTFE capillary tubes at a controlled flow rate of 1000 μL h^{-1}. Measurements on the influence of flow rate on the sensor response showed no significant variations. Data acquisition and injection parameters are fully controlled by a single interface developed under a CVI/Labwindows environment, providing the ability of a fully automatic process. This experimental set-up is summarized in Fig. 3.

The following protocol is applied for each measurements: the microfluidic chip microchannel is filled with deionized water to obtain a stable reference, providing the frequency baseline f_{ref}. An aqueous PEG sample is then injected in the microchannel, until a steady state of the oscillation frequency is achieved. Frequency shift and additional insertion losses are measured, and the microchannel is rinsed with deionized water until the frequency gets back to f_{ref}. This cycle is repeated three times to ensure repeatability, and each measurement is an average value of the variations observed. An example of a measurement cycle is given in Fig. 4. All of the

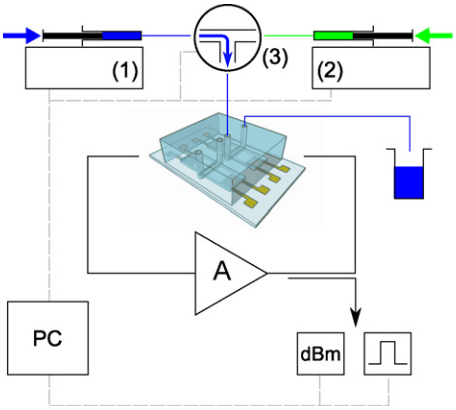

Fig. 3. Description of the experimental microfluidic monitoring apparatus. Two syringe pumps (1), (2) linked to an actuated valve (3) inject the selected liquid into the microfluidic chip, while a frequency counter and a power meter retrieve informations about the oscillation loop. Each device is controlled and monitored with a single PC.