

Dependence of Brillouin frequency shift on temperature in poly(pentafluorostyrene)-based polymer optical fibers estimated by acoustic velocity measurement

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Abstract: Poly(pentafluorostyrene) (PPFS), which can be easily synthesized and has a low optical loss window at 850 nm, is a promising alternative for a costly perfluorinated polymer as a base material of polymer optical fibers (POFs). To investigate the potential of a PPFS-POF as a Brillouin-based temperature sensing fiber, the Brillouin frequency shift and its temperature dependence of PPFS were measured using an ultrasonic pulse-echo technique. The temperature coefficient, which determines the sensitivity of the temperature sensing, was approximately -7.1 MHz/K independently of the molecular weight and was nearly identical to that in perfluorinated POFs.

Keywords: polymer optical fiber, Brillouin scattering, fiber-optic temperature sensor, poly(pentafluorostyrene)

Classification: Fiber optics, Microwave photonics, Optical interconnection, Photonic signal processing, Photonic integration and systems

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1 Introduction

Compared to conventional temperature sensors (thermocouples, thermistors, etc.), fiber-optic temperature sensors have many inherent advantages such as immunity to electromagnetic interference noise and capability of (quasi-)distributed measurement. In particular, distributed temperature sensors based on Brillouin scattering in optical fibers have gained a great deal of attention for the past several decades because of their truly distributed measurement capability with high stability [1, 2, 3, 4, 5, 6, 7, 8]. In conventional fiber-optic

Brillouin temperature sensors, their sensing heads comprise glass optical fibers such as silica single-mode fibers (SMFs) [1, 2, 3, 4, 5, 6], tellurite glass fibers [7], and photonic crystal fibers [8], which are so fragile that they cannot withstand strains of over several percent.

To extend the measurable strain region, our research efforts have focused on the sensor applications of Brillouin scattering in polymer optical fibers (POFs) [9, 10, 11, 12, 13], which are in general sufficiently flexible to withstand large strains of up to tens of percent. We have studied Brillouin scattering in perfluorinated graded-index (PFGI-) POFs and reported their fundamental properties at 1.55 μm [10, 11, 12, 13], which is a common telecommunication wavelength. The Brillouin frequency shift (BFS) in PFGI-POFs at room temperature was approximately 2.8 GHz ($\sim 1/4$ of that in silica fibers) [10] and was strongly dependent on temperature with a proportionality constant of -4.1 MHz/K [11]. The absolute value of the temperature dependence constant was 3.5 times as large as that in silica fibers, and a potential application of PFGI-POFs for high-precision temperature sensing has been discussed [11].

The PFGI-POFs were originally developed as a communication medium and have been continuing to break records for the lowest propagation loss and highest data transmission speed of all the POFs [14]. However, despite their impressive performance, the PFGI-POFs have not been widely utilized because of the prohibitive costs. The base material is a homopolymer made by the cyclopolymerization of perfluoro(butenyl vinyl ether) prepared by a complex process [15], which makes it one of the most expensive synthetic polymers.

In this study, we investigate a partially fluorinated polymer, poly(pentafluorostyrene) (PPFS) as a possible low-cost alternative. Partially halogenated styrene monomers are easily prepared via dehydration of the corresponding alcohols, which are synthesized via Grignard reactions with acetaldehyde [16]. Because of the carbon-hydrogen bonds at the main chain, PPFS and its POF absorb infrared light [17] and exhibit a considerably higher propagation loss at 1.55 μm . However, PPFS-POFs have a low-loss window at 850 nm instead [16], which is also a common optical transmission wavelength used in Gigabit Ethernet and compatible with commercial light sources including vertical cavity surface emitting lasers [18]. Unfortunately, at this moment, Brillouin scattering in POFs at other than 1.32–1.55 μm cannot be directly measured because some of the measurement devices such as optical amplifiers and circulators are unavailable. Thus, we estimate the BFS and its temperature dependence in PPFS-POFs at 850 nm using an ultrasonic pulse-echo technique [19, 20]. In addition, we study the influence of molecular weight of the base polymer on the Brillouin properties for the first time.

2 Principle

When propagating in an optical fiber, incident pump light interacts with acoustic phonons, generating backscattered Stokes light; this phenomenon is known as Brillouin scattering. The central frequency of the Stokes light

spectrum shifts to lower frequency than the pump frequency by the amount called BFS v_B , which is given by [21]

$$v_B = \frac{2nv_a}{\lambda_p}. \quad (1)$$

where n is the core refractive index, v_a is the acoustic velocity in the fiber, and λ_p is the pump wavelength. When the refractive index of a fiber core material is known, the BFS at an arbitrary pump wavelength can be calculated by measuring the acoustic velocity in the fiber sample (as well as in the bulk sample for POFs with relatively large core diameters [19]). The acoustic velocity is further related to the Young's modulus E , density ρ , and Poisson's ratio σ by [22, 23]

$$v_a = \sqrt{\frac{1 - \sigma}{(1 - 2\sigma)(1 + \sigma)} \frac{E}{\rho}}. \quad (2)$$

Since the Young's modulus has a relatively strong temperature dependence [24], the acoustic velocity and the BFS shift toward higher or lower frequency depending on the environmental temperature, which is the principle of Brillouin-based temperature sensing. To develop high-precision temperature sensors, fibers with strong BFS dependences on temperature are desirable.

3 Methods

3.1 Preparation of polymer samples

We prepared four PPFs samples with different molecular weights. PFS monomer and all other chemicals were purchased from SynQuest Laboratories and Sigma Aldrich, respectively. The monomer was freshly distilled using a spinning band column before use, and the others were used as received. For the polymerization, we used glass ampoules with 10 mm inner diameters. The monomer mixtures, which contained di-*tert*-butyl peroxide as the free-radical initiator, were transferred into the glass ampoules and subjected to repeated freeze-pump-thaw cycles. The ampoules were then flame-sealed in vacuo. The polymerizations were carried out in an oil bath at 120 °C for 90 h. The glass ampoules were carefully broken, and the polymer rods were obtained.

The molecular weights and distributions of the polymers were measured using gel permeation chromatography (GPC). All GPC analyses of the polymers in tetrahydrofuran were performed at a flow rate of 1.0 mL/min at 40 °C. The chromatograms were calibrated using polystyrene standards. The refractive indices were measured using a prism coupler with an accuracy of ± 0.0005 . The probe wavelengths were 409.2, 650.3, 833.7, and 1546 nm. The measured values were fitted to the three-term Cauchy's equation [25], and the refractive indices at 850 nm were obtained. The molecular weights (M_w : weight average, M_n : number average) and refractive indices at 850 nm of PPFs samples are summarized in Table I. We varied the molecular weights by adjusting the concentration of initiator, and M_w was in the range of $5.96 - 8.13 \times 10^5$. The refractive indices were independent on the molecular weights as expected.

Table I. The amount of initiator for polymerization, molecular weights, and refractive indices of PPFS bulk samples

Sample	Initiator [mol %]	$M_w (\times 10^5)$ [g/mol]	$M_n (\times 10^5)$ [g/mol]	M_w/M_n	Refractive index at 850 nm
P-1	0.20	8.13	4.13	1.97	1.467
P-2	0.30	7.69	3.99	1.93	1.467
P-3	0.40	6.84	3.57	1.92	1.466
P-4	0.50	5.96	2.65	2.25	1.467

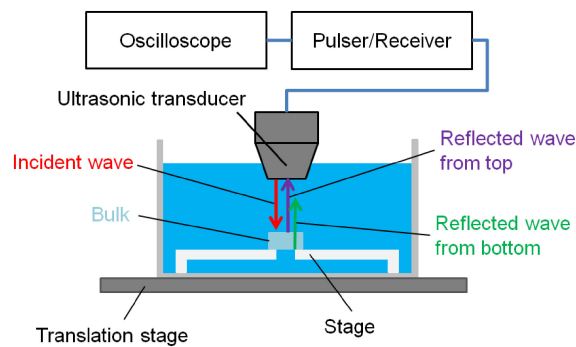


Fig. 1. Experimental setup for acoustic velocity measurement in PPFS bulk samples.

3.2 Brillouin frequency shift measurements

For BFS measurements, the obtained polymer rods were cut into 4-mm-thick 10-mm-diameter cylinders with flatly-polished bottom and top surfaces. The sample was placed on a stage with an 8-mm-diameter hole at the center, which was fixed in degassed water as shown in Fig. 1. A pulsed converging ultrasonic wave with 20-MHz center frequency (note that MHz ultrasonic wave has been experimentally shown to be available for BFS estimation [19]), which was generated with a focus-type transducer connected to a pulser/receiver, was launched into the sample, and the reflected waves from the top and bottom surfaces were detected with the same transducer. The small hole below the sample avoided the interference with the other wave reflected from the stage. The time delay between the reflected waves was observed with an oscilloscope. The acoustic velocity v_a in the sample was calculated from the time delay Δt and the sample thickness l by

$$v_a = 2l/\Delta t. \quad (3)$$

By substituting Eq. (3) into Eq. (1), the BFS at 850 nm was obtained. These steps were repeated at different temperatures to investigate the temperature dependence of the BFS.

4 Results

Fig. 2 shows the temperature dependence of the BFS at 850 nm in sample P-2 as an example. The temperature was increased from room temperature to

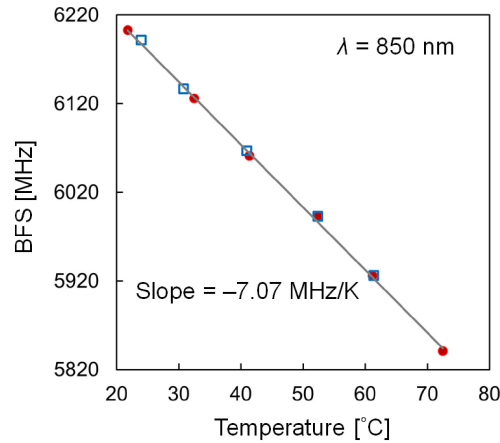


Fig. 2. BFS dependence on temperature in sample P-2 at 850 nm. The solid circles and hollow squares indicate the measured points with increasing and decreasing temperature, respectively.

Table II. BFSs at room temperature (RT) and their temperature coefficients of the PPFs samples, silica SMF, and PFGI-POF at 850 nm. Note that the values for the silica SMF and PFGI-POF have been recalculated using Eq. (1)

Sample	BFS at RT [GHz]	Temperature coefficient [MHz/K]
P-1	6.16	-7.27
P-2	6.17	-7.07
P-3	6.16	-7.18
P-4	6.18	-7.12
Silica SMF	19.7	2.2
PFGI-POF	5.1	-7.5

75 °C, and then decreased to room temperature. The BFS at room temperature was ~ 6.2 GHz, and its temperature dependence was linear with a proportionality constant of approximately -7.1 MHz/K irrespective of increasing or decreasing temperature. The BFS at room temperature and the temperature coefficient of the four samples are summarized in Table II. Both values were nearly independent of molecular weight. As the Young's modulus, Poisson's ratio, and density of polymers, which determine the acoustic velocity (Eq. (2)), generally have little dependences on molecular weight when the molecular weight is sufficiently high [26], no correlation between the BFS and molecular weight was predictable. However, this relation had not been experimentally investigated, and we believe that the finding of this study will be of great help in designing and preparing POFs for Brillouin-based temperature-sensing applications. The estimated BFS and the temperature coefficient in PPFs-POFs at 850 nm were close to those in PFGI-POFs as listed in Table II. The BFS in PPFs-POFs, which was 1.2 times as high as that in

PFGI-POFs, may contribute to the mitigation of the Brillouin signal deterioration caused by Rayleigh noise [27]. Although the absolute value of the temperature coefficient in PPFS-POFs was slightly lower than that in PFGI-POFs, it was still approximately 3.3 times as large as that in a standard silica SMF.

5 Conclusion

We synthesized PPFS polymers with different molecular weights by free-radical polymerization in bulk and studied their BFS properties. The BFS and its temperature dependence in PPFS-POFs were estimated from the bulk samples using the ultrasonic pulse-echo technique. The BFS and the temperature dependence were independent of the molecular weight over the range investigated. The BFSs of PPFS samples at room temperature were 6.2 GHz at 850 nm and linearly changed with temperature at the ratio of -7.1 MHz/K. The absolute temperature coefficient was nearly identical to those of PFGI-POFs and 3.3 times as large as those of silica SMFs. As mentioned in the introductory part, since the production cost of PPFS-POFs could be considerably lower than that of PFGI-POFs, PPFS-POFs might be a promising alternative of PFGI-POFs for high-precision temperature sensing at 850 nm in the near future.

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