Giant elasticity of photopolymer nanowires

Sana Nakanishi, Satoru Shoji, and Satoshi Kawata[a]
Department of Applied Physics, Osaka University, Suita, Osaka 565-0872, Japan

Hong-Bo Sun
State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Qianjin Street, Changchun 130012, China

Giant elasticity, reflected by a shear modulus three order smaller than seen in the bulk of the same materials, is found in polymer nanowires, which are prepared by two-photon polymerization into a shape of spring: geometry capable to magnify mechanical deformations. An approach intervening the competitive processes of dissolving and polymerization in the course of rinsing of written structures was proposed for continuously tuning the shear modulus and fixing them at desired level. These results not only reveal a characteristic of polymers when the material size enters into the regime of hundreds of nanometers but also indicate prospect polymer microelectromechanical system for biocompatible applications. © *2007 American Institute of Physics.*
[DOI: 10.1063/1.2767995]

The nanomechanical properties of photopolymers are attracting more research efforts because a path has been recently paved to biocompatible micronanomachines or even polymer microelectromechanical system (MEMS) owing to femtosecond laser micronanofabrication technology.[1–5] Since the feature sizes in these polymer structures have reached sub-100 nm level,[6,7] it is no longer possible to properly design and fabricate more complicated machines and systems with desired function without a deep understanding of the nanoscale behaviors of polymers. In this letter, we study the mechanical characteristics of polymer nanowires, of which the radius is around 100 nm. We find that the strain tensile of polymer abides by a linear law, but the magnitude of the shear modulus is three order smaller than that of the bulk, meaning a giant elasticity of the polymer nanowires. Furthermore, the shear modulus could be freely adjusted within a certain range by controlling a progression of polymerization, as is enabled due to the size effect.

Figure 1 illustrates a schematic [the inset of (b)] and experimentally produced (a) spring-shaped nanowires, or nanosprings, with coil radius R of 2.5 μm, pitch P of 2.0 μm, and the number of turns N of 4. For applying force to the spring by laser tweezers, a bead of 1.0 μm radius was attached to one end of the nanospring. The other end was connected to an anchor affixed to the glass substrate, and the connection point was 7.0 μm above the substrate. The entire structure including the anchor, the spring, and the bead were fabricated by two-photon-absorption-induced photopolymerization (TPP) of urethane acrylate photopolymerizable resin (SCR500, JSR). A 780 nm wavelength mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) that delivered 80 fs at a repetition rate of 82 MHz was utilized as an exposure source. The laser beam was focused into the resin on a glass substrate by an objective lens [numerical aperture (NA) =1.4, oil immersion, Olympus]. A three-dimensional (3D) piezoelectric stage moved the resin relative to the focal spot according to a preprogramed pattern of a nanospring, and a galvanometer shutter controlled the exposure time, 2.5 ms, at

each point. The distance between each point was 50 nm. After the nanosprings were written, unpolymerized resin was removed by ethanol. After exchanging the solution with fresh ethanol sometimes we kept ethanol solution surrounding the nanosprings, and performed all the following experiments with nanosprings immersed in ethanol.

In order to measure the tensile strain of the nanosprings, we focused the light beam from a 1064 nm cw Nd doped yttrium aluminum garnet laser by an objective lens (NA =1.35, oil immersion, Olympus) onto the bead and pulled it aside by moving the focal position [insets of Fig. 1(b)]. The movement until the maximum extension of the spring, where the bead escaped from the trap, is sufficiently slow so that the effect of viscous resist is negligible. Calibration method of the laser trapping force is shown in detail in Ref. 8. We used 1 μm radius beads made of polystyrene dispersed in water. Since refractive index ratio of polystyrene and water, 1.59/1.33, is larger than that of photopolymerized resin and ethanol, 1.55/1.36, this refractive index difference was compensated by ray optics theory.[8]

The pair of springs shown in Fig. 1(a) was prepared on neighbored anchors: one of them is under going trapping [top of (a) and inset B of (b)] while the other has been relaxed
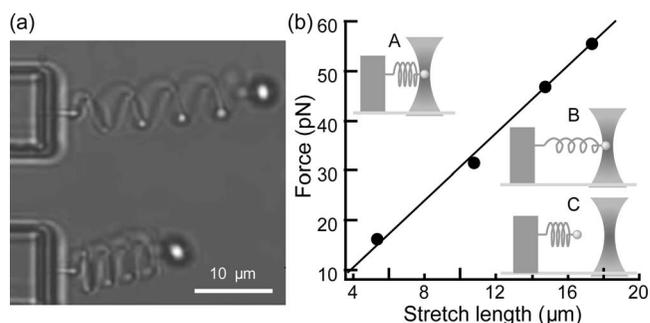

FIG. 1. Polymer nanowires created by TPP of resin, which are designed into spring shape. (a) Optical microscopic image of the nanosprings. The top spring is being stretched, and the bottom spring has been relaxed and restored to the original position. (b) The tensile strain curves of the nanosprings, from which a linear dependence is found. The insets illustrate how a spring was pulled.
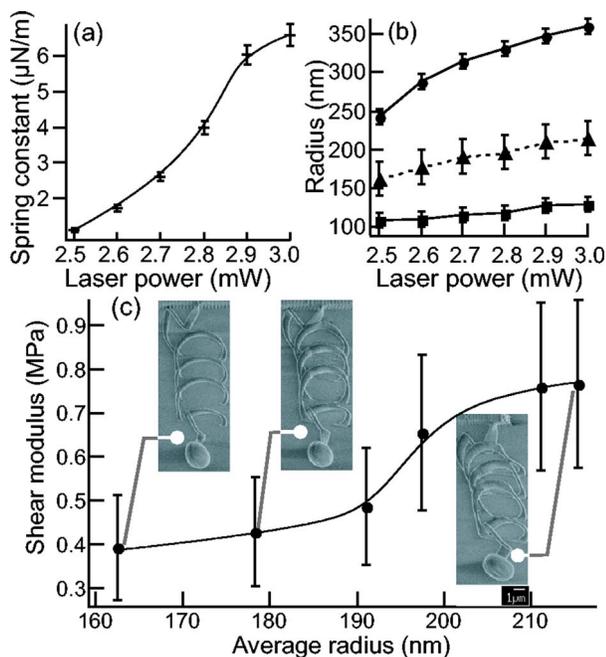
[a]Electronic mail: skawata@skawata.com

FIG. 2. Laser power dependent behaviors of nanosprings. (a) Spring constants from nanosprings of the same design as that in Fig. 1(a) but written by different laser powers. (b) Radius of the nanowires of each spring. Squares and circles show the half of lateral and vertical lengths. Triangles show averaged radius calculated from lateral and vertical lengths. (c) Shear modulus of nanosprings calculated with the value shown in (a) and (b) and the inset are SEM images of the springs.

FIG. 3. (a) Raman spectra of photopolymerized and unpolymerized resins. The peak at 1638 cm^{-1} assigned to C=C stretching mode from unsaturated monomer and oligomer molecules disappears after polymerization. (b) Intensity of 1638 cm^{-1} peak in polymers solidified at different laser powers. The upper and lower dotted straight lines are the intensity from the unpolymerized resin and that fully polymerized under UV light exposure.

[bottom of (a) and inset C of (b)]. The displacement-force curve in Fig. 1(b) exhibits a *linear* tensile-strain behavior across the entire range of spring extension. The spring constant determined according to Hooke's law, $F=kx$, was 3.3 ± 0.1 $\mu N/m$, consistent with our previous results.[1,3]

The spring constant k is correlated with the shear modulus G_s and geometrical parameters of the spring R and N, as well as the radius of nanowire r, with the following equation;[9] $G_s=4NR^3k/r^4$. Shear modulus, which is an intrinsic property of materials and is defined as the ratio of shear stress to shear strain, is generally constant for bulk materials prepared by identical technical procedure. It is interesting to know the characteristics of G_s in the nanometer regime. Experimentally we fabricated nanosprings of the same design as Fig. 1 but with different wire widths by changing the laser power from 2.5 to 3.0 mW, measured at the focal plane of objective lens. Figure 2(a) shows that a significant laser power dependent spring constant k increases by six times from 1.1 to 6.6 $\mu N/m$ as the laser power rises by 20% from 2.5 to 3.0 mW. For evaluation of G_s, the value of nanowire radius r as well as spring constant k is required. For size measurement, a particular set of springs were fabricated, of which the bottom sides of nanosprings sit on the glass substrate for protection from being destructed during the solvent evaporation process. Typical scanning electron microscopic (SEM) images of these springs are shown as the insets of Fig. 2(c). The averaged nanowire radius is defined as $r_s=\sqrt{r_l r_v}$, where r_l and r_v are lateral (inside the focal plane) and vertical (along the laser beam propagation) widths, considering that the focal spot of the fabrication laser is of elliptical shape. We measured the half of minimum and maximum thicknesses of the nanowire in the SEM image as r_l and r_v. In Fig. 2(b), r_l, r_v, and r_s are shown as squares, circles, and
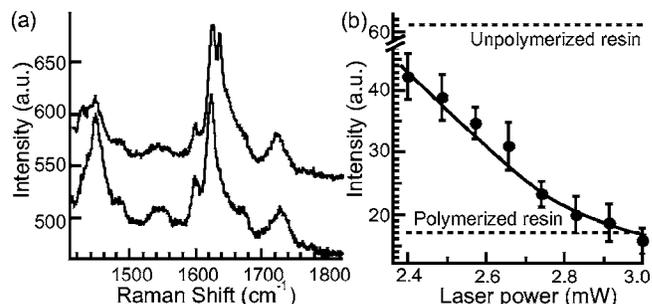
triangles, respectively. After adjusting for the effects of structural parameters, we find that the shear modulus undergoes a change: it increases from 0.39 to 0.77 MPa and is then saturated [Fig. 2(c)], although saturated value of G_s in nanowires was still three order smaller than shear modulus of bulk status of the same material (150 MPa).

An immediate question is as follows. What causes the variation of the shear modulus? We have to consider the intrinsic material properties. The 3D molecular network is formed by photopolymerization of monomer, oligomer, and cross-linker. The density of cross-linking and the polymerization degree are crucial factors to the mechanical properties of materials.[10] Since the polymerization occurs accompanied with the opening of unsaturated bonds, C=C for urethane acrylate resin, the process could be monitored by the consumption of C=C.[11] Raman spectroscopy was implemented to reach the above end. As test samples for Raman spectroscopy, rectangular solid structures were fabricated by TPP with different laser powers. Each structure was 4 μm in square and 5 μm in height, consisting of nanowires with regular intervals of 100 and 200 nm in lateral and vertical directions, respectively. Using a confocal Raman microscope (Raman-11, Nanophoton Corp.), a 785 nm wavelength solid-state cw laser with the power of 20 mW, which is not sufficient to initiate additional TPP, was focused in the deep inside of the structures by the objective lens (NA=0.9) to take Raman spectra. The measurement was conducted immediately after the structures were polymerized and rinsed, which takes typically in less than a total of 10 min. A Raman shift assigned to C=C was observed at 1638 cm^{-1} [Fig. 3(a)]. Its intensity is larger at low fabrication laser power [Fig. 3(b)], implying that the higher laser power is exerted the higher percentage of C=C are reacted. It is seen from Fig. 3(b) that the Raman shift intensity approaches the level of a resin that was uniformly polymerized under UV exposure when the laser power reaches 3.0 mW, where the shear modulus was saturated.

So far the laser power dependent G_s could be attributed as the factor causing the variation of the shear modulus in the polymer nanowires. However, due to dark reaction and ambient light illumination, photopolymerization reaction proceeds for reactions in bulk volume, and G_s ultimately reaches a fixed level.[12] In the case of nanowires, will the same happen and is it feasible to set and stabilize the shear modulus at different levels? To answer this question, one needs to consider size effects. After the two-photon polymerized nano-
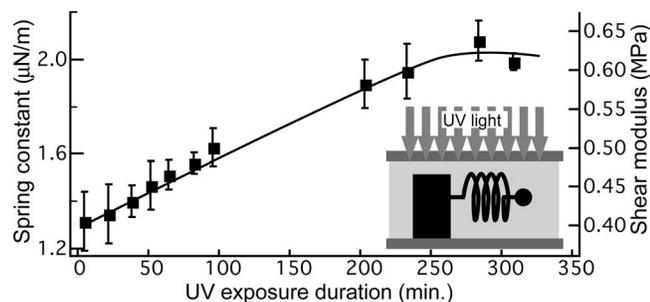
FIG. 4. Saturated spring constants by exposing the nanosprings with additional UV light for different durations, which were written by TPP and then immersed into ethanol.

wires are immersed into ethanol for rinsing, two competitive processes occur: dark reaction due to the remnant radicals and ambient light-aided polymerization promote the progression of polymerization while the attack of solvent molecules removes the remnant molecules of monomer, oligomer, and radical pieces from the polymer network. For polymerization in a bulk volume, the latter is negligible while this becomes dominant at the nanosize due to the large relative percentage of the surface to the volume, where solvent molecules can penetrate easily. The post-TPP ends with complete removal of small molecules. This suggests a possibility to control the ultimate degree of cure, and thefore G_s of nanopolymer, and fix them at a desired level by accelerating or decelerating one of the two processes: polymerization and dissolving of remnant small molecules. This was confirmed experimentally, for which the TPP created nanosprings soaked in ethanol are further illuminated with UV light (center wavelength was 370 nm) for different periods. When the additional UV exposure time increases from 0 to 4.5 h, the saturated spring constants of nanowires fabricated with identical design and under the same conditions range from 1.3 to 2.0 μN/m (Fig. 4), and the shear modulus varies from 0.40 to 0.64 MPa, while the change of wire width was not observed after 5 h UV exposure. It is noteworthy that the maximum of the saturated shear modulus (0.64 MPa) is 0.13 MPa smaller than the saturated value from solely under TPP (0.77 MPa). This further proves the model of competitive polymerization-dissolving processes.

In order to examine whether giant elasticity is a general performance when the size of polymer materials step into the hundreds of nanometer regime, springs of 1 μm diameter are fabricated and found not drivable by laser trapping even when the maximum of trapping force was applied. Bayindir, *et al.* also reported that Young's modulus of a polymer cantilever with the size of several microns was the same order of magnitude as that of bulk polymer.[13] It is obvious that more efforts should be paid to clarify the details of the shear

modulus jump from megapascal order at nanosize to gigapascal order in macrosize. The following factors could cause the large reduction of elasticity observed in our experiment. The first possible factor is swelling of polymer induced by the penetration of solvent into polymer network. Since the size of the polymer studied here is a few hundreds of nanometer, ethanol could penetrate into the entire polymer structure immediately and the reduction of elasticity by the swelling of polymer is not negligible anymore. Another possible factor is a difference of glass transition temperature T_g. The resin consisting of nanowires studied here has $T_g=152$ °C. It has been reported that T_g of a freestanding polymer thin film was significantly reduced when thickness is reduced to less than 300 nm.[14] If a further reduction of T_g to a level lower than room temperature could occur as result of dimension decrease from two dimension for thin film to one dimension in the nanowires studied here, the reduction of T_g would lead to one possible explanation of the giant elasticity of polymer nanowire. The giant elasticity of nanopolymers offers the promise that the technology of TPP of resins and micronanomachines and polymer MEMS produced this way promising for detecting weak interactions in biocompatible applications.

[1]S. Kawata, H. B. Sun, T. Tanaka, and K. Takada, Nature (London) **412**, 697 (2001).
[2]P. Galajda and P. Ormos, Appl. Phys. Lett. **78**, 249 (2001).
[3]H. B. Sun, K. Takada, and S. Kawata, Appl. Phys. Lett. **79**, 3173 (2001).
[4]H. B. Sun, H. Masuo, and H. Misawa, Appl. Phys. Lett. **74**, 786 (1999).
[5]S. Maruo, K. Ikuta, and H. Korogi, Appl. Phys. Lett. **82**, 133 (2003).
[6]K. Takada, H. B. Sun, and S. Kawata, Appl. Phys. Lett. **86**, 071122 (2005).
[7]S. H. Park, T. W. Lim, D. Y. Yang, N. C. Cho, and K. S. Lee, Appl. Phys. Lett. **89**, 173133 (2006).
[8]K. Svaboda and S. M. Block, Annu. Rev. Biophys. Biomol. Struct. **23**, 247 (1994).
[9]C. J. Ancker and J. N. Goodir, J. Appl. Mech. **25**, 466 (1958).
[10]E. Nielsen, *Mechanical Properties of Polymer and Composites* (Dekker, New York, 1974), Vol. 1, pp. 48–54.
[11]C. Esen, T. Kaiser, and G. Schweiger, Appl. Spectrosc. **50**, 823 (1996).
[12]F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed. (Wiley, New York, 1984), pp. 262–290.
[13]Z. Bayindir, Y. Sun, M. J. Naughton, C. N. LaFratta, T. Baldacchini, J. T. Fourkas, J. Stewart, B. E. Saleh, and M. C. Teich, Appl. Phys. Lett. **86**, 064105 (2005).
[14]M. Alcoutlabi and G. B. McKenna, J. Phys.: Condens. Matter **17**, R461 (2003).