Elastic coefficient of a single polymer chain by using Brownian dynamics analysis

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The elastic coefficient of a single polystyrene chain has been experimentally evaluated by using Brownian dynamics analysis. The Brownian motion of the chain is probed using a particle trapped by optical tweezers with a negligibly small spring constant. The displacement of the particle due to Brownian motion is measured by an interferometer assembled using the same laser beam as the optical tweezers. Two methods are employed for Brownian dynamics analysis: (1) the analysis of the time course of the displacement of the particle and (2) the fitting of the power spectrum of Brownian motion with a Lorentzian. The elastic constant of a polystyrene chain in dichloromethane at 21 °C is estimated to be 6.4×10^{-6} and 1.1×10^{-5} N/m when methods (1) and (2) are employed, respectively. The elastic constant obtained by approximating the polystyrene chain to a freely jointed chain is in agreement with the experimentally evaluated elastic constant. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2756527]

I. INTRODUCTION

A flexible polymer chain in solution behaves like a soft spring in the mechanical sense.[1] For example, the force f that is required to extend a freely jointed chain (FJC) having n number of bonds with the bond length b is given by

$$f = \frac{3k_B T}{nb^2} \boldsymbol{R} \tag{1}$$

in the small deformation regime.[2] Here, $\boldsymbol{R}$, k_B, and T are the end-to-end vector of the chain, the Boltzmann constant, and the absolute temperature, respectively. Equation (1) indicates that a FJC can be considered to be a Hookean spring with the elastic coefficient $k = 3k_B T/nb^2$. However, it is difficult to experimentally evaluate k due to its small magnitude. For example, for a FJC with $b = 10^{-9}$ m and $n = 10^2$, both of which are typical values for FJC models of real synthetic polymers, k is estimated to be of the order of 10^{-5} N/m at room temperature. For the measurement of such a small k, it is necessary to determine $|f|$ and $|\boldsymbol{R}|$ at high resolutions. Since $|\boldsymbol{R}|$ is of the order of 10^{-8} m for a single polymer chain in the small deformation regime, the measurement system used for the evaluation of k requires a resolution in $|f|$ of 10^{-13} N. A scanning probe microscope (SPM) is a promising tool for the mechanical measurement of single polymer chains due to the high resolution in $|\boldsymbol{R}|$. However, in a SPM, the resolution in $|f|$ is at best 10^{-12} N;[3–7] this means that a SPM has insufficient force resolution for the evaluation of k for single polymer chains in the small deformation regime. A system that uses optical tweezers is also a promising tool for the evaluation of k due to the high resolution in $|f|$ because a particle trapped by optical tweezers behaves like a spring with a very small spring constant.[8–10] However, in practice, it

is difficult to determine $|\boldsymbol{R}|$ at a high resolution by using the optical tweezers system. To our knowledge, there are still no apparatus available for examining the elastic constant of a flexible polymer chain in the small deformation regime with a sufficient resolution both in $|f|$ and $|\boldsymbol{R}|$. Consequently, there are no experimental data on the elastic constant of a flexible polymer chain in the small deformation regime

Instead of measuring $|f|$ and $|\boldsymbol{R}|$, the elastic constant of a polymer chain in the small deformation regime can be obtained from Brownian dynamics analysis. A polymer chain in solution exhibits a conformational change, and this Brownian dynamics reflects the elastic constant of the chain in the vicinity of the equilibrium state. Our strategy is as follows. Since the direct observation of the Brownian motion of a polymer chain is almost impossible, a particle that is employed as a probe for the Brownian motion is bound to the free end of a polymer chain tethered to an immovable plate. This particle is trapped in the very weak potential of the optical tweezers so that it is not allowed to escape from an interferometer equipped for the measurement of its displacement. It is noted that, as shown later, optical tweezers have a significantly smaller spring constant than a flexible polymer chain. Therefore, the trapping of the probe particle does not significantly affect the Brownian dynamics of the polymer chain.

II. PRINCIPLES OF MEASUREMENT

Firstly, consider a laser beam of the wavelength λ focused on the center of a spherical particle with diameter $d > \lambda$ in solution. When the refractive index of particle n_1 is sufficiently greater than that of solvent n_2, the particle is trapped by the optical tweezers formed in the vicinity of the focal point, as shown in Fig. 1.[11–13] By considering the direction of the trapping beam as the z axis and the equilibrium
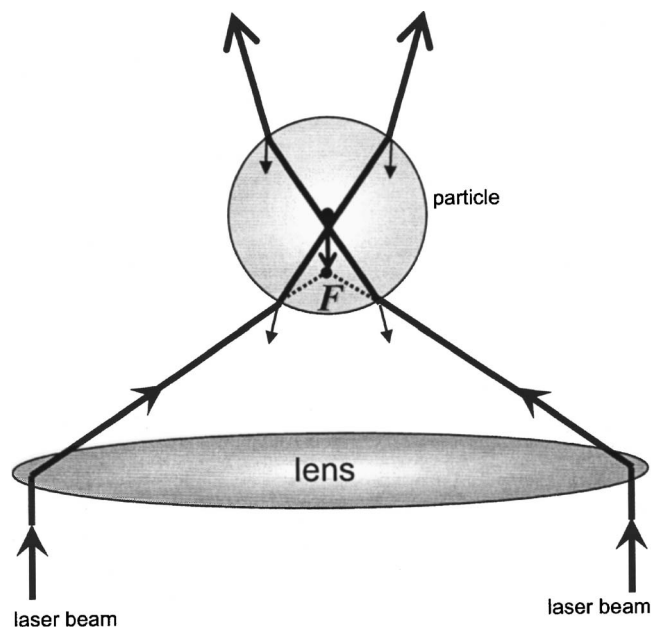
FIG. 1. Illustration of the optical trapping of a particle in solution by a focused laser beam. Under the condition that the effect of the gravity force is negligible, the focal point becomes the trapping center.
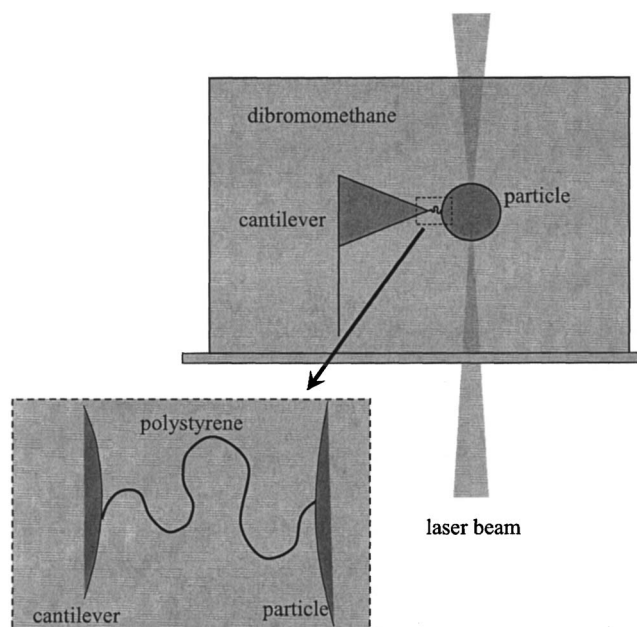

FIG. 2. Illustration of a polymer chain confined between a cantilever and a particle. In fact, the dimension of the polymer chain is significantly smaller than the dimensions of the cantilever and particle; this means that the geometrical condition of the chain corresponds to confinement between two planes, as shown in the magnified illustration.

point (center) of the optical trap as the origin, the trapping force F acting on a particle moving on the xy plane is given by[12]

$$F = Q(r)\frac{n_1 P}{c}. \tag{2}$$

Here, $Q(r)$, P, and c are the trapping efficiency at position r, the power of the focused beam, and the velocity of light, respectively. When $|r| \ll d$, F is approximately represented as

$$F = k'r, \tag{3}$$

where k' is a constant. The particle trapped in the potential of the optical tweezers fluctuates around the equilibrium point due to Brownian motion. For simplicity, we consider the fluctuation of the particle along the x axis. Under the condition $|\Delta x| \ll d$, the fluctuation can be represented as

$$U_1(x) = \tfrac{1}{2}k'(\Delta x)^2 + A_1. \tag{4}$$

Here, Δx, $U_1(x)$, and A_1 are the deviation of the particle from the equilibrium point, the potential of the optical tweezers along the x axis, and a constant, respectively.

Next, consider a polymer chain that is tethered to a plane at one end and a particle at the other end, as shown in Fig. 2 (Figure 2 illustrates the experimental setup. See below.) Since the dimension of the polymer chain is significantly smaller than that of the particle, the polymer chain behaves as if it is confined between two planes. In the absence of any external forces, the equilibrium dimension of the confined polymer chain is determined by the balance between the elastic force due to chain extension based on the distance between the planes and the steric repulsion force due to confinement. Then, the Brownian motion of the particle is dominated by the potential formed as a result of the abovemen-

tioned force balance for the polymer chain. The fluctuation of the particle in such a potential can be approximately represented as

$$U_2(x) = \tfrac{1}{2}k(\Delta x)^2 + A_2. \tag{5}$$

Here, $U_2(x)$ is the potential due to the force balance for the polymer chain, and A_2 is a constant. When the particle that is tethered to the polymer chain is trapped by the optical tweezers with potential $U_1(x)$, the Brownian motion of the particle is given by

$$U(x) = U_1(x) + U_2(x) = \tfrac{1}{2}K(\Delta x)^2 + A, \tag{6}$$

where $K = k + k'$ and A is a constant. The equation of the Brownian motion of a particle in potential $U(x)$ is given in the Langevin form

$$m\frac{d^2x}{dt^2} = -\frac{dU(x)}{dx} - f_r\frac{dx}{dt} + F_R(t). \tag{7}$$

Here, m, t, f_r, and $F_R(t)$ are the mass of the particle, the time, the friction coefficient for the translational motion of the particle, and the random force due to the collision of the solvent molecules with the particle, respectively. The solution of Eq. (7) is given by an autocorrelation function $C(t)$ with a time constant τ,

$$C(t) = \langle \Delta x(0)\Delta x(t)\rangle = [\Delta x(0)]^2 \exp(-t/\tau). \tag{8}$$

According to Wiener-Khinchin's theorem, the power spectrum $S(\omega)$ of Brownian motion is written as

$$S(\omega) \equiv \int_{-\infty}^{\infty} C(t)e^{i\omega t}dt = \frac{A'}{1 + \omega^2 \tau^2}, \qquad (9)$$

where A' is a constant. From the equipartition law of energy, K in Eq. (6) is given by

$$K = \frac{k_B T}{\langle (\Delta x)^2 \rangle}, \qquad (10)$$

where $\langle \ \rangle$ denotes the ensemble average. By using the relation $\tau = f_r / K$, K is also written as

$$K = \frac{f_r}{\tau} = \frac{6\pi\eta r}{\tau}, \qquad (11)$$

where η and r are the viscosity of the solvent and the radius of the particle, respectively. Equation (9) can be rewritten as

$$S(\omega) \rightarrow \begin{cases} \propto \omega^2, & \text{for } \omega \gg \tau^{-1} \\ = A', & \text{for } \omega \ll \tau^{-1}. \end{cases} \qquad (12)$$

Equation (12) indicates that when two lines obtained in the $\omega \gg \tau^{-1}$ and $\omega \ll \tau^{-1}$ regions of the log $S(\omega)$ vs log ω plot are extrapolated to the $\omega \approx \tau^{-1}$ region, the intersection is found to be at $\omega = \tau^{-1}$. Once τ is determined, K is obtained using Eq. (11). Thus, K can be evaluated from the power spectrum as well as the average fluctuation of Brownian motion. As described below, $k \gg k'$, i.e., $K \approx k$ in this study, and the elastic coefficient k is evaluated from the Brownian motion of the particle that is tethered to the polymer chain in solution.

III. EXPERIMENT

Borosilicate glass particles (mean diameter: 9.6 ± 1.0 μm; Duke Scientific, USA) were mixed with a silane coupling agent, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (Shin-Etsu Chem., Japan), in water containing a trace of acetic acid at room temperature to allow the coupling agent to be fixed on the surface of the particles. Then, the particles were stored in an oven at 110 °C for 5 min. The resultant particles were immersed in a chloroform solution of α-amino-ω-thiol-terminated polystyrene (PS) ($M_w = 148\,000$, $M_w / M_n = 1.10$; Polymer Source, USA) at 40 °C to allow the PS chain to be tethered to the particles through the coupling agent. To prepare particles for which the PS chains were sparsely distributed (to avoid the mechanical measurement of several PS chains), this tethering reaction was ended in a few minutes. The thiol group at the other end of the PS chain was bound with gold that was coated on a cantilever (SI-AF01-A, spring constant: 0.2 N/m; SII, Japan) just before the measurement.[14]

We assembled a measurement system, as illustrated in Fig. 3.[8] The linearly polarized beam of the second harmonic of a Nd-yttrium aluminum garnet laser (wavelength: 532 nm; Millennia Pro, Spectra-Physics, USA) was expanded with a beam expander; then, it was slightly split along the x axis into two beams with orthogonal polarization. The two beams were focused on a quartz cell by an objective to form optical tweezers for a particle dispersed in dibromomethane that filled the cell. The density of dibromomethane is 2.5 g/cm³—nearly equal to that of the particle used in this study. This means that the influence of gravity on the motion
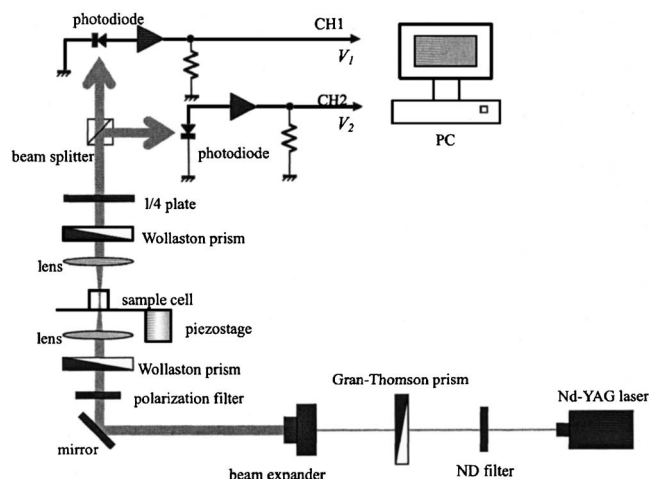

FIG. 3. Block diagram of the measurement system assembled in this study. By using a common laser beam, the optical tweezers and the interferometer are combined.

of the particle is negligible. After the particle was transmitted, the two beams were again merged into a single linearly polarized beam. When the particle moved along the x axis to generate a difference in the optical length of the split beams traveling through the particle, the merged beams became elliptically polarized. The ellipticity was evaluated as the difference in the intensity measured by two photodiodes. On the basis of the two components of the voltages, V_1 and V_2, that are obtained using the photodiodes, the position of the trapped particle is given by

$$x = \frac{a(V_1 - V_2)}{V_1 + V_2}, \qquad (13)$$

where a is an apparatus constant that is determined to be 2.1×10^{-5} m by moving a particle quantitatively. The value of k' was evaluated using borosilicate particles not tethered to PS chains, while K was measured using the PS-tethered particles prepared as described above. For the measurement of K, the cantilever to be bound to the PS chain at the thiol end was fixed to the bottom of the quartz cell positioned on a piezostage (P-753 1CD, PI, Germany) that moved the cantilever along the x axis. After the PS chain was tethered to the cantilever and the particle, the fluctuation of the particle along the x axis was monitored. All measurements were conducted at 21 ± 1 °C.

To estimate the end-to-end distance of the chain at the equilibrium point, where the Brownian motion of the particle was measured as described above, the mechanical measurement of a single PS chain was also conducted using a SPM (SPA300HV, SII, Japan). The cantilever used in this measurement had a spring constant of 0.08 N/m and a gold-coated tip. The method used to tether a PS chain was the same as that described above, except that the borosilicate glass particle was replaced by a quartz plate. Force curves were measured against the tensile length for the PS chain in cycloheptane at 19 ± 1 °C near the Θ state.[15]
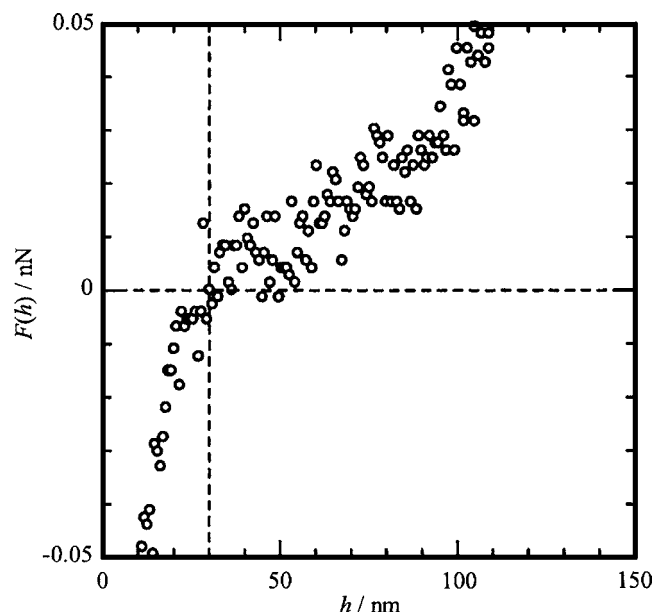
FIG. 4. Force curve of a PS chain measured in cycloheptane using the SPM. The intersection of the broken lines indicates the equilibrium point.

IV. RESULTS AND DISCUSSION

Figure 4 shows the force curve of a PS chain plotted against the end-to-end distance measured using the SPM. Here, h is the distance between the surface of the quartz plate and the cantilever, where the bending of the cantilever is corrected using the detected force and the spring constant of the cantilever. The value of $F(h)$ is positive when it acts as a repulsive force to separate the tip from the quartz plate and vice versa. The force curve shows that on separating the tip from the plate, $F(h)$ sigmoidally increases with h. In the small h region, where $F(h)$ is negative or nearly zero, the geometrical condition of the polymer chain can be approximated to correspond to the confinement of the chain between two parallel planes, as considered in the measurement of Brownian motion. The force curve shows that $F(h)$ becomes zero at around $h=30$ nm; in other words, the elastic and steric repulsion forces of the PS chain are balanced at this point. This means that the measurement of Brownian motion described above has been conducted at around $|R|=30$ nm, where the PS chain is in the equilibrium state.

Figure 5(a) shows the time course of x for a particle not tethered to a PS chain; the laser power $I=1.0\times10^{-1}$ W. According to Eq. (10), k' is estimated to be 1.9×10^{-7} N/m. Figure 5(b) illustrates the power spectrum calculated from the data shown in Fig. 5(a). The power spectrum can be fitted by two lines, as expected from Eq. (12), and k' is determined to be 6.1×10^{-7} N/m from the intersection of the two lines, as indicated by a broken line in the figure. The two k' values obtained are somewhat different, but it is noteworthy that the elastic coefficient of the optical tweezers is significantly smaller than that of the abovementioned FJC. This very small elastic coefficient ensures that the cantilever can be considered as an immovable plate in the measurement of the PS chain tethered to the cantilever and particle. Figure 6 shows the (a) time course of x and (b) power spectrum of the Brownian motion measured at $I=3.0\times10^{-2}$ W for a particle
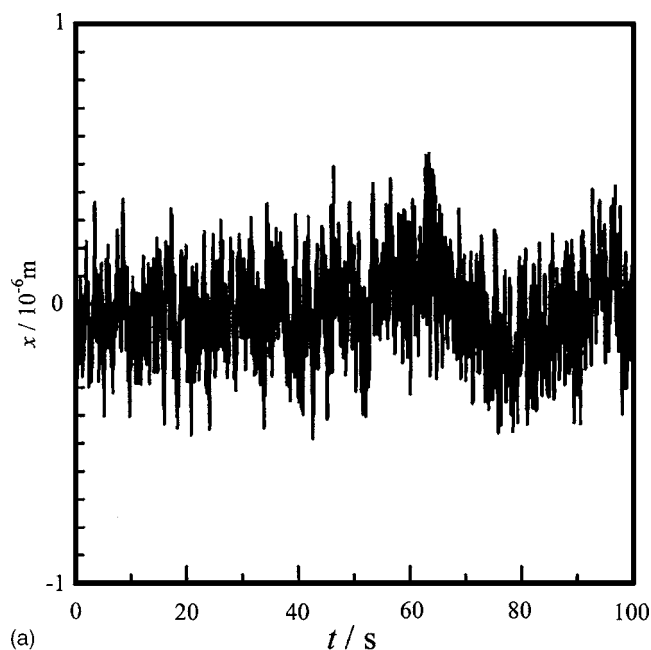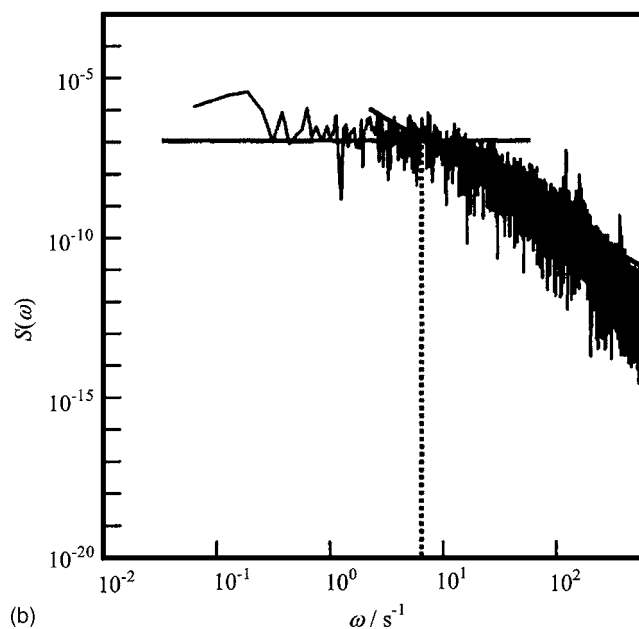
FIG. 5. (a) Time course of x measured at $I=1.0\times10^{-1}$ W for a particle not tethered to a PS chain. (b) Power spectrum calculated from the data shown in Fig. 5(a). Two solid lines are drawn for the fitting of the data by Eq. (12), and the intersection is indicated by a broken line.

not tethered to a PS chain. The k' values estimated using Eqs. (10) and (12) are 7.8×10^{-8} and 2.1×10^{-7} N/m, respectively. The values of k' obtained using Eq. (12) are plotted against I in Fig. 7. It is seen that k' is proportional to I within the range of $0\leq I\leq1.0\times10^{-1}$ W, as expected from Eq. (2). Here, we confirm the validity of the use of Eq. (11) in this study. It is known that Stokes' approximation for drag is valid for a particle traveling in a medium under the condition of a low Reynolds number (approximately <1). On the basis of the velocity of translational motion at 21 °C, as shown in Fig. 5(a), the Reynolds number for this particle is estimated to be of the order of 10^{-4}, which means that Eq. (11) holds.
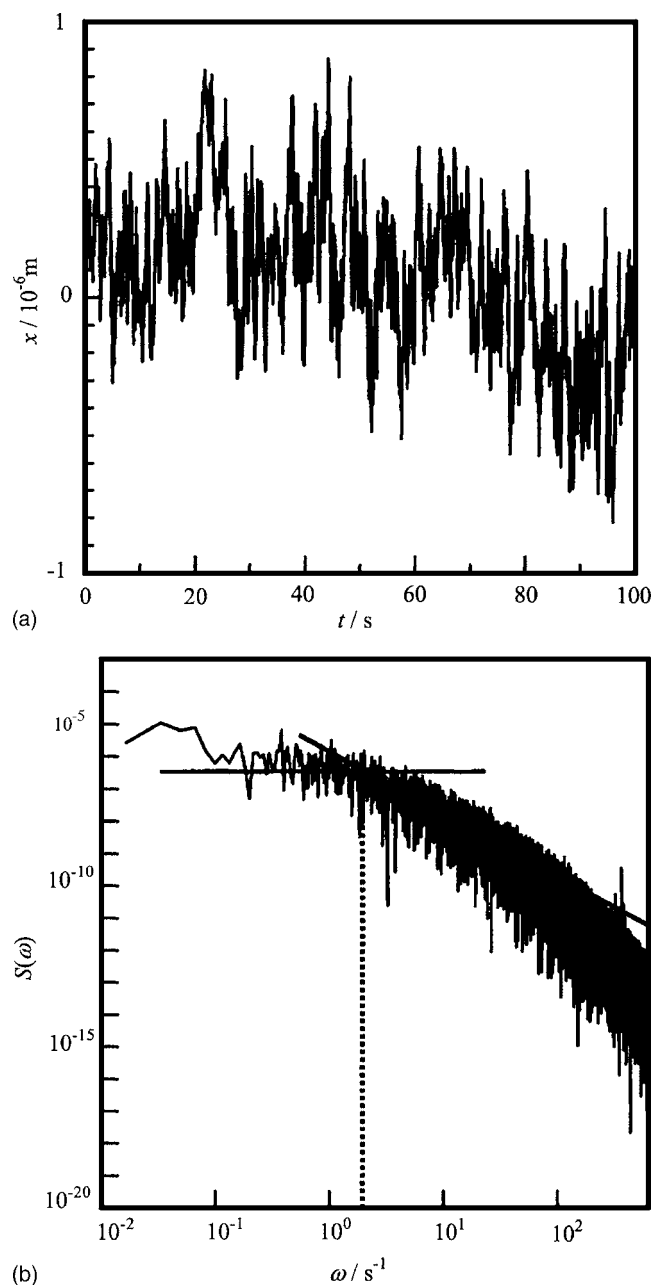
(a)

(b)

FIG. 6. (a) Time course of x and (b) power spectrum measured at $I=3.0 \times 10^{-2}$ W for a particle not tethered to a PS chain. The lines drawn in this figure have the same meaning as those drawn in Fig. 5.

Figure 8(a) shows the time course of x at $I=1.5 \times 10^{-3}$ W, i.e., $k'=9.3 \times 10^{-9}$ N/m, for a particle tethered to the PS chain. The value of K is estimated to be 6.4×10^{-6} N/m according to Eq. (10). The value of K can also be determined as 1.1×10^{-5} N/m based on the power spectrum shown in Fig. 8(b), although the power spectrum shows a weak ω dependence, even in the low ω region. Since $K(=k+k') \gg k'$, K is approximately equal to k; thus, we obtain the elastic coefficient of a PS chain. The average of three K values obtained in this study from the time course of the displacement is 4.0×10^{-6} N/m with the standard deviation $\sigma=1.7 \times 10^{-6}$ N/m. The average K based on the power spectrum is 5.7×10^{-6} N/m with $\sigma=3.8 \times 10^{-6}$ N/m.

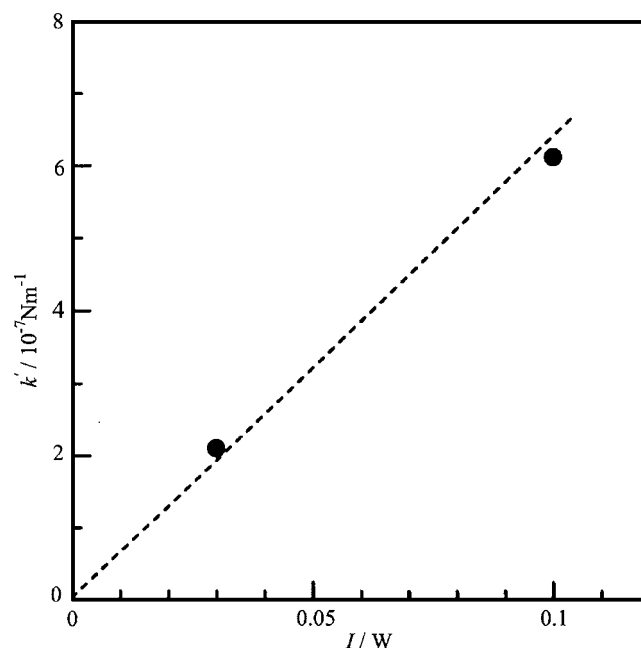In fact, the particle also fluctuates along the y and z axes

FIG. 7. Plot of k' against I. The value of k' is proportional to I within the range $0 \le I \le 1.0 \times 10^{-1}$ W, as expected from Eq. (2).

on account of the Brownian motion of the PS chain; such motion may affect V_1 and V_2, which are monitored using the system described above. When considering these facts, the k value obtained in this study is not rigorously equal to the elastic coefficient of a single PS chain. However, we emphasize that the measurement system used in this study primarily detects the fluctuation of the particle along the x axis. Therefore, the k value obtained in this study is acceptable as a reasonable value of the elastic coefficient of a single polymer chain.

To further check the reasonableness of the elastic coefficient evaluated in this study, the elastic coefficient of the PS chain is also obtained by a calculation in which the PS chain is approximated to a FJC. By using the characteristic ratio $C_\infty=10.7$ that is reported for PS in the Θ state in cyclopentane at 20.5 °C (Ref. 15) and by assuming a constant contour length, the PS chain measured in this study in the equilibrium state is found to be equivalent to a FJC with $b=1.6$ nm and $n=266$. Here, we assume that the chain dimension of PS in dibromomethane is approximately the same as that in cyclopentane and that the influence of confinement between the cantilever and the particle on the chain dimension is negligible. Equation (1) gives $k=1.7 \times 10^{-5}$ N/m for the FJC, suggesting that the elastic coefficient evaluated in this study for a PS chain is a reasonable value, although the k value of the FJC is somewhat larger than the experimentally obtained elastic coefficient. The difference in k may be attributed to the error arising from the assumptions considered above, namely, the value of C_∞ reported for PS in the Θ state in spite of the fact that dichloromethane is a good solvent for PS and the negligible influence of confinement. The dimension of a polymer chain in a good solvent is larger than that in the Θ state.[16] The existence of impenetrable planes that confine a polymer chain enlarges the dimension of the chain due to the decrease in the conformational entropy.[17–21]
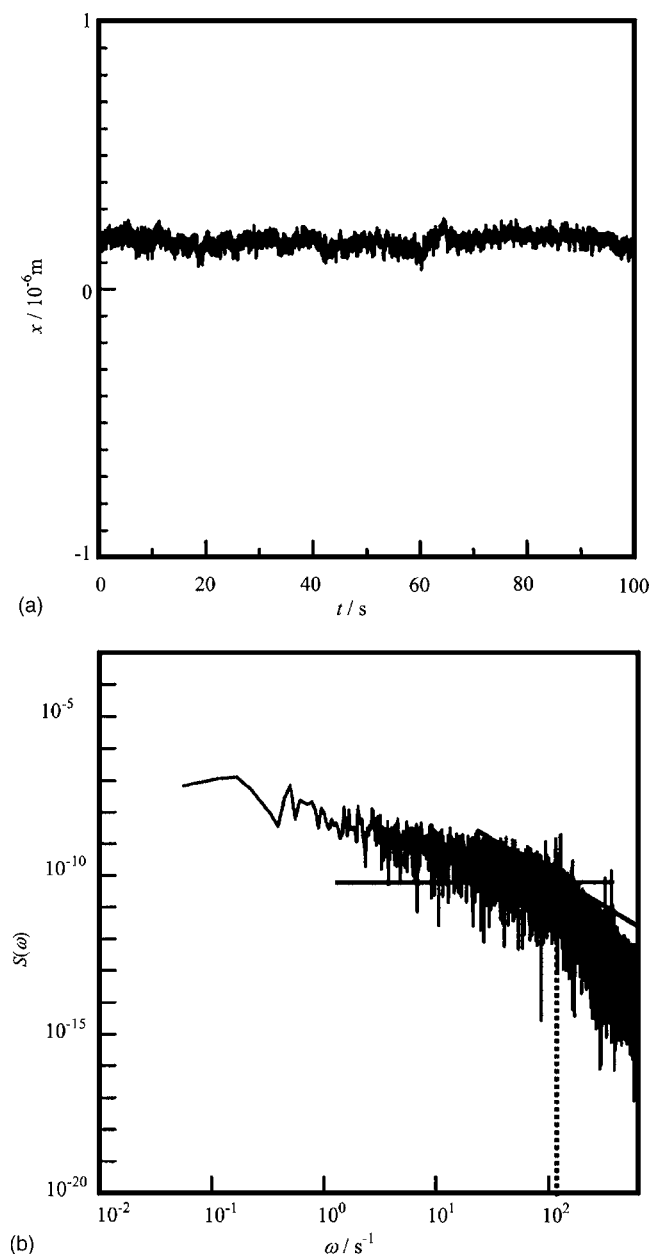
FIG. 8. (a) Time course of x and (b) power spectrum measured at $I=1.5 \times 10^{-3}$ W for a particle tethered to a PS chain. The lines drawn in this figure have the same meaning as those drawn in Fig. 5.

From these facts, it is considered that the PS chain measured in this study has a larger chain dimension than that of the FJC model. It is impossible at present to quantitatively estimate the increase in the chain dimension by these effects, but the calculated k value should be less than the value given above $(k=1.7\times10^{-5}$ N/m) so as to approach the k value experimentally evaluated in this study.

Finally, we comment on the applicability of our system to other polymers of different chain stiffness. According to Eq. (10), the upper limit of measurable K is determined by the resolution in Δx. Since the resolution in Δx of our interferometer system is 10^{-8} m at present, our system is appli-

cable to a polymer chain with $k(\approx K)$ smaller than about 4×0^{-5} N/m, which is somewhat stiffer than the PS chain used in this study. In the case of a polymer chain of small k, the approximation that $K\approx k$ no longer holds and k should be obtained from $K=k+k'$. The lower limit of k is therefore expected to be comparable with $k'(\approx10^{-8}$ N/m), which is probably smaller than the elastic coefficient of almost all the polymer chains. The range of k estimated above again indicates that our system is suitable for measurement of the elastic coefficient of flexible polymer chains.

V. CONCLUSIONS

A new method was developed to measure the elastic coefficient of a polymer chain. The PS chain was tethered to a borosilicate particle at one end and a cantilever at the other end. The value of k for the PS chain was measured by using optical tweezers as well as an interferometer. The optical tweezers used in this study had a very small spring constant, allowing the Brownian motion of the PS chain to be probed by trapping the PS-tethered particle. The two methods employed in this study for Brownian dynamics analysis provided reasonably similar elastic coefficients.

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