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Nanomechanical Thermal Analysis of Photosensitive Polymers

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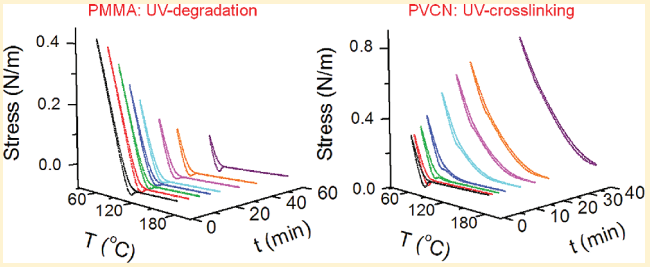
Supporting Information

ABSTRACT: A few nanograms of poly(methyl methacrylate) (PMMA) or poly(vinyl cinnamate) (PVCN) was coated onto one side of a silicon cantilever, and the photodegradation of PMMA or photo-cross-linking of PVCN was investigated as a function of UV irradiation time. After UV irradiation, the resonance frequency and deflection of the polymer-coated silicon cantilevers were measured as a function of temperature, and these properties were found to be related to changes in the modulus and surface stress of the coated polymers, respectively. A decrease in the modulus and tensile surface stress was observed for PMMA under UV exposure due to photodegradation, whereas an increase in the modulus of PVCN was observed due to photo-cross-linking. In addition, the influence of UV exposure on the glass transition of the PMMA and PVCN was investigated using deflection measurements. Whereas a single glass transition was observed for PMMA, two distinctive glass transitions were observed for PVCN due to the copresence of cross-linked and un-cross-linked of PVCN. Variations in the polymer structures were also investigated as a function of UV irradiation time using Fourier transform infrared spectroscopy and compared with the results obtained using the cantilever measurements.



1. INTRODUCTION

Photoinduced changes in the thermomechanical properties of polymers are important not only in fundamental science but also in industrial applications, including photoresists and adhesives.[1,2] Photoresists are light-sensitive polymers used to form a patterned coating on a substrate and have been extensively studied because they have played a key role in the modern electronic revolution. Two types of photoresists, positive or negative, are in widespread use. Positive photoresists degrade upon exposure to UV light, whereas negative photoresists cross-link under the same conditions.[3] The cross-linking and degradation processes both affect the thermomechanical properties of a photoresist and induce changes in the glass transition temperature (T_g),[4] modulus,[5] and stress in a photoresist.[6]

Several studies have investigated changes in the glass transition temperatures and moduli of photoresists using differential scanning calorimetry (DSC) or dynamic mechanical analyzers (DMA).[4,7] Residual stresses due to a photoresist coating on a silicon wafer may be measured using double laser beam reflections, interferometry, or profilometers.[8−10] However, no methods have measured changes in both the thermodynamic and mechanical properties of a photoresist over time. Furthermore, thermomechanical changes in photoresists coated onto flexible substrates have not been extensively investigated, possibly due to the absence of appropriate measurement methods. However, such measurements are important for the fabrication of flexible electronic devices, such as organic field effect transistors.[11]

Cantilever sensors consist of miniaturized bimaterial structures and are extremely sensitive to any changes in the material coated on the cantilever. These structures have mainly been used as sensors for the detection of gases and biomolecules.[12,13] Only a few studies have used cantilevers to monitor light-induced changes in the moduli of polymers. Thundat et al. used microcantilevers to investigate the degree of cross-linking in UV-cured glues,[14] and Haramina et al. used macrocantilevers to investigate the dynamics of poly(vinyl cinnamate) (PVCN) upon UV irradiation.[15] These studies focused on changes in the stiffness of the polymers during cross-linking and did not measure changes in the stress or thermodynamic properties. Igarashi et al. measured the influence of humidity on the surface stresses of an allylamine-coated cantilever under UV irradiation, but they did not investigate the thermomechanical properties of the polymer either.[16]

In this study, we coated a few nanograms of positive or negative photoresist on a silicon cantilever and measured the temperature-dependent deflections and resonance frequencies as a function of UV irradiation time. The glass transition temperature of the photoresist was determined from the temperature-dependent deflections of the cantilever. To the best of our knowledge, this study reports the first use of silicon microcantilevers for

Received: September 29, 2011
Revised: November 6, 2011
Published: November 21, 2011

investigating the thermomechanical properties of photosensitive polymers.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(methyl methacrylate) (PMMA) and PVCN were purchased from Aldrich (Saint Louis, MO) and were used without further purification. As indicated by the manufacturer, the weight-average molecular weight of PMMA and PVCN were 120 000 and 200 000 g/mol, respectively. Anhydrous toluene was purchased from Aldrich and was used without further purification to prepare 0.5 wt % PMMA and PVCN solutions. Rectangular silicon cantilevers with a triangular free end were obtained from Nanoworld (Neuchatel, Switzerland). Each cantilever was 500 μm in length, 100 μm in width, and 1 μm in thickness and had a spring constant of 0.03 N/m. One side of each cantilever was coated with PMMA or PVCN using inkjet printing methods (Cantispot, Cantion, Denmark). The polymer coatings were sufficiently thick (~1 μm) to avoid complications from thin film effects.

2.2. Microcantilever Measurements. The photoresist-coated cantilever was mounted on a thin aluminum holder, and the temperature was controlled using a resistance heater with a programmable temperature controller (Hanyoung, Inchon, Korea). The temperature was cycled between 60 and 180 °C several times to relieve any stress developed during the polymer coating process. The heating and cooling rates were maintained at 10 °C/min. The temperature-dependent changes in the resonance frequency and deflections of the cantilever were measured as a function of UV irradiation time using optical beam techniques. In brief, after UV irradiation for a certain period of time, a focused laser beam was reflected off the free end of the cantilever onto a duo-lateral position-sensitive detector (SiTek Electro Optics, Partille, Sweden). The resonance frequency of the thermally vibrating cantilever (without actuation) was calculated using a fast Fourier transform (FFT) algorithm. The absolute deflection of the cantilever was calibrated using a Wyko NT1100 profilometer (Veeco, Santa Barbara, CA).

2.3. FT-IR Measurements. The polymer samples on the microcantilevers were too small to characterize by standard FT-IR techniques. Solutions of 0.5 wt % PVCN or PMMA were spin-coated onto a silicon wafer, and the FT-IR spectra were obtained using a Thermo Nicolet NEXUS 670 spectrometer in reflection mode as a function of UV irradiation time. The power of a UV lamp (254 nm) was measured to be 4.5 mW/cm^2 at a distance of 2.54 cm (1 in.), which is similar to the value used in conventional photolithography (~10 mW/cm^2).

3. RESULTS AND DISCUSSION

Figure 1a shows the variations in the resonance frequency of the PMMA-coated cantilever during heating and cooling thermal cycling after UV irradiation at 60 °C for various lengths of time. The resonance frequency of the cantilever (f) depended on its dimensions (w: width; t: thickness; l: length), effective mass (m), and effective Young's modulus (E), that is, $f = (1/2\pi)(Ewt^3/4ml^3)^{1/2}$, where w, t, l,and m are constants, indicating that the resonance frequency was proportional to the square root of E. It is important to note that the frequency change of a polymer-coated cantilever is affected by the position of the coating.[17] If a sample is coated on the free end of a cantilever, the frequency change is mostly governed by the mass change of the sample, whereas the frequency change is governed by the modulus change (or volume change) of the sample if it is coated on the clamped end of the cantilever. Because we coated PMMA on the clamped end of the cantilever, the frequency change can be related to the modulus change of PMMA. Given that changes in the resonance frequency of an uncoated silicon cantilever were negligible over this temperature

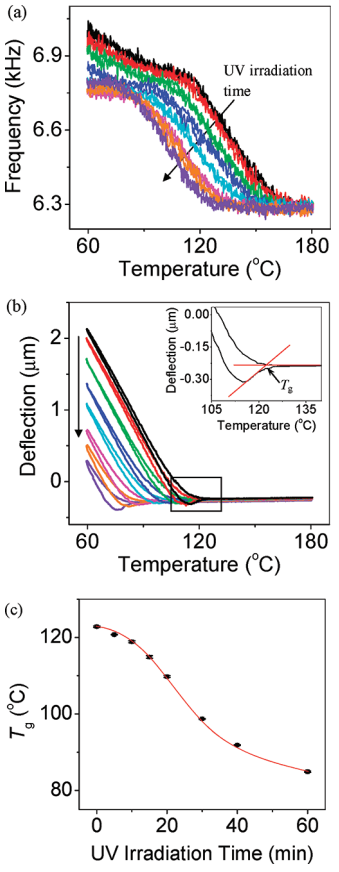


Figure 1. Temperature-dependent variations in (a) the resonance frequency and (b) the deflection of the PMMA-coated cantilever after various periods of UV irradiation time: 0 min (black), 5 min (red), 10 min (light green), 15 min (blue), 20 min (sky blue), 30 min (magenta), and 40 min (orange), and 60 min (violet). The inset of (b) shows a magnified image of the boxed area. The T_g was determined from the intersection of two tangents to the curves. (c) Variations in the T_g of PMMA as a function of UV irradiation time. The curve was made to guide the eyes.

range, the frequency changes could be attributed to changes in the Young's modulus of the coated PMMA.[18]

Viscoelastic responses typical of glass polymers were observed for the unirradiated PMMA-coated cantilever: a gentle decrease in the glass region (<120 °C), a steep decrease in the glass transition region (<160 °C), and negligible changes in the rubbery plateau region (>160 °C). The negligible changes in the rubbery plateau region were attributed to the limited sensitivity of the cantilever sensors above the T_g of PMMA.[18] UV irradiation on the PMMA-coated cantilever induced a shift in the glass transition region toward lower temperatures, and the resonance frequency in the glass region decreased, indicating that the molecular weight and modulus of PMMA decreased due to photodegradation.[19,20]

Note that it was not straightforward to determine T_g from the dynamic resonance frequency measurements.[21] In addition, T_g obtained using the resonance frequency measurements did not agree with the value of T_g typical of the bulk polymer because T_g depended on the rate of applied stress.[22] The typical applied frequency in a DMA experiment was 1 Hz, whereas the resonance frequency of the cantilever in this study was 6.9 kHz. The time—temperature superposition principle indicates that the rate of applied stress (i.e., time) is equivalent to temperature because

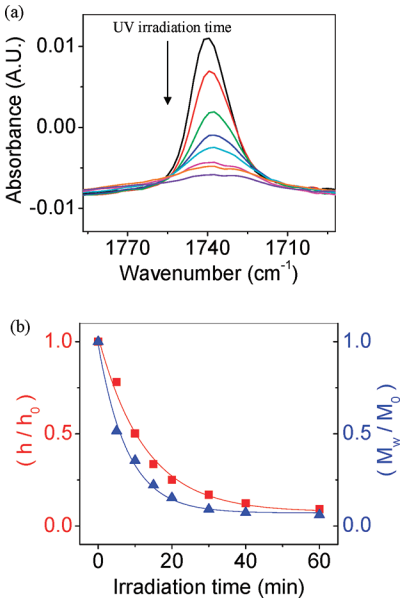


Figure 2. (a) FT-IR absorption spectra of PMMA as a function of UV irradiation time: 0 min (black), 5 min (red), 10 min (light green), 15 min (blue), 20 min (sky blue), 30 min (magenta), 40 min (orange), and 60 min (violet). (b) Variations in the intensity of FTIR absorption peak of PMMA (red square) and calculated molecular weight of PMMA (blue triangle) as a function of UV irradiation time.

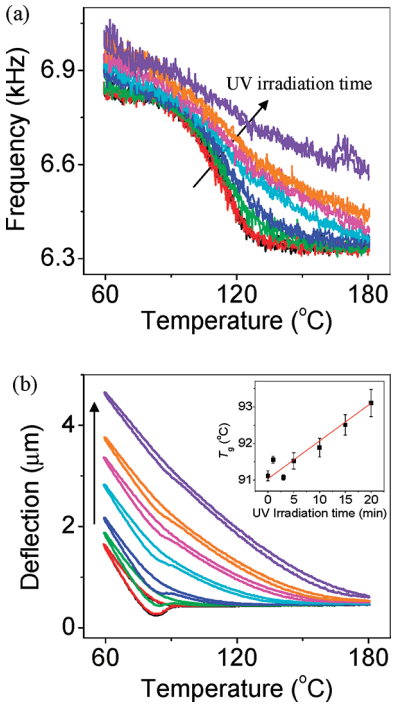


Figure 3. Temperature-dependent variations in (a) the resonance frequency and (b) the deflection of the PVCN-coated cantilever after various periods of UV irradiation time: 0 min (black), 1 min (red), 3 min (light green), 5 min (blue), 10 min (sky blue), 15 min (magenta), 20 min (orange), and 40 min (violet). The inset of (b) shows variations in the T_g of PVCN as a function of UV irradiation time.

molecular motion is faster at higher temperature. As a result, the T_g determined from the resonance frequency measurements produced a higher T_g than the value measured using DMA techniques.

In contrast, T_g was accurately determined using static cantilever deflection measurements. Figure 1b shows the temperature-dependent changes in the deflection of the PMMA-coated cantilever as a function of UV irradiation time, which was measured at the same time as the resonance frequency. The cantilever was initially bent toward the PMMA side at 60 °C due to the tensile stress that developed during PMMA coating.[23] Note that the cantilever bending implies that a spring force is applied to the PMMA coating by the cantilever. As the cantilever was heated, the PMMA-coated cantilever bent toward the silicon side at temperatures up to 110 °C due to differences in the thermal expansion coefficients of the PMMA and silicon cantilever. A decrease in the deflection of the cantilever was attributed to volume expansion of PMMA because volume changes in the silicon cantilever and modulus changes in the PMMA at this temperature range were not significant. Once the cantilever reached the lowest degree of bending, i.e., a maximum compressive stress, σ_{max}, it began to bend toward the PMMA side at temperatures up to 120 °C due to the substantial decrease in the modulus of PMMA.

Further heating did not induce notable changes in the deflection because the PMMA was too soft above 120 °C. The T_g was determined to be 120 °C from the intersection of the tangents to the curves corresponding to the glass transition regime and rubbery plateau regime. This value was close to that obtained from DSC measurements.[24] Once the temperature reached 180 °C, the cantilever was cooled to 60 °C. A substantial hysteresis was observed in the deflection during heating and cooling due to physical aging effects, whereas no hysteresis was observed in the resonance frequency.[25]

As with the resonance frequency changes, the temperature-dependent changes in the cantilever bending were affected by the UV irradiation time. The tensile stress of the cantilever at 60 °C decreased with the UV irradiation time, indicating that the modulus of PMMA decreased due to photodegradation. Figure 1c shows variations in T_g as a function of UV irradiation time. The decrease in T_g with UV irradiation time indicates that the molecular weight of PMMA decrease due to photodegradation.

Figure 2a presents the FT-IR absorption spectra of PMMA as a function of UV irradiation time. Main-chain and side-chain scission events occurred in PMMA under UV irradiation.[19] The peak in Figure 2a corresponds to an ester group of PMMA, and the peak intensity (h) can be used to estimate the degree of the PMMA degradation.[26] The peak intensity was normalized with the maximum peak intensity (h_0) and plotted in Figure 2b. The peak intensity decreased with UV irradiation time, indicating that the molecular weight of PMMA decreased.

Changes in the molecular weight of PMMA (M_w) with UV irradiation time may be estimated using the Fox−Flory equation:[27]

$$T_g = T_{g,\infty} - \frac{K}{M_w} \quad (1)$$

where K and $T_{g,\infty}$ are a polymer-specific constant (2902 for PMMA)[27] and the glass transition temperature of PMMA with an infinitely high molecular weight, respectively. After 1 h UV irradiation, the average molecular weight of PMMA decreased to 7200 g/mol, which corresponded to 6% of the initial molecular weight of PMMA (120 000 g/mol). Figure 2b shows that variations in the normalized peak agree with variations in the molecular weight of PMMA as a function of UV irradiation time.

Figure 3a shows the temperature-dependent variations in the resonance frequency of the PVCN-coated cantilever as a function

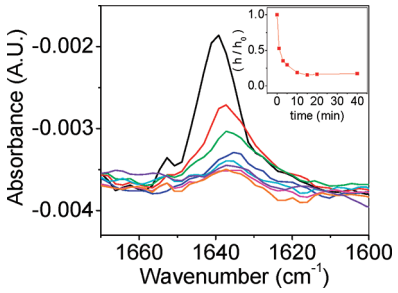


Figure 4. FT-IR absorption spectra of PVCN as a function of UV irradiation time: 0 min (black), 1 min (red), 3 min (light green), 5 min (blue), 10 min (sky blue), 15 min (magenta), 20 min (orange), and 40 min (violet). Inset shows variations in the intensity of the normalized FTIR absorption peak of PVCN as a function of UV irradiation time.

of UV irradiation time. In contrast with the trend observed for the PMMA-coated cantilever, the resonance frequency of the PVCN-coated cantilever increased with UV exposure time due to an increase in the modulus of PVCN upon photo-cross-linking. In addition, the glass transition region disappeared as photo-cross-linking progressed, as typically observed in cross-linked polymers.[22]

The temperature-dependent changes in the deflection of the PVCN-coated cantilever were measured as a function of UV irradiation time and are plotted in Figure 3b. Because photo-cross-linking of PVCN induced the formation of chemical bonds, its stiffness increased. Consequently, the tensile stress of the cantilever increased with UV irradiation time. Note that σ_{max} decreased with UV irradiation time, indicating that cross-linking restricted the physical aging of the PVCN chains.[28] The inset of Figure 3b shows variations in T_g as a function of UV irradiation time. Compared to the substantial decrease in T_g of PMMA by photodegradation, T_g of PVCN was not significantly affected by photo-cross-linking, which does not agree with the FT-IR experiments.

Figure 4 shows the FT-IR absorption spectra of PVCN (C═C stretch) as a function of UV irradiation time. Upon exposure to UV light, the decrease in the intensity of C═C peak was observed with increasing UV irradiation time due to C═C bond scission, indicating that the peak intensity is related to the degree of photo-cross-linking of PVCN.[15,29] The inset of Figure 4 shows that the intensity of the peak decreased by 70% after 40 min of UV irradiation. This substantial change in the peak intensity indicates that the degree of photo-cross-linking of PVCN must be high, and the resulting T_g should be higher than the values obtained from the deflection measurements.

In order to investigate the origin of the discrepancy between the FT-IR and deflection measurements, variations in the deflections of the PVCN-coated cantilever were measured after annealing. Annealing at temperature below T_g induces the increase of the σ_{max} peak due to the physical aging of polymers, whereas the annealing at temperature higher than T_g does not induce any change in the deflection profile.[25] Figure 5a shows the deflection profiles of the fresh PVCN-coated cantilever during the heating and cooling cycles. Annealing of the cantilever at 80 °C for 2 h induced the increase in σ_{max} due to the physical aging of PVCN. Similar results were observed for the partially cross-linked PVCN-coated cantilever (5 min of UV irradiation) when annealed at 80 °C for 2 h as shown in Figure 5b.

However, the annealing of the partially cross-linked PVCN-coated cantilever at 120 °C which is higher than the glass transition temperature of un-cross-linked PVCN produced a new σ_{max} peak at ~140 °C (Figure 5c), indicating that there exist some PVCN chains experiencing glass transition. It is interesting to note that this deflection profile having two distinctive σ_{max} peaks is typically observed from a polymer blend-coated cantilever,[25] indicating that the partially cross-linked PVCN behaves as a polymer blend of un-cross-linked and cross-linked PVCN chains. As a result, the negligible change in T_g observed in Figure 3b can be attributed to the un-cross-linked part of PVCN. The T_g of the cross-linked part of PVCN cannot be determined because the corresponding σ_{max} peak appears at a different temperature as the annealing temperature varies, indicating the presence of PVCN chains with a wide molecular weight distribution. Note that the intensity of the σ_{max} corresponding to the cross-linked PVCN is much smaller than that corresponding to the un-cross-linked PVCN because the cross-linking restricts the physical aging of polymer chains.[28]

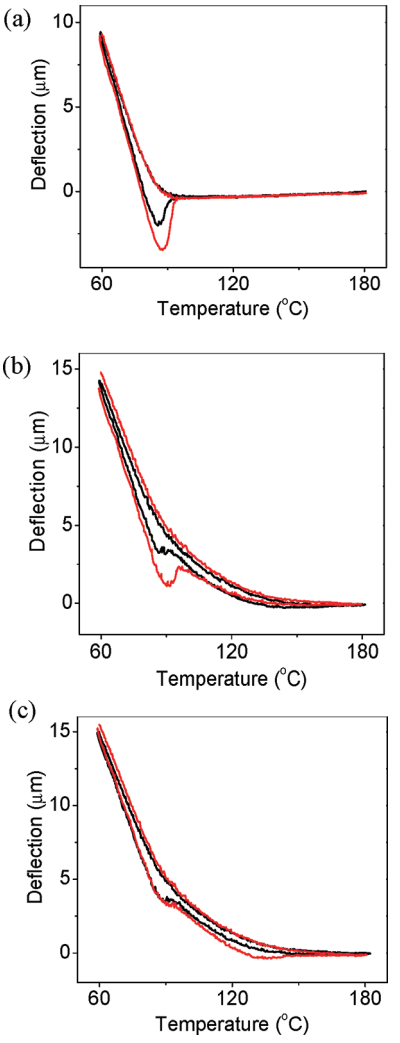


Figure 5. Temperature dependence of the deflection profiles of a fresh PVCN-coated microcantilever annealed at 80 °C (a), partially cross-linked PVCN-coated microcantilevers annealed at 80 °C (b) and 120 °C (c) for 0 h (black) and 2 h (red).

Figure 6 compares variations in the surface stress of the PMMA- and PVCN-coated cantilevers as a function of UV irradiation time. Assuming that the polymers are uniformly coated

dx.doi.org/10.1021/ma202194e |*Macromolecules* 2011, 44, 9661–9665

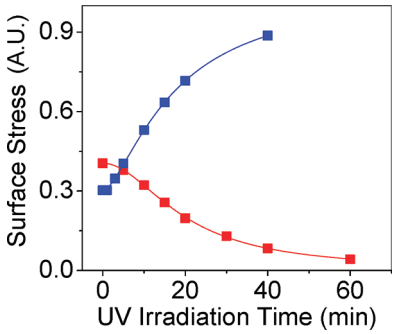


Figure 6. Variations in the surface stress of the PMMA-coated cantilever (red) and PVCN-coated cantilever (blue) as a function of UV irradiation time.

on the cantilever, surface stress (σ) is related to deflections (z) in a cantilever via Stoney's equation, that is

$$\sigma = \frac{E_{\text{eff}} t^2}{3L^2(1-\nu)} z \tag{2}$$

where E_{eff}, t, L, and ν are the effective modulus, thickness, length, and Poisson's ratio of the polymer-coated cantilever. E_{eff} of the bilayer cantilever is obtained as[30]

$$E_{\text{eff}} = \left\{ {E_{\text{p}}}^2 \left(\frac{t_{\text{p}}}{t}\right)^4 + {E_{\text{s}}}^2 \left(\frac{t_{\text{s}}}{t}\right)^4 + 2E_{\text{p}}E_{\text{s}} \left(\frac{t_{\text{p}}}{t}\right)\left(\frac{t_{\text{s}}}{t}\right) \left[2\left(\frac{t_{\text{p}}}{t}\right)^2 + 2\left(\frac{t_{\text{s}}}{t}\right)^2 + 3\left(\frac{t_{\text{p}}}{t}\right)\left(\frac{t_{\text{s}}}{t}\right) \right] \right\} \Big/ \left[E_{\text{p}}\left(\frac{t_{\text{p}}}{t}\right) + E_{\text{s}}\left(\frac{t_{\text{s}}}{t}\right) \right] \tag{3}$$

where the subscripts "s" and "p" represent the silicon cantilever and polymer, respectively. The surface stresses after UV irradiation for various lengths of time were calculated using the deflection results at 60 °C. Although the surface stresses of the two coated cantilevers evolved in the opposite direction, the trends were quite similar. The surface stress change was not noticeable during the early stages of UV irradiation but became significant during the middle stages. Further UV irradiation resulted in saturated surface stress.

4. CONCLUSIONS

In summary, we used flexible silicon cantilevers to investigate the influence of UV irradiation on the thermomechanical properties of PMMA and PVCN samples. By measuring the temperature-dependent variations in the resonance frequency and deflection of polymer-coated cantilevers, we obtained the temperature dependence of the effective modulus and glass transition temperatures of the polymers as a function of UV irradiation time. In addition, the surface stresses during photo-cross-linking of PVCN and photodegradation of PMMA were measured. Although the results were qualitative due to difficulties associated with achieving a uniform polymer film coating on the silicon cantilevers, this method provides a promising technique for investigating the thermomechanical properties of photosensitive polymers using a few nanograms of the samples.

■ ASSOCIATED CONTENT

Supporting Information. Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This research was supported by the Future-based Technology Development Program (Nano Fields) through the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science and Technology (Grant 2011-0019126).

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