Relaxation Phenomena observed for Single Polymer Chains

Kenji Watanabe,* *Naoto Ohno, Ken Nakajima, Toshio Nishi,*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan
watanabe@polymer.titech.ac.jp

Introduction

A method, which is called as "nanofishing," enables us to stretch a single polymer chain with picking it at its two modified termini using atomic force microscope (AFM) [1]. A stress-strain curve obtained for a single polystyrene chain with thiol termini in a Θ (cyclohexane) solvent showed a good agreement with a so-called worm-like chain model, and thus gave microscopic information about entropic elasticity. Solvent effects on the statistical properties of single polymer chains were also investigated [2, 3].

In this study, we extended the capability of nanofishing to the phenomena far from equilibrium state by giving much faster pulling speeds. We also measured the dynamic sinusoidal response, as in macroscopic rheological studies, repeatedly at several extension lengths before full stretching or rupturing, by a "nanorheology AFM" constructed in our laboratory [4]. It enabled us to design any required movements on a z-piezoelectric scanner, especially sinusoidal movements. The rheological properties of a single polymer chain were discussed from the frequency-dependent measurement.

Experimental

A SH-terminated PS was used as a sample. It was based on living-polymerrized COOH-terminated PS. The degree of polymerization was about 900 and thus its contour length was 220 nm. The thiol groups were substituted for the COOH ends using 1,10-decane dithiol by means of thiolester bonding. Au (111) surface on mica substrates were prepared as described [4]. The polymer was dissolved in a good solvent, N,N-dimethylformamide (DMF).

All AFM experiments were performed by NanoScopeIV and PicoForce (Veeco Metrology Group, USA). In order to pick up the SH-modefied terminal, a gold coated cantilever, OMCL-BLRC150VB-C1 (OLYMPUS Co. Ltd., Japan), was used.

In this study, we applied a repetitive staircase movement on a piezoscanner instead of the triangular movement that was commonly used during a single polymer chain stretching as shown in Figure 1.

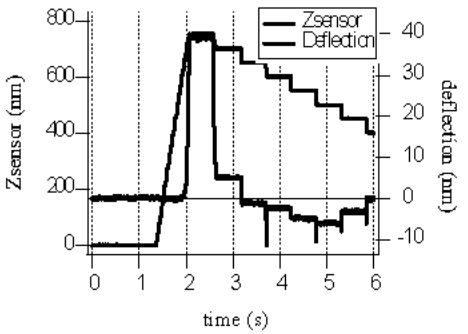

Figure 1. The time-course changes of the input z-scanner movement signal and the output cantilever deflection signal.

Results and discussion

Figure 2 (a), (b) are force-extension curves of single polystyrenes at the pulling speed of (a) 3 μm/s and (b) 10 μm/s. The result similar to the case of the quasi-static stretching was obtained in Figure 2 (a). Thus, we could conclude that the case corresponded quasi-static stretching as well as usual nanofishing even it. On the other hand, in Figure 2 (b) we observed a force-extension curve different from the quasi-static stretching. It was thought that when the cantilever was pulled at the high pulling speed the tension increased momentarily because of a rapid conformational change. We could also observe the successive relaxation process as shown in Figure 3. Interestingly, the relaxation was not gradual but stepwise, which might be related to the local unwinding of internal entanglement of a single polymer chain.

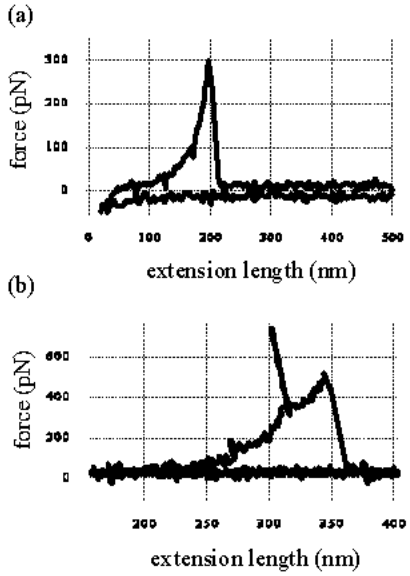

Figure 2. Force-extension curves of single polystyrenes at the pulling speed of (a) 3 μm/s and (b) 10μm/s.

Conclusions

We could realize an extended capability of nanofishing by giving staircase stretching, which was similar to macroscopic stress relaxation experiment. In addition, and the behavior against a sinusoidal oscillation during a stretching process will be reported at the site.

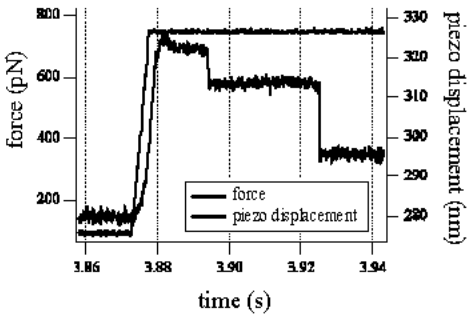

Figure 3. Relaxation process of observed after momentary stress increase in Figure. 2 (b).

References

[1] Binnig, G.; Quate, C.F.; Gerber, Ch.; Weibel, E. *Phys. Rev. Lett.* **1986**, 56, 930.
[2] Nakajima, K.; Watabe, H.; Nishi, T. *polymer* **2006**, 47, 2505.
[3] Nakajima, K.; Watabe, H.; Nishi, T. *Kautsch. Gummi Kunstst.* **2006**, 59, 256.
[4] Sakai, Y.; Ikehara, T.; Nishi, T.; Nakajima, K.; Hara, M. *Appl. Phys. Lett.* **2002**, 81, 724.