Relaxation Phenomena observed for Single Polymer Chains

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

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan.

watanabe@polymer.titech.ac.jp

Introduction

A method, which is called “nanofishing,” enables us to stretch a single polymer chain with pulling it at its two modified terminals using atomic force microscope (AFM) [1]. A stress-strain curve obtained for a single polystyrene chain with thiol terminals in a 2-(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 stress-relaxation response, as in macroscopic rheological studies, repeatedly at several extension lengths before full stretching or rupturing, by a “nano-rheology AFM” constructed in our laboratory [4]. It enabled us to design any required movements on a stop-eddy elevator, especially uniaxial movements. The rheological properties of single polymer chains were discussed from the frequency dependent measurement.

Experimental

A SH-terminated PS was used as a sample. It was based on a living-terminated COOH-terminated PE. The degree of polymerization was about 500 and thus its contour length was 220 nm. The thiol groups were substituted for the COOH ends using 1,1-dioctadecyl disiloxane by means of thiol-ene bonding. Au (111) surface on silicon substrates were prepared as described [4]. The polymer was dissolved in a good solvent, N,N-dimethylformamide (DMF).

All AFM experiments were performed by NanoScope IV and PicoForce (Veeco Metrology Group, USA). In order to pick up the SH-modified terminal, a gold coated cantilever, OMCOS-89MB (Hi-Micro, Japan), was used.

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

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 is similar to the case of the quasi-static stretching was obtained in Figure 2 (a). Thus, we could conclude 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 winding of internal entanglement of a single polymer chain.

Conclusions

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

References


Figure 1. The time course change of the input strain and the output cantilever deflection signal.

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

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