

Temperature-dependent Conformational changes of Single Polymer Chains

*Naoto Ohno**, Kenji Watanabe, 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
nohno@polymer.titech.ac.jp

Introduction

Atomic force microscope (AFM) enables us to stretch a single polymer chain by picking it at its two modified termini. Using this method called “nanofishing,” we have studied statistical properties of single polymer chains. A force-extension curve obtained for a polystyrene with thiol termini in a cyclohexane near the Θ temperature had showed a good agreement with a worm-like chain (WLC) model, and thus gave microscopic information about entropic elasticity [1, 2].

In this report, with a newly installed heater/cooler unit, the experiments were performed at wide-range temperatures, resulting in wide-range solvent qualities from poor to good solvent condition. Temperature dependence of statistical properties of polystyrene was investigated. Solvent effect was also observed.

Experimental

A SH-terminated PS was used as a sample. It was based on a living-polymerized COOH-terminated PS with $M_n = 93,800$ and $M_w = 100,400$. The polydispersity was $M_w / M_n = 1.07$. The degree of polymerization was about 900 and thus its contour length was about 220 nm. The thiol groups were substituted for the COOH ends using 1,10-decane dithiol by means of thioester bonding with anticipating the preferential interaction between thiol and gold. The polymer was dissolved in a cyclohexane, and the solution was cast on a Au(111) substrate. After 10 minutes of incubation, the surface was rinsed with a pure solvent.

All experiments were performed by using NanoScopeIV and MultiMode Heater/ Cooler (Veeco Metrology Group, USA). In order to pick up the SH-modified terminal, a gold-coated cantilever, OMCL-RC800PB-1 (OLYMPUS Co. Ltd., Japan), was used. The value of their spring constants were 0.02-0.05 N/m, which were experimentally measured by thermal fluctuation method [3]. Distilled water and cyclohexane were used as a poor solvent and a Θ solvent, respectively.

Results and discussion

Temperature dependence. Figure 1 shows the temperature dependence of the persistence length. At each temperature, about 10 of fishing results were averaged. The value of persistence length rose remarkably at 35°C (Θ temperature) while it was almost constant and independent of temperature at lower temperatures. This indicated that the conformational change of polymer chain between poor and good regions was probed at a single molecular level.

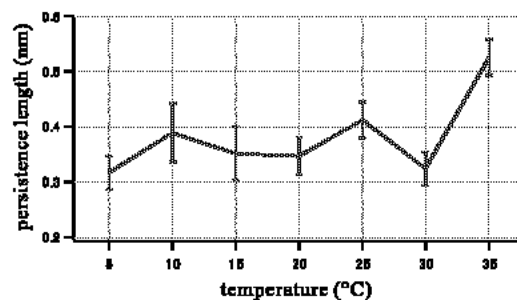


Figure 1. The temperature dependence of persistence length.

Nanofishing in poor condition. M. Wittkop and coworkers examined the deformation behavior of a single polymer chain below the Θ temperature using Monte Carlo simulation [4]. They reported that the deformation was represented by coil-strand coexistence and the attractive force was constant and independent of the extension. As

shown in Figure 2 (b), we could reproduce a very similar force-extension curve for a single polystyrene chain, which was sometimes observed in cyclohexane below the Θ temperature (35°C). Because of large non-specific adsorption between a substrate and a probe, initial behavior on extension was hidden. Contrary to the case of nanofishing at Θ temperature shown in figure 2(a), the force was kept constant during the extension length from about 50 nm to 150 nm. Such constant force was also observed in water. This could be related to the extraction of monomers one by one from collapsed globule into stretched strand. After that, the system became unstable, resulting in a force-extension relationship similar to the case of Θ solvent. A similar experimental evidence had already reported for physisorbed poly(N-isopropylacrylamide) [5], however, our result would be the first result of this instability observed for a single isolated polymer chain.

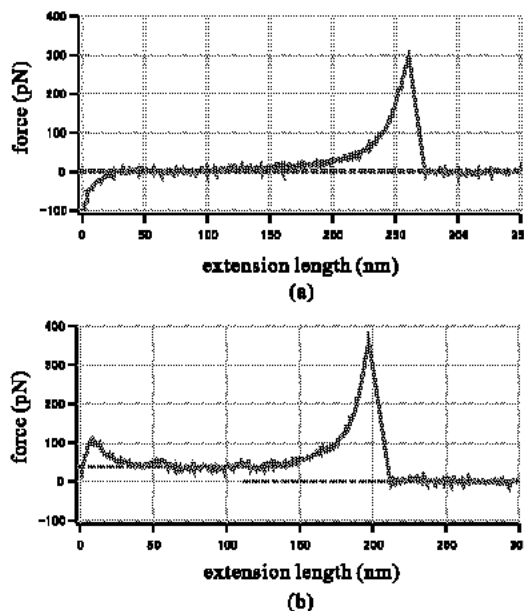


Figure 2. Force-extension curves obtained for single polystyrene chain in cyclohexane (a) at 35°C and (b) at 5°C. The coil-strand coexistence was revealed in (b).

Conclusions

“Nanofishing” realized by AFM gave a force-extension curve for a single polystyrene chain with thiol termini in a Θ solvent (cyclohexane). This showed a good agreement with a WLC model, and thus gave microscopic information about entropic elasticity. The temperature dependence of persistence length in cyclohexane was examined at a single polymer basis. The coil-strand transformation realized in a poor solvent region was also evident.

References

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