Polymer 52 (2011) 5644–5647

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Mechanical behavior of a single polymer chain in a non-solvent

Jun-ichi Horinaka*, Tomohiro Takaki, Toshikazu Takigawa

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan

ARTICLE INFO

Article history:
Received 13 April 2011
Accepted 26 September 2011
Available online 1 October 2011

Keywords:
Single polymer chain
Non-solvent
Force relaxation

ABSTRACT

Mechanical properties of a single polystyrene chain in mixtures of dioxane and methanol were measured with AFM. The effect of the solubility of the surrounding liquid on mechanical behavior of a polymer chain was examined. In good and Θ solvents, the force-extension curves exhibit a freely jointed chain (FJC)-like trend with good reproducibility. In a non-solvent, the profile of force-extension curve was dependent on the extension speed: an FJC-like nature emerged at the lower speed of 200 nm/s while saw-toothed curves were obtained at the higher speed of 2000 nm/s. The shape of saw-toothed curves varied from measurement to measurement. A force relaxation was also observed in the non-solvent under a fixed extension distance after 2000 nm/s extension. The mechanical behavior in non-solvents suggests that inhomogeneous deformation of a PS chain occurs due to reduction of the chain mobility.

1. Introduction

Conformation of polymer chains in a liquid is strongly affected by how strong the interaction between polymers and solvent molecules is, and the degree of interaction is reflected in the solubility or miscibility. For example, the conformation changes from a random-coil to a globule; if the liquid changes from a good solvent to a "non-solvent" [1,2]. This means that mechanical properties become different if the solubility of the surrounding liquid is different. However, the effect of the solubility on mechanical behavior of a polymer chain is not fully understood, since the studies on the mechanical properties in a non-solvent are quite limited [3,4]. An atomic force microscope (AFM) is a powerful tool to investigate mechanical properties of a single chain. Many research groups have reported the force-extension curves, the force (F) plotted against the extension distance (d), for a single chain in various solvents with AFM [3–10]. In a non-solvent, however, there are few studies on the force-extension curves [3,4]. The force relaxation process, the time (t) dependence of F after a constant distance (d) elongation, may bring useful information on mechanical properties of a polymer chain, but no data exist in non-solvent.

In this study, mechanical properties of a single polystyrene (PS) chain were examined with AFM in liquids. By using mixtures of a good solvent and a non-solvent, the force-extension curves as well as the force relaxation curves at various compositions were compared.

2. Experimental

Samples were prepared as follows. A cleaned quartz substrate was immersed in an aqueous solution of a silane coupling agent 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (Shin-Etsu Chem., Japan) to activate the surface with epoxy groups. After drying in an oven at 110 °C, the substrate was put in a chloroform solution of α-amino-ω-thiol-terminated PS (Polymer Source, USA). In this process, the PS chain was bonded with the epoxy group. The weight and number average molecular weights of the polymer were 3.4×10^5 and 3.1×10^5, respectively. The substrate was washed with chloroform and toluene repeatedly to remove unreacted PS chains. Mixtures of dioxane (Wako, Japan) and methanol (Wako, Japan) were prepared at various compositions. The volume fractions of dioxane (φ) employed are $\varphi = 1$, 0.714, 0.35, and 0. Here, dioxane is a good solvent for PS, but methanol is a non-solvent for PS. When $\varphi = 0.714$, the mixture is reported to be the Θ solvent for PS at 25 °C [11]. Hereafter, "non-solvent" corresponds to the liquid of $\varphi = 0.35$ as well as $\varphi = 0$. This is because the mixture of $\varphi = 0.35$ was also unable to dissolve PS at measurable concentrations, although the solvent quality may be better than pure methanol ($\varphi = 0$). A laboratory-made AFM was used for mechanical measurements of a single PS chain. The experimental setup is illustrated in Fig. 1. A gold-coated cantilever with the spring constant of 0.03 N/m (Olympus, Japan) was used. In the liquids, an AFM image of the substrate was taken to know the position of tethered PS chains. When a PS chain to be examined is determined, the substrate was firstly moved with the piezo stage so that the thiol group at the free end of the chain was bonded with gold on the cantilever [12]. Then, the PS chain was extended by moving down the piezo stage at 200

---

* Corresponding author. Tel.: +81 75 383 2455; fax: +81 75 383 2458.
E-mail address: horinaka@rheogate.polym.kyoto-u.ac.jp (J.-i. Horinaka).

0032-3861/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2011.09.042

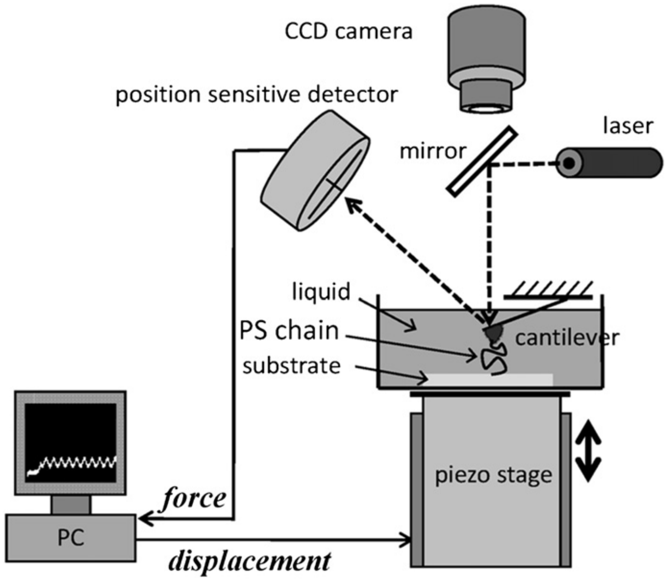

Fig. 1. Experimental setup for mechanical measurement of a PS chain with a laboratory-made AFM.

or 2000 nm/s. It was possible to extend the same PS chain by repeating the contact and extension procedure. The force from the chain was detected by the cantilever. The measurement temperature (T) was settled at 25 °C.

3. Results and discussion

Fig. 2(a) shows an AFM image of the substrate in the liquid of $\varphi = 1$ (i.e., in a good solvent). The height above the surface is represented by a gray scale: The lighter color is applied to a higher projection. To avoid extension of two or more chains, we chose a projection separating from others, as indicated by an arrow in the image. The vertical sectional view taken on line A–B of Fig. 2(a) is shown in Fig. 2(b), where the peak height is 18 nm. By using the characteristic ratio $C_\infty = 10.7$ that is reported for PS in the Θ state in cyclopentane at 20.5 °C [13], the root-mean-square radius of gyration, $\langle S \rangle^{1/2}$, of the PS chain measured in this study in the equilibrium state is calculated to be 16 nm. This suggests that the chain dimension measured by the AFM is roughly reasonable, although the chain dimension on a substrate may differ from that in a dilute solution and may depend on solvent and temperature [14].

Fig. 3 shows the force-extension curves for a PS chain in the liquid of $\varphi = 1$ measured at (a) 200 nm/s and (b) 2000 nm/s. The reproducibility for the curves was very good. The curves exhibit a freely jointed chain (FJC)-like trend: Initially F gradually increases with d but the slope becomes steep in the high d region [6]. To quantify the FJC-like trend, each curve was fitted by the modified-FJC (m-FJC) model [6]:

$$d = L\left[\coth\left(\frac{Fa}{k_{\mathrm{B}}T}\right) - \left(\frac{k_{\mathrm{B}}T}{Fa}\right)\right]\left(1 + \frac{NF}{K}\right) \qquad (1)$$

Here, L is the contour length, a is the Kuhn length, $N = L/a$, k_{b} is the Boltzmann constant, and K is the segment elasticity. As drawn in Fig. 3(a) and (b), the force-extension curves, obtained for the same PS chain, can be fitted by a model with the same parameters: $L = 570$ nm, $a = 0.71$ nm, and $K = 5.4$ N/m. This indicates that the curve profile is independent of the extension speed. The similar FJC-like force-extension curves were obtained for a PS chain in the Θ solvent ($\varphi = 0.714$ and $T = 25$ C), although the data are not shown here.

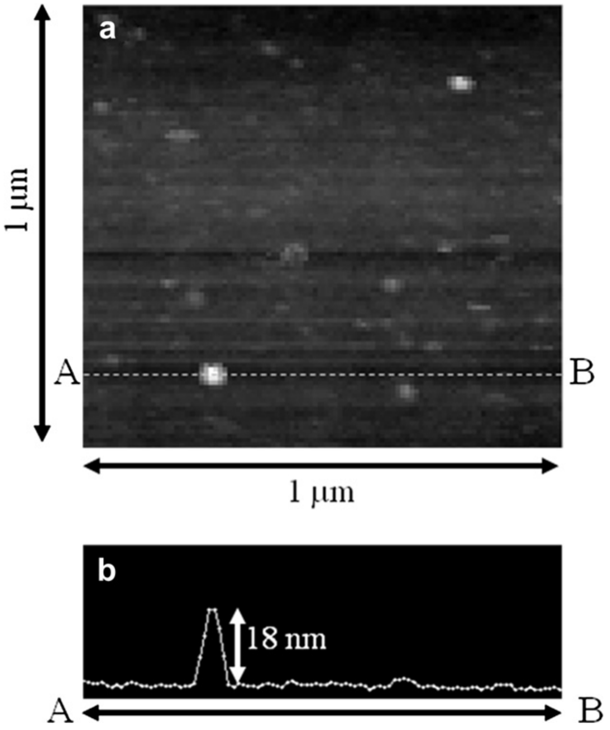

Fig. 2. (a) AFM image of a substrate with PS chains tethered on the surface. The arrow indicates a PS chain suitable for measurement. (b) Cross section along A–B indicated by a broken line in (a).

The force-extension curves for $\varphi = 0.35$ are shown in Fig. 4. The curve profiles are clearly different to each other depending on the extension speed: an FJC-like nature emerges on the curve at the low extension speed of 200 nm/s (Fig. 4(a)) while a saw-toothed curve is obtained at the high extension speed of 2000 nm/s (Fig. 4(b)). Fig. 4(a) also shows an m-FJC model with $L = 600$ nm, $a = 0.55$ nm, and $K = 6.5$ N/m. The differences in a and K from those in Fig. 3 indicate that the chain properties vary with the solvent quality. It was confirmed that a saw-toothed curve is obtained only for the latter case and the shape of curve varies from measurement to measurement. The extension speed dependence suggests that the chain mobility is rather reduced in the mixture of $\varphi = 0.35$ (in a non-solvent). An inhomogeneous extension tends to occur for the high-speed extension, but a homogeneous deformation is realized at the low speed extension. This may be generalized as follows: The deformation becomes homogeneous when the product of a characteristic time of the chain motion and the deformation rate is small enough, but the deformation is inhomogeneous when the product is large enough. It should be noted that the saw-toothed profile observed in this study is not merely due to measurement in a mixed solvent, because saw-toothed curves are also obtained in the liquid of $\varphi = 0$ (i.e., in pure methanol), as shown in Fig. 5. This suggests that the mechanical properties of a PS chain in the non-solvents $\varphi = 0$ and 0.35 are similar to each other. Here, the force-extension curves are compared with those reported by other research groups [3,4]. The force-extension curves measured in water are different in shape from those obtained in this study: a plateau force in the middle extension regime is characteristic of the curves in water whereas no plateau force is observed in this study. The meaning of these observations is not clear at the moment, but the interaction between polymers and solvent molecules might be responsible for the difference.