

## Direct Observation of Random-Coil Conformations of a Synthetic Polymer with Atomic Force Microscopy

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**Abstract:** The random coil conformations of single synthetic polymer chains were clearly imaged by atomic force microscopy for the first time.

### Introduction

The conformational characteristics of linear macromolecules is one of the most important physical factor for an understanding of polymer properties. It would be extremely stimulating for new insights into polymer behavior if we can directly observe a single chain conformation of macromolecules with microscopy. Since the invention of scanning probe microscopy, such as STM and AFM, observations in atomic or molecular scale became a routine work. However these observations have usually been limited in crystalline or liquid crystalline structures. Reliable observation of random coil conformations of flexible amorphous polymer molecules has not yet been achieved, except for the case of large biomolecules such as DNA [1].

We will report that the random coil conformations of single synthetic polymer molecules frozen on a substrate were successfully identified with microscopy for the first time [2].

### Experimental

The sample used was a poly(styrene)-*block*-poly(methylmethacrylate) diblock copolymer (PS-*b*-PMMA, Mn(PS):  $1.548 \times 10^5$ , Mn(PMMA):  $3.923 \times 10^5$ , Mw/Mn:1.08). The polymer was spread from a very dilute benzene solution ( $4 \times 10^{-6}$  g/mL;  $<C^*/1000$ ) on water surface and deposited onto mica at a surface pressure less than 0.1 mN/m. Kumaki reported that PS *monomolecular* particles were obtained from polystyrene solutions in the same conditions [3]. As shown in Figure 1, we expected to obtain PS *monoblock particles* from which single PMMA polymer chains emanated, and tried to use the PS

particles as a probe to observe and identify PMMA single chains [4].

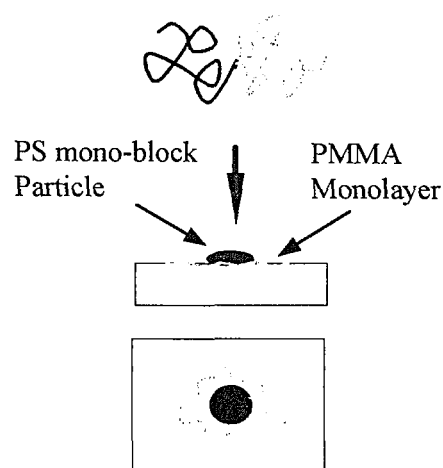


Fig. 1. Strategy to observe PMMA conformations. PS-*b*-PMMA on water surface.

(NanoScopeIII) using the tapping mode. AFM images are shown in the height mode without any image processing except flattening.

## Results and Discussion

As expected, AFM observation of the deposited samples showed a single PS block chain aggregated itself into a single PS particle (*PS monoblock particle*, diameter: 14nm, thickness: 2.5nm), from which the single PMMA block chain emanated as a monolayer (thickness: 0.2 -0.5 nm). Immediately after the deposition, the single PMMA block chain was aggregated to form a condensed monolayer around the PS particles. However after exposing the deposited film to highly humid air, the PMMA chains were dramatically elongated from the particle. Figure 2(a) shows the AFM image of a structure composed of three polymer molecules.

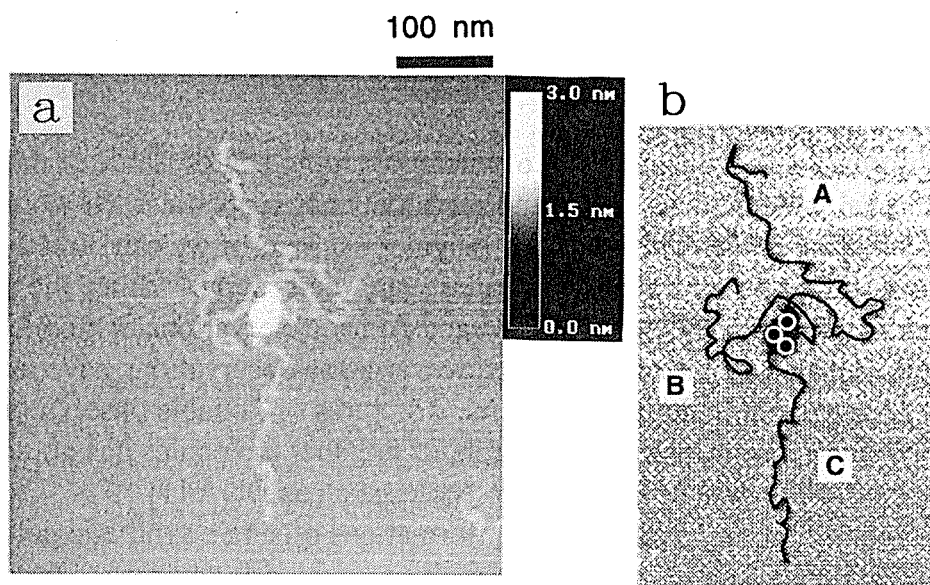


Fig.2 (a) AFM image of an aggregate composed of three PS-b-PMMA molecules, observation was done after keeping in 100%RH for one hour and in 79.3%RH for further 26 hours. (b) A schematic representation of molecular arrangement. Curvilinear lengths are A: 549, B: 403 and C: 314 nm. End-to-end distances are A: 122, B:73, and C:189 nm.

As shown in the schematic representation (Fig. 2(b)), the central core is the aggregation of the three *PS monoblock particles*, thus the three strings emanated from them (A,B,C) are the PMMA block chains. The curvilinear lengths of them are 31 to 55% of that of the fully stretched PMMA block chain (1000nm). The observed length should be shorter than the real because all small kinks of chains are ignored due to a limited resolution; the lengths observed here agree within the order of magnitude. Figure 3 shows another example of AFM image.

Figure 4 shows the end-to-end distance distribution of the PMMA blocks directly determined with AFM. The average root-mean-square end-to-end distance was 132 nm; this is 3.3 times larger than that expected for the  $\Theta$  state in three dimensions for the same PMMA molecules. We believe this quite large expansion is because the chains take the conformations highly restricted in two dimensional space on mica. We believe thin absorbed water layer (0.5nm at 79%RH[5]) formed on the mica

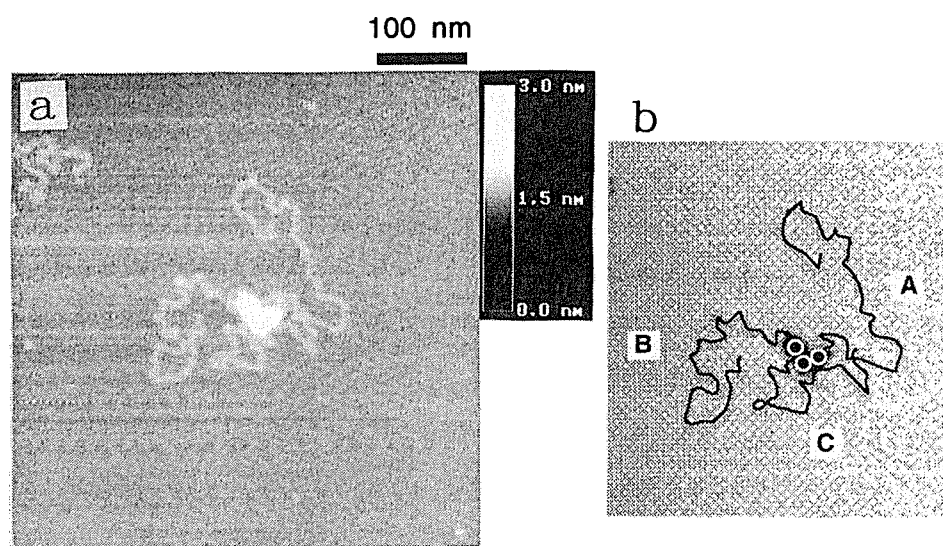


Fig.3 Another AFM image of the same sample as Figure 2. The aggregate is composed of three PS-*b*-PMMA molecules. Curvilinear lengths are A:503, B:455 and C:350nm. End-to-end lengths are A:90, B:63 and C:66nm.

substrate due to high humidity may enhance motion of the PMMA chains and constrain the chain conformations in two dimensions, leading to the dramatic conformation rearrangement.

We have developed a method to observe individual polymer chains on two-dimensional surface by AFM. Our understanding of polymers will be improved with an aid of molecular level information as shown here. [6]

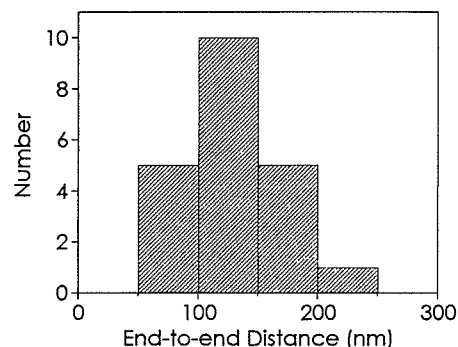


Fig. 4 End-to-end distance distribution directly determined with AFM.

## References

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- (4) Immediately after the invention of SPM, people tried to observe polymer LB films, but no meaningful image was observed in the case of amorphous polymers, for example, see PMMA LB films, T. R. Albrecht, et al., *J. Appl. Phys*, **64**, 1178 (1988).
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