Visualization of Single-Chain Conformations of a Synthetic Polymer with Atomic Force Microscopy

Jiro Kumaki,*,† Yukihiro Nishikawa,† and
Takeji Hashimoto*,†,‡

Hashimoto Polymer Phasing Project, ERATO, JRDC
Keihanna Plaza, Seika, Kyoto 619-02, Japan
Department of Polymer Chemistry
Graduate School of Engineering, Kyoto University
Kyoto 606-01, Japan

Received November 17, 1995

The conformational characteristics of linear macromolecules are one of the most important physical factors for an interpretation and understanding of their properties. Numerous works have in fact been reported along this line since the early stages of polymer science.[1] It would be extremely stimulating for new insights into polymer behavior if we could directly observe a single-chain conformation of macromolecules with microscopy. We report here our experimental result that the random coil conformations of single synthetic polymer molecules frozen on a substrate were successfully identified for the first time.

Recent developments in scanning probe microscopy, such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), enable us to identify structures of single molecules (or atoms) in organic and inorganic materials.[2] However, these observations have usually been limited to the molecular structures in crystalline and liquid crystalline orders. Reliable observation of random coil conformations of amorphous polymer molecules has not yet been achieved[3,4] except for the case of large biomolecules such as DNA.[5]

The sample used was a polystyrene-*block*-poly(methyl methacrylate) diblock copolymer which has the number average molecular weights of 154 800 for polystyrene (PS) and 392 300 for poly(methyl methacrylate) (PMMA) with the polydispersity index of 1.08 (Polymer Source Inc.). The polymers were spread from solutions with a polymer concentration of 4×10^{-6} g/mL in benzene (spectroscopic grade) onto a water surface at 25 °C in a commercial LB trough (FSD-50, USI). This spreading condition is similar to that used for obtaining PS monomolecular particles.[6−8] A single layer formed on the water surface was deposited onto a freshly cleaved mica by pulling it out of the water while compressing the film at constant pressure (the vertical dipping method). In order to observe individual molecules, we have tried to transfer monolayers at the extremely low surface pressure less than 0.1 mN/m. Therefore, the area was not well-controlled during the deposition, and the deposition ratio could not be determined. However, the deposition was always reproducible. The samples were observed in air by a commercial AFM (NanoScopeIII, Digital Instruments) with a silicon cantilever (resonance frequency, 300−400 kHz; spring constant, 70−90 N/m) using the tapping mode. AFM images are shown in the height mode without any image processing except flattening.

The surface pressure of the block copolymer increased monotonically with decreasing area. The conventional linear extrapolation of the high-pressure limb of the curve to zero pressure yields a limiting area, A_0, of 6.96×10^2 nm^2/molecule (0.709 m^2/mg).[9] Figure 1a shows an AFM image of a sample transferred at an area of 1.7 A_0. PS monoblock particles (diameter, 11−15 nm; thickness, 2.5 nm) such as those shown by A, B, and C are formed on mica. They tend to aggregate to form stringlike structures such as those shown by D, E, F, G, and H; for example, the stringlike structures D and E contain five and three monoblock particles, respectively (see Figure 1b). These particles or strings are surrounded by a condensed PMMA monolayer (thickness, 0.2−0.5 nm). This monolayer on the mica should reflect the condensed monolayer formed on the water surface.[10] Figure 1c is a schematic representation of a single block copolymer on mica which is actually seen as A in the micrograph. A small number of large particles seen as I, J, and K are multimolecular particles which could be easily distinguished from the smaller and thinner PS monoblock particles. The smaller PS particles were identified to be monoblock particles because of their size.[9] If we assume that the PS monoblock particles are flat ellipsoidal shapes with the measured thickness of 2.5 nm and that they have the same density as bulk PS (1 g/cm^3), from the molecular weight of the PS block the diameter of the particles is expected to be 14 nm, in good agreement with the observed diameters.[11]

Figure 2a is an example of AFM images of a sample prepared under the same conditions as in Figure 1, but observation was done after keeping the specimen in Figure 1 in 100% relative humidity (RH) air for 1 h and 79.3% RH air for an additional 26 h. Surprisingly, the PMMA molecule was significantly elongated, and the thicknesses of the PMMA molecules were reduced to 0.1−0.2 nm. Figure 2b shows a schematic representation of a possible molecular conformation. Both the sizes of the PS core and the number of chains consistently indicate that the aggregate contains three molecules. The curvilinear lengths along PMMA molecules correspond to 314−549 nm. From the molecular weight, the length of the fully stretched PMMA block is expected to be 1000 nm. The observed curvilinear length should be shorter than the expected, because small kinks of chains parallel and perpendicular to the substrate are all ignored due to a limited resolution; the lengths observed here agree within an order of magnitude. The average root-mean-square end-to-end distance observed for 21 single PMMA molecules was 132 nm; this is 3.3 times larger than that expected for the θ state in three dimensions for the same PMMA molecules (40 nm). This quite large expansion was unusual

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* Address correspondence to J.K. at Plastics Research Laboratories, Toray Industries, Inc., 9-1, Ooe, Minato-ku, Nagoya 455, Japan, and to T.H. at Kyoto University.

† JRDC.

‡ Kyoto University.

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[11] In AFM observations, lateral widths of polystyrene aggregates such as those shown in the images D and E in Figure 1a may be broadened due to the finite size of the probe tip, but the spacing, periodicity, and step height are unaffected by this.[18] In the present measurement, the diameters of the particles are measured precisely from the distances between contacting particles. Now that the diameters measured for the individual particles in Figure 1 were nearly identical to those measured from the distances, we can conclude that the effect due to the finite tip size appears to be small in this observation.

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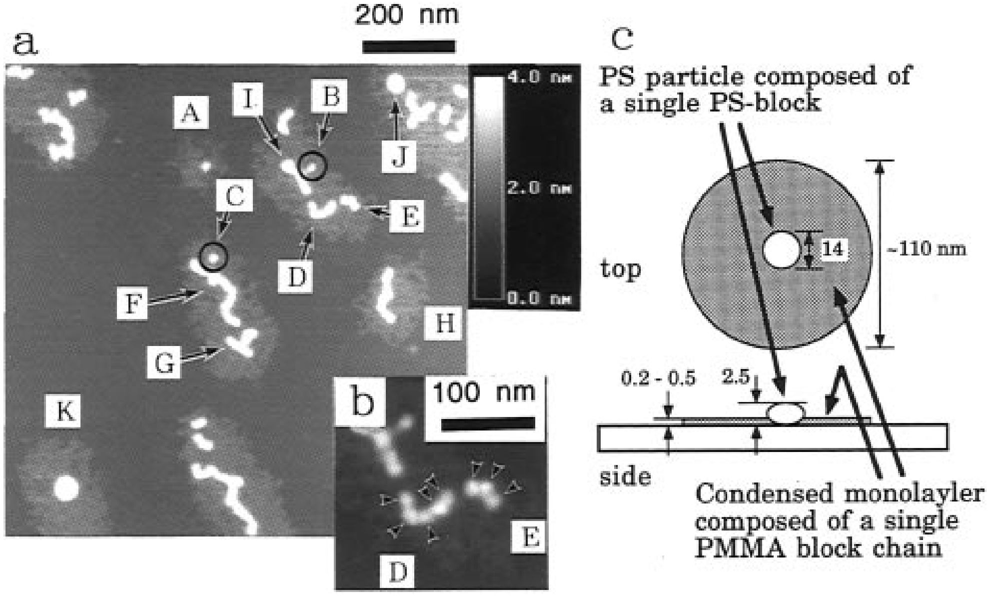

Figure 1. (a) AFM image of a PS-*b*-PMMA monolayer immediately after deposition on mica, (b) an enlarged and contrast-enhanced image of the stringlike structures of D and E in a, which are composed of PS monoblock particles indicated with the arrows, and (c) a schematic representation of a condensed monolayer composed of a single block copolymer, which is actually seen in region A in a.

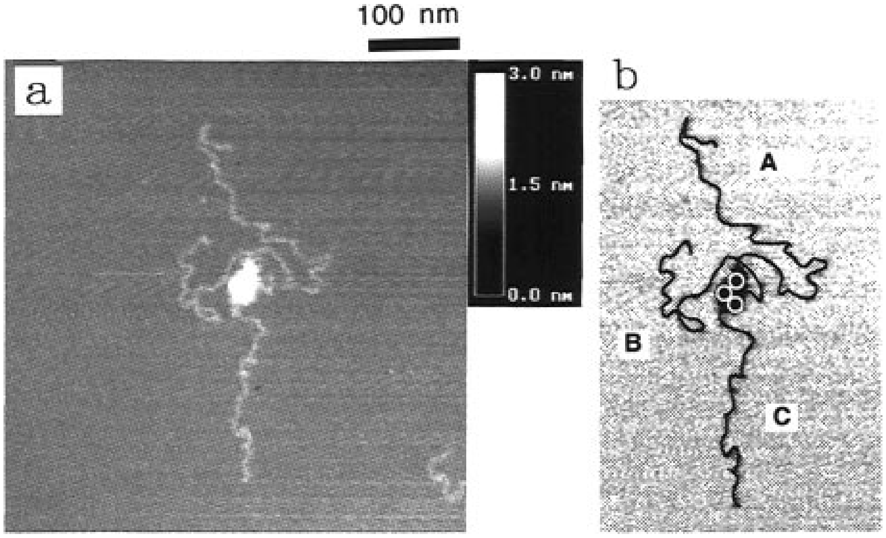

Figure 2. (a) AFM image of a PS-*b*-PMMA monolayer deposited on mica under the same conditions as in Figure 1. However, the AFM observation was done after keeping the sample in 100% RH air for 1 h and 79.3% RH air for an additional 26 h. (b) Schematic representation of a possible molecular conformation. The curvilinear lengths of the lines are A, 549; B, 403; C, 314 nm. The end-to-end distances are A, 122; B, 73; C, 189 nm.

for nonionic polymers. We believe that this is because the chains take the conformations highly restricted in two-dimensional space on mica. The thin absorbed water layer formed on the mica surface due to high humidity (thickness, 0.5 nm at 79% RH[12,13]) may enhance motion of the chains and their conformational rearrangements on the substrate. The rearrangement should depend on detailed balances between the segment–segment interactions of the PMMA, segment–substrate interactions, and segment–water interactions, as well as the thickness of the water layer absorbed on the substrate. We may propose a coarse-grained picture for the rearrangement such that the attractive interactions between the segments are outweighed by those between the segments and substrate.

In conclusion, we have developed a method to observe individual polymer chains on a two-dimensional surface by AFM. In this report we used PS-*b*-PMMA as a model polymer to identify the single molecules. It is probably not necessary to use block copolymers; the technique should be applicable to a wide variety of polymers which are known to spread as monolayers on the water surface.[14–17] Our understanding of polymers, especially in two-dimensional space, will be improved with the help of molecular level information as shown here.

JA9538593

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