

The AFM Observation of Single Polyethylene Molecules in Coiled State on Mica

V.V. Prokhorov ¹, I. V.Yaminsky ²

¹ *Microscopy group, Institute of Bioorganic Chemistry, 16/10 Miklukho-Maklay str, Moscow, 117871, Russia, vprokh@mail.ibch.ru.*

² *Department of Chemistry, Moscow State University, Moscow, 119922, Russia*

Abstract. Single polyethylene molecules and their small aggregates have been deposited on mica from diluted solutions at elevated temperatures and visualized by AFM in coiled and crystalline states. Coils have two-dimensional conformations with both highly tangled sites and locally extended segments with a length much exceeding the persistent length in a solution. The length measurements of coils reveal a wide distribution with the length of a maximum much smaller than the length of fully stretched molecules, moreover the long coils have been observed indicating the existence of linear multimolecular aggregates. Two models have been considered for the explanation of the observed deficit in the coils length, correspondingly the model implying the substantial smoothing of a winding chain trajectory due to the lack of the AFM resolution and the model of locally extended surface conformations with the long intramolecular folds. The roots of the apparent negative AFM height contrast of coils have been discussed.

INTRODUCTION

Direct microscopic observations of single polymer molecules in coiled state have the intrinsic scientific interest as well as the practical importance in a polymer characterization. Up to nowadays the microscopic visualization of polymer coils were conducted intensively mainly for macromolecules with a large persistent length L_p such as stiff DNA [1] ($L_p = 50$ nm) or wormlike polyelectrolyte brushes [2]. There are very few studies in which polymers with a short persistent length have been visualized in coiled state. In a recent study [3] AFM has been used for the observation of two hydrophobic flexible polyelectrolyte molecules trapped and frozen due to adsorption on mica surface in different conformational states. Many of synthetic polymers such as polyolefins (particularly polyethylene) are electrically neutral, hydrophobic and intrinsically flexible with a persistent length of the order of 1 nm [4]. The first study in which such polymers have been observed in coiled state was made in [5] where isolated poly(methyl methacrylate) (PMMA) chains in polystyrene-block-poly(methyl methacrylate) copolymer have been visualized by AFM being deposited on mica using a spreading procedure in a Langmuir-Blodgett trough. An anomalously high extension of adsorbed chains much exceeding the dimension of polymer coils in a solution has been noted. However the use of Langmuir-Blodgett trough for a deposition essentially limits the applicability of this approach for the routine applications especially at elevated temperatures needed for coiled states of many polymers and further use of this technique haven't been published. It has been shown in [6] that the molecules of polyethylene and isotactic polypropylene can be observed in coiled and compact states by AFM using a procedure of the direct deposition on mica from diluted solutions at elevated temperatures. The deposition procedure turned out to be very simple and quick and can be routinely used for the observation of molecules of other polyolefins, particularly polymer coils of a block-copolymer

polypropylene-block-poly(ethylene-co-propylene) were visualized in [7]. The underlying physics of the adsorption to mica of single molecules of flexible electrically neutral hydrophobic polymers resulting in the formation of surprisingly various surface structures of a molecular size is still not clear however. The present research is an attempt to give the interpretation of some quantitative and qualitative dependencies for coiled conformations.

MATERIALS AND METHODS

Materials and samples preparation: The sample preparation was in accordance with [6]. Standard PE grade with narrow molecular weight distribution $M_N=11400$ $M_W/M_N=1.19$ was used. The deposition was done by dropping of 20 μl of 10^{-4} wt.% hot polymer solution in ortho-dichlorobenzene (ODCB) on a surface of freshly cleaved mica sheet placed in a hot stage with a temperature of 150-160 $^{\circ}\text{C}$. The time of drop evaporation was within several seconds, then the sample was withdrawn from a hot stage for the AFM observations.

AFM and the analysis of AFM images: AFM images were recorded with a Nanoscope III multimode AFM (Digital Instruments) operated in a tapping mode at ambient conditions. Silicon cantilevers with spring constants of 30 N/m were used. The scanning was conducted with low amplitudes of a probe oscillation in the range of several nm. The specialized software packages were used for the routine off-line analyses of AFM images and for semiautomatic measurements of the length of linear objects: Femtoscan Online (A.Filonov, I.Yaminsky, <http://www.nanoscopy.net>) and DNA-calc (G.Gluschenko, V.Prokhorov, gena@nanko.ru, V.Prokhorov, vprokh@mailcity.com).

RESULTS AND DISCUSSION

AFM reveals the coexistence on mica surface of both extended coils and compact crystallites with a complex structure (Fig.1). Generally a lot of different morphological states coexisting within the same sample is observed [6] at such depositions which are coils, crystallites with regular shapes morphologically similar to those of represented in Fig.1 and long isolated lamellae in “edge-on” orientation.¹ The crystallites are folded states adopted by single PE molecules or their small aggregates at deposition on mica substrate, the models of their structure will be considered elsewhere. The coils have the negative apparent height of 0.2-0.5 nm and the apparent width of about 5 nm. The surface conformations of polyethylene coils considered as a whole on a macroscale are much more tangled than those of adopted by polymers with a large length of Kuhn statistical segment [1,2]. This feature is evidently related with a relative freedom of rotations along -C-C- bonds resulting in an intrinsic flexibility of a molecular backbone [4]. A high degree of entanglement was observed also for coils of other polyolefins [6]. The appearance of multiple

¹ In the classification made in [6] the isolated lamellae were called erroneously “nanofibers” due to a characteristic morphology with two close narrow stripes. Now we consider this term irrelevant [8].

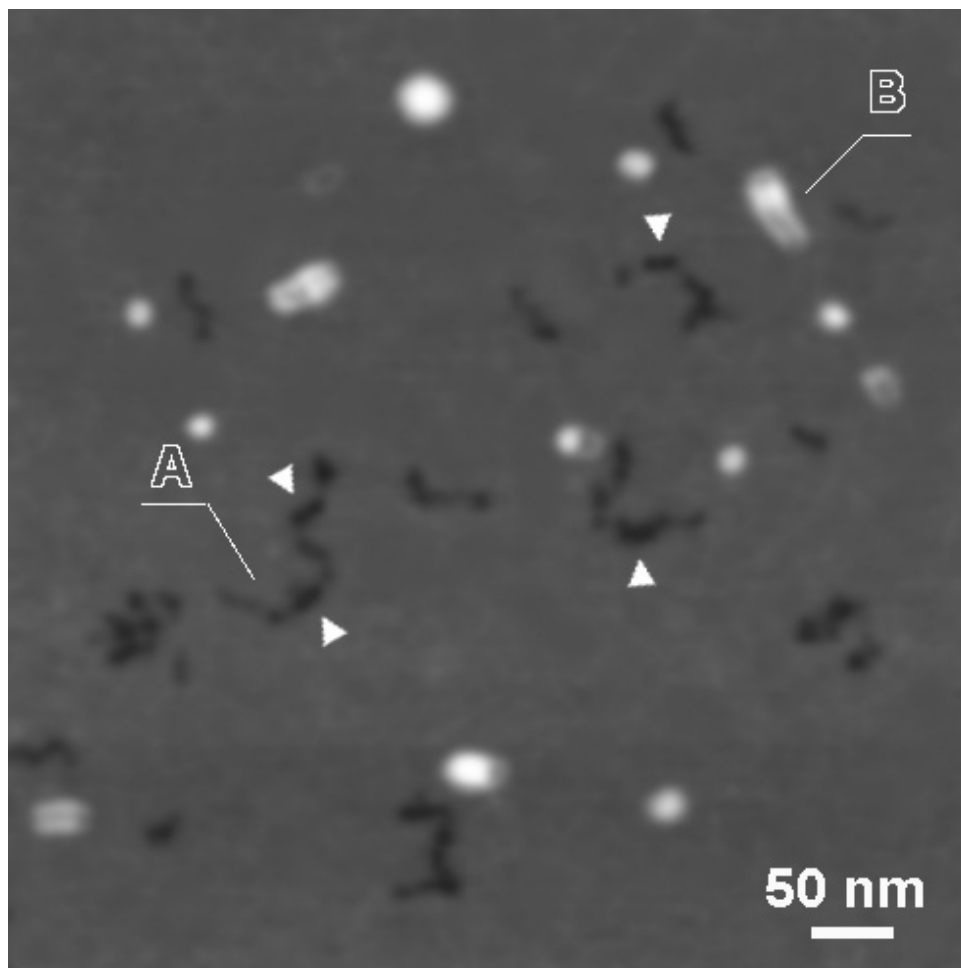


FIGURE 1. The AFM height image of polyethylene single- and few- molecular surface conformations on mica: A – extended coils, B – folded compact crystallites. The coils have the intrinsically negative apparent height with some segments accentuated (shown by arrows).

crossovers highly complicates the tracing of the observed chain trajectories and the length measurements for polymers with chains length of several hundreds nm. It should be specially noted that the coiled conformations didn't changed during observations, the repeating scans resulted in essentially the same AFM pictures. On a local scale the characteristic feature of coils surface conformations is observed: they include both tangled sites with crossovers and extended straight segments with a length of 5-15 nm. This value seems anomalously large in a comparison with the polyethylene persistent length in a solution of 1 nm. It should be kept in mind however that a common broadening of lateral dimensions due to a final probe curvature R must take place, very roughly it can be estimated from common geometrical considerations as $\delta x \sim \sqrt{2 R \cdot h}$, where $h \sim 0.5$ nm is a height (diameter) of a polymer chain and typically $R \sim 10-20$ nm what gives δx of several nm. Although this value is in the agreement with experimentally observed chain width on AFM images, at the same time it greatly exceeds the persistent length. It means that the

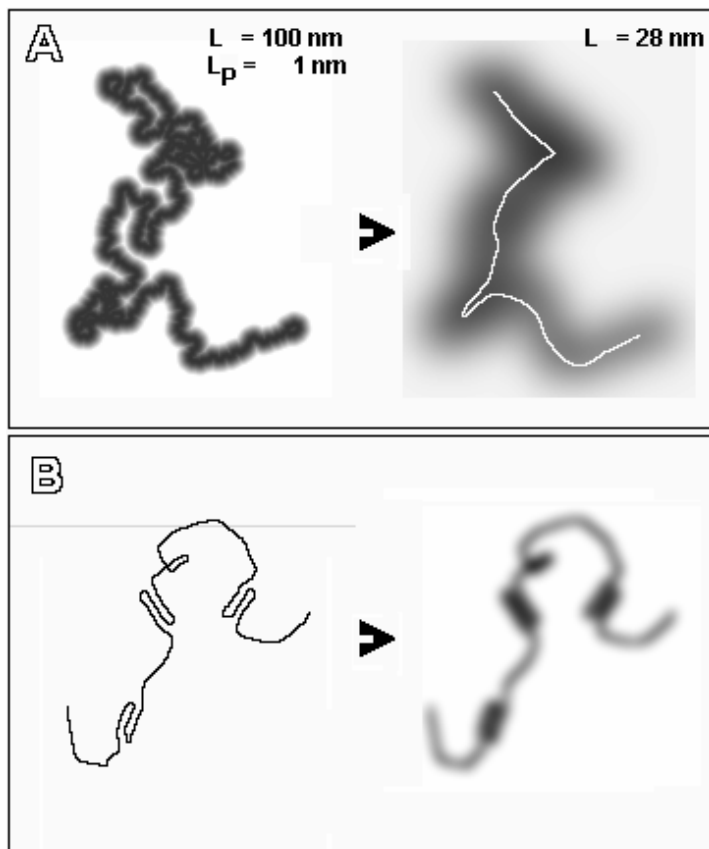


FIGURE 2. Two models of the interpretation of AFM images of coils: A – the model of the chain with a small two-dimensional persistent length, its AFM image is highly smoothed by a probe, B - the model of locally extended chains with intramolecular folds. The left images are model images; the right images are obtained by their spatial averaging and correspond to the smoothing by a probe. In the model A the coil trajectory with the length of 100 a.u. and the diameter of 0.5 a.u. was simulated by a two-dimensional random walk with the persistent length of 1 a.u., then it was spatially averaged by Gaussian filter with a radius of 1 a.u.. The length of convoluted thread in the right is of 0.28 original chain length. The left image for the model B was drawn schematically without any simulations.

interpretation of AFM images of coils of flexible polymers should be done with a caution because the fine details of chain trajectories within the size of the resolution spot could be slashed and only the result of a “spatial averaging“ by the AFM probe will be observed. The concomitant consequence of this effect of a «poor resolution» could be the inevitable large decrease in the observed chain length in comparison with the length of fully stretched chains. Fig.2A schematically illustrates such an effect of a shortening with the expectable magnitude of the order of several times.

To test this prediction the measurements of a curvilinear length of coils have been done (Fig.3) for PE grade with a narrow molecular weight distribution and with a small chain length (of about 105 nm in a stretched state) providing the surface conformations with a relatively small degree of entanglement. The histogram in Fig.3 was obtained from measurements of about 150 coils from 15 different images. Coils with a complex structure such as shown in lower left part of Fig.1 were excluded from

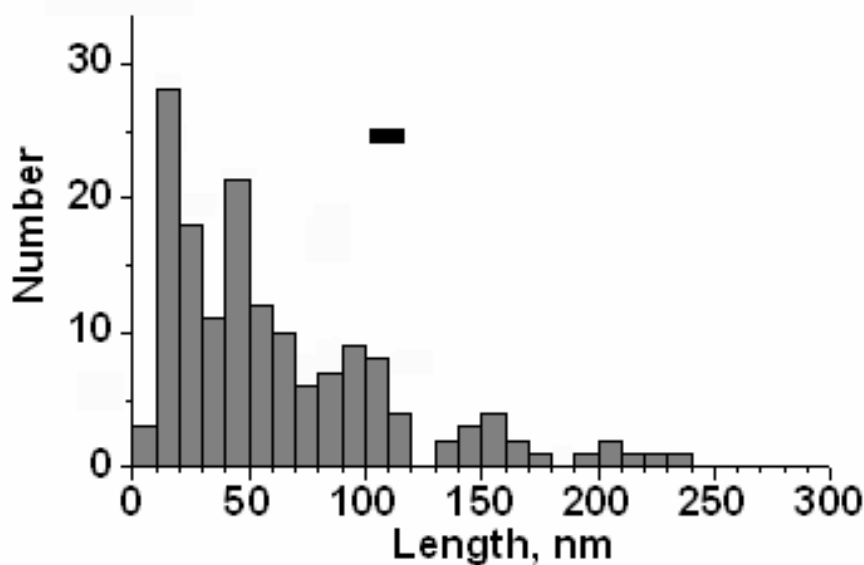


FIGURE 3. The histogram of the length distribution of PE coils. The horizontal bar at about 105 nm corresponds to the length dispersion of fully stretched molecules calculated from a molecular weight distribution.

the analyses to avoid the ambiguity in the length measurements. The prominent feature of the histogram in Fig.3 is that the most of coils have the apparent length several times smaller than the length of a stretched molecule, however a small fraction has the length exceeding this value. For the comparison the (narrow) lengths distribution of a fully stretched molecules derived for this grade from the known molecular weight distribution is shown by bar placed at 105 nm. Moreover, in contrast to the expectations of a continuous distribution the histogram in Fig.1 reveals the sequence of several peaks decreasing in the amplitude. The position of the 3rd (from the left) peak corresponds approximately to the length of a fully stretched molecule, the positions of the 2nd and the 1st peaks are approximately half and fourth of the

length of fully stretched molecule correspondingly. It is worth to notice also that the peaks couldn't appear from the degradation of PE molecules in shorter fragments in our specimens preparations. Common procedures of the molecular weight distribution analyses in a gel-permeation chromatography imply no polymer degradation at much more longer time of the elution of polymer solutions at elevated temperatures.

We suggest that there are two ways to interpret these results. In the first model (Fig.2A) it is supposed that the surface conformations of adsorbed molecules could be described by a small apparent persistent length of the order of 1 nm (like in solution). In this case in dependence on the size of the resolution spot provided by the probe (which is anyway of the order of several nm-s) the AFM measurements would give a single peak in a distribution of the length of (single) molecules with a maximum at the length which is several times smaller than the length of fully stretched molecules. The typical shortening is demonstrated in Fig.2A in which it is of the order of a factor

of 3.6. In this model the appearance of the long right tail in Fig.3 indicates that most of observed coils are in fact the linear aggregates of several (2-10) PE molecules. The physical reasons resulting in such a long linear aggregates are not clear however.

The second model (Fig.2B) implies that the coils surface conformations are locally extended at a scale of several nm-s however coils may have a number of relatively long intramolecular folds along the chain trajectory with the length of the order of ten or several tens nm. The deficit in the length of coils contributing to the distribution in Fig.3 in the range smaller than 100 nm results from poor AFM resolution so that adjacent polymer stems forming folds are indistinguishable in AFM images. In dependence on the number of folds and the number of polymer stems inside them the continuous distribution in the observed length could be generated. The appearance of peaks in the histogram of Fig.3 indicates however that some “preferable” types of folding probably take place. Namely, the peak at about 50 nm could correspond to the molecules folded twice on themselves whereas peaks corresponding to three- and four- times folded molecules could merge and produce the single peak at about 20-30 nm in Fig.3. The appearance of coils with the length (> 100nm) exceeding the length of a single PE molecule indicates that the linear aggregates of a few PE molecules are formed in this case also.

The model B seems more preferable for several reasons. First, the wide two-dimensional extension and the length comparable with the length of stretched molecules have also been observed for coils of other neutral flexible polymers deposited on mica such as polypropylene-block-poly(ethylene-co-propylene) in [7] and PMMA in [5]. Second, the model B is indirectly supported by AFM pictures of coils by a frequent observation of segments with an apparent length within 5-15 nm which are accentuated in height images by their distinctively different (also negative) heights, some of such segments are shown by arrows in Fig.1. Such an inhomogeneity in the apparent height contrast could indicate that a coil has sites of variable width, which can't be detected laterally due to the lack of resolution however for some reasons these sites manifest themselves in the observed height. Third, the idea of intramolecular folds is in agreement with many computer simulations of the crystallization of single polymer molecules [9]. The intrachain van-der-Waals attraction between different chain segments drives this folding with a formation of metastable folds for molecules placed in a solution. It may be supposed that polyethylene molecules approaching mica had such intramolecular folds before adsorption or, similarly, the folds were formed during or after adsorption to mica.

In addition and irrespectively to these two models of the internal structure of observed coiled conformations there is a possibility that some close coils are linked with each other but the linker is invisible in AFM images. This assumption is difficult to test at present but anyway if it is true the statistics of coils with a larger length in the distribution in Fig.3 will be increased.

The high expansion of surface conformations of adsorbed polymer molecules in comparison with coils dimensions in a solution assumed in the model B implies some physical mechanism. We suppose that this mechanism is based on the existence of short-range van der Waals surface force field of a sufficient strength in the vicinity of the crystal substrate. The energy of short polyethylene segments in the vicinity (and on) the surface of crystal substrates such as alkali halides and graphite has been calculated in [10,11]. It is of the order of several kT per methylene unit and is concentrated in the vicinity to the surface in a narrow layer with a thickness of the

order of 1 nm. The corresponding strong force gradient may have a sufficient strength to overcome cis-trans potential barriers along the molecule backbone and to rearrange the random coil conformation in such a way that the straight all-trans segments (having the lowest energy in this field) will have the increased statistical weight. As a result the molecule will be laterally expanded locally and globally. The high surface force field and similar behavior may be expected for mica. Many studies based on statistical mechanical theory also predict the increase in the radius of gyration at the adsorption of a single polymer chain on a flat homogeneous surface at a sufficient strength of attraction [12]. In recent molecular dynamic simulations [13] of the adsorption of single polyethylene molecule onto a solid surface the substantial increase in the component of the gyration radius parallel to a surface has been found in the case of a “strong” and “medium” vdW attraction between a polymer and a substrate. However the simulations in [13] predict the different two-dimensional morphology, namely the stretched monolayer-like or polylayer-like structures, instead of tangled coiled conformations found in the present research and in [5-7]. We suggest that this disagreement may result from the disregarding in the theoretical calculations and computer simulations two in-plane periodic components of the surface force field of crystal substrate. Despite the weakness of these two components (which are of the order of several percents in the magnitude in comparison with a normal component [10,11]) their integral effect could be important for the formation of a particular two-dimensional morphology. Particularly the long molecular segments could be laterally fixed in a substrate periodic crystal field and this fixation could prevent them from further collapse on the surface to the folded ordered crystallite. We think that some strong fixation mechanism is necessary anyway for the explanation of the very fact that the observed coiled two-dimensional conformations were surprisingly stable. They didn't changed after multiple scans, neither lateral diffusion nor even minor changes in a conformation due to the local segments rearrangements have been observed within the times of many hours. Further experimental and theoretical efforts are necessary to clarify these details.

Both coils and compact crystallites in Fig.1 have small dimensions indicating that they consist of very few (often single) polyethylene molecules. Moreover it is clearly seen with the achieved resolution that the compact crystallites reveal complex internal structure. The observation of these fine structural details is interesting from the fundamental point of view for the theories and computer simulations of a crystallization single polymer molecules in a solution [9] and on a substrate and for the theories of coil-to-globule transition in most complex case of highly crystalline polymers such as polyethylene. Although it should be noted firstly that the important relevant details of the procedure of the specimens preparations must be preliminary clarified, particularly the exact temperatures and the temperature intervals at which the molecules acquire coiled and/or crystalline states in a solution and on a substrate as well the characteristic times of intramolecular transformations on the surface. This could be the subject of further studies.

We have found that the observed negative apparent height of coils is a stable anomaly of our AFM observations. We assume at present that this artifact could be explained on a base of two different assumptions. Firstly, it is well known that the scanning of heterogeneous samples (hydrophobic polymer vs hydrophilic mica in our case) could result in a tapping mode in offsets in a vertical cantilever position [14]. If these offsets had a value of about 1 nm (what is a common case) they could in some

conditions imitate the negative height of polymer coils having the diameter of only about 0.5 nm. Secondly, the presence of a thin water film on the mica surface could have a great influence at the observation of hydrophobic molecules. In several AFM and SPFM studies [15,16] this film has been observed directly. Particularly in a recent study [16] the patterned water films have been observed on mica in a contact AFM mode with a height (in dependence on a humidity treatment) within 0.3-1 nm. Moreover, the study in [16] implies that the formation of a thin water layer on mica surface is accompanied with a localized exchange of hydrogen ions for potassium ions and the formation of potassium bicarbonate islands. The viscoelastic response at scanning for such a film may differ from that of for the purely fluid film. At this assumption the observed negative heights of polymer coils could be explained from purely geometrical difference in the heights of the water film and adsorbed polymer molecules if we assume that the probe scans over the surface of the water film and the latter is absent nearby and below hydrophobic polymer. If this model is true the negative apparent height of hydrophobic coils is a one more manifestation of the ubiquitous water films.

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