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Research Article

Detecting van der Waals forces between a single polymer repeating unit and a solid surface in high vacuum

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ABSTRACT

Ubiquitous van der Waals (vdW) forces are very important for nanostructures. Although the vdW forces between two surfaces (or two layers) have been measured for several decades, a direct detection at the single-molecule level is still difficult. Herein, we report a novel method to solve this problem in high vacuum by means of AFM-based single-molecule force spectroscopy (SMFS). Solvent molecules and surface adsorbed water are removed thoroughly under high vacuum so that the situation is greatly simplified. A constant force plateau can be observed when a polymer chain is peeled off from a substrate in high vacuum. Accordingly, the vdW forces between one polymer repeating unit and the substrates can be obtained. The experimental results show that the vdW forces (typical range: 21–54 pN) are dependent on the species of substrates and the size of polymer repeating unit, which is in good accordance with the theoretical results. It is expected that this novel method can be applied to detect other non-covalent interactions (such as hydrogen bond and π-π stacking) at the single-molecule level in the future.

KEYWORDS

van der Waals forces, high vacuum, atomic force microscopy, single-molecule studies, polymer desorption

1 Introduction

Non-covalent interactions, such as van der Waals (vdW) forces [1, 2], hydrogen bond [3] and hydrophobic interaction [4], are very important for the bottom-up fabrication of nanostructures [5, 6]. For this reason, precise measurements of noncovalent interactions have been long desired. However, it is difficult to measure vdW forces since they are the weakest noncovalent interactions in most cases. In the last three decades, experimental techniques, such as surface force apparatus (SFA) and atomic force microscopy (AFM), have been successfully utilized to detect vdW forces in surface/surface [7–9] and AFM tip/surface [10–13] systems, respectively. However, direct detection of the vdW forces acting on a small molecule is still difficult. The main obstacle in this regard is that the manipulation of a small molecule is hard due to the very tiny size, which usually requires a complex detecting system and strategy [14, 15]. For instance, ultra-high vacuum, extremely low temperature and AFM with extremely sensitive force detection are necessary; accurate location and manipulation of target single molecule are also required. When the AFM tip is very close to the substrate surface, the interactions between the tip and the substrate are unavoidable, which will strongly disturb the detection of vdW forces.

Herein, we propose a facile strategy to directly detect the vdW forces between a polymer repeating unit and a solid surface. Similar to a necklace, a polymer chain strings the repeating units together. Compared with a small molecule, the force signals of the polymer chain desorption event will last a much longer time due to the lengthened molecular length. Thus, the desorption event of the individual polymer chain may be easily distinguished in this case.

Besides the selection of target molecule, the micro-environment of force measurement is also crucial to the detection of the vdW forces. Molecular force measurements were usually carried out in a liquid environment [16–33]. Since various forces (vdW forces and etc.) are involved in the molecular adsorption in a liquid environment, it is hard to differentiate each of the forces clearly (Fig. S1 in the Electronic Supplementary Material (ESM)). For the target molecule, the vdW forces from the substrate will be counteracted to a large extent by the vdW forces from the solvent molecules. Thus, even if the force signal is successfully obtained in a liquid environment, it represents the resultant force rather than the vdW forces from the substrate (Fig. S1 in the ESM). Therefore, it is very difficult to directly detect vdW forces at the single-molecule level in a liquid environment.

To directly detect vdW forces at the single-molecule level, the disturbance from the liquid environment should be eliminated. We expect that a vacuum environment would be helpful for this purpose. Solvent molecules and surface adsorbed water are removed almost thoroughly under high vacuum so that the situation is greatly simplified [34]. It is expected that the vdW forces may be detected at the single-molecule level when a polymer is used as the target molecule in high vacuum (Fig. S1 in the ESM). In this study, atomic force microscopy (AFM)-based single-molecule force spectroscopy (SMFS) is exploited to detect the vdW forces between a single polymer repeating unit and a solid surface in high vacuum. The experimental results show that the vdW forces (typical range: 21–54 pN) are dependent on the species of substrates and the size of polymer repeating unit, which is in good accordance with the theoretical results.

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2 Experimental

2.1 Materials and sample preparation

Freshly cleaved highly oriented pyrolytic graphite (HOPG, ZYH grade, Bruker Inc.), paraffin wax (Adamas-beta Inc., reagent grade) and quartz slide are used as the substrates in force measurements, respectively. The paraffin slide is prepared by melting the paraffin wax on a clean glass slide. The quartz slide is treated by a hot piranha solution for 30 min (98% H_2SO_4 and 35% H_2O_2, 7:3, v/v) and extensive DI water rinsing to obtain a clean surface. PEG (BioUltra grade, M_W 35 kDa) is purchased from Sigma Corp. Poly(2,3-dihydrofuran) (PDHF, M_W 100 kDa) is purchased from ZZBio Co., Ltd (Shanghai, China). The details of synthesis and purification of poly(N,N-ethylmethylacrylamide) (PEMA, M_W 230 kDa) can be found elsewhere [35]. DI water (> 15 MΩ·cm) is used when water is involved. PEMA or PEG is dissolved in DI water to a concentration of 50 μg/mL. A drop of the target polymer solution is deposited onto the substrate for 10 min. PDHF is dissolved in dichloromethane to a concentration of 100 μg/mL. A drop of the target polymer solution is deposited onto the substrate and exposed in low vacuum (~ 20 Pa), so that the dichloromethane will be volatilized within 1 min. Then, the samples are rinsed with their solvents to remove the loosely adsorbed polymer and dried by air flow.

2.2 Force measurements

All force measurements in high vacuum are carried out on an AFM (SPI3800N, Seiko Inc., Japan), which is equipped with an environment chamber with an external vapor control system. Prior to the force measurements, the AFM chamber is pumped down to ~ 7.0×10^{-4} Pa to achieve high vacuum, where almost all adsorbed water molecules can be removed from the substrate. The AFM setup is earthed before vacuum degassing, and the tip and substrate are sat in high vacuum for a relatively long time (~ 2 h) before force measurements. Thus, no static electricity is expected to remain on the tip and the substrate [36]. Force measurements are carried out at room temperature (~ 22 °C). During the AFM manipulation, data are recorded at the same time and converted to force–extension curves (in brief, F–E curves) subsequently. The spring constant of each AFM cantilever is calibrated by the thermo-fluctuation method, and the values ranges between 500 and 800 pN/nm. The stretching velocity is 1.0 μm/s unless mentioned otherwise.

The force measurements in liquid environments are carried out on another AFM (NanoWizard II, JPK Instruments, Germany). Prior to the measurements, a drop of liquid is injected between the Si_3N_4 AFM cantilever (MLCT model, Bruker Corp., CA) and the sample. The process of the force measurements is similar to that mentioned above. The instrumentation of AFM-based SMFS can be found elsewhere [19, 21, 37–39].

3 Results and discussion

Herein, poly(N,N-ethylmethylacrylamide) (PEMA) is used as the target polymer chain, while a nonpolar material, highly oriented pyrolytic graphite (HOPG), is used as the substrate. Figure 1(a) shows the force-extension (F–E) curve of PEMA obtained in high vacuum (see the Experimental section for details), where a long plateau with a height of ~ 67 pN can be observed. The long plateau in the F–E curve can be attributed to one of the three possible scenarios: (i) The desorption of a polymer chain with a train-like conformation from the substrate [40]; (ii) The polymer chain forms a globule in its poor solvent and the segments are pulled out of the globule consecutively [4]; (iii) The repeating units of a polymer chain are pulled out of the polymer crystal one by one [41]. Water is a good solvent for PEMA. Therefore, the PEMA chain should not adopt a globule conformation on the sample surface, since an aqueous solution is used in the sample preparation. A prolonged time is needed to grow a polymer crystal under relatively high concentration, which is clearly not the case in our experiments: 10 min of physisorption from a dilute PEMA solution. Since the scenarios of (ii) polymer globule and (iii) polymer crystal are excluded, only scenario (i) is left. Experimentally, the train-like conformation of the polymer chain is confirmed by AFM imaging, see Fig. 2.

When stretched by an AFM tip, the PEMA repeating units will be peeled off from the substrate surface one by one. The HOPG surface is homogeneous, and PEMA is a homopolymer. Therefore, the desorption force of all the repeating units should be virtually identical, resulting in a long plateau in the F–E curve (Fig. 1(a)). Both the polymer and the substrate are neutral, hence electrostatic force can be ignored in this case. Under ambient condition, the surface of a substrate may be covered by a thin layer of adsorbed water. It is expected that the surface adsorbed water can be removed in high vacuum [34]. To confirm this, a set of control experiments have been carried out, where the AFM chamber is blanketed by dry

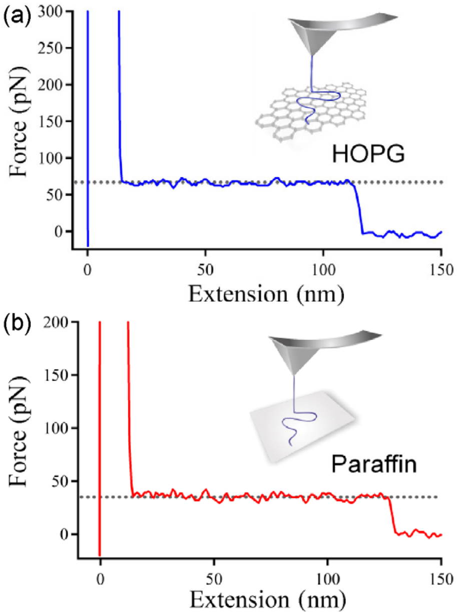

Figure 1 Typical single-chain F–E curve of PEMA obtained in high vacuum on the HOPG (a) and the paraffin substrate (b), respectively. The dotted line locates at 67 and 34 pN in (a) and (b), respectively. The complete F–E curve is shown in Fig. S2 in the ESM.

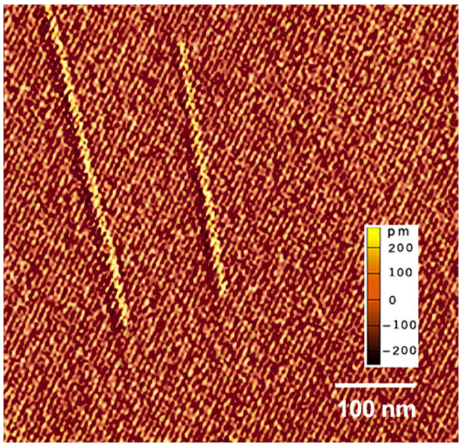

Figure 2 AFM image (Cypher, Asylum Research, CA) of single PEMA chains adsorbed on the HOPG substrate (scan size: 0.6 μm × 0.6 μm, measured in air). The PEMA chains adopt a train-like conformation on the substrate. The polymer chains are stretched due to the effect of molecular combing in the sample preparation [42]. AFM image of a blank HOPG substrate is shown as a reference in Fig. S3 in the ESM.

nitrogen before degassing. The mean desorption force of PEMA obtained in the control experiments is similar to that obtained previously (Fig. S4 in the ESM), indicating that the surface adsorbed water is removed in high vacuum. Force measurements of another polymer, poly(ethylene glycol) (PEG) [19], are also carried out in high vacuum, which confirm that the surface adsorbed water in the system is removed completely (Fig. S5 in the ESM). Therefore, the hydrophobic effect will not contribute to the desorption force in high vacuum [43]. According to the above results and analysis, the desorption force observed from Fig. 1(a) can be preliminarily attributed to vdW forces between a single PEMA chain and the HOPG substrate.

A paraffin slide is used as another substrate in the high vacuum force measurements. As shown in Fig. 1(b), a long plateau is also observed in this case. Similar to HOPG, the paraffin surface is also nonpolar and homogeneous. With the same reasons, the desorption force of PEMA from paraffin surface can also be preliminarily attributed to the vdW forces. Statistical analysis shows that the desorption forces (vdW forces) of PEMA chain obtained in high vacuum on HOPG and paraffin substrates are 67.4 ± 15.8 and 34.2 ± 9.9 pN, respectively (Fig. 3). The different desorption forces may result from different properties (i.e., Hamaker constants, A) of the substrate materials [1]. According to the literature [1], the vdW forces for the same polymer are proportional to $A^{1/2}$ of the substrate. The larger Hamaker constant of HOPG will result in a larger vdW forces on it. The details of the theoretical calculations can be found in the ESM.

To assess the measurement accuracy and precision, the potential errors and the corresponding influence factors are analyzed (see the ESM for details), which suggest a total random error of 30%–40% in the force measurements. However, due to the large sample size (N > 400), the standard errors of the mean in all the force measurements are lower than 1 pN, indicating that the effects of random error are greatly reduced (see Table S1 in the ESM). Besides, the already desorbed adjacent repeating units can be regarded as an ultra-sharp AFM tip, which will induce a very limited, however, nonnegligible systematic error (+20%, see the ESM for details) in the force measurements (Fig. 4(a)). Accordingly, the vdW forces of an individual PEMA repeating unit on HOPG and paraffin substrates are corrected to be 53.9 ± 12.6 and 27.4 ± 7.9 pN, respectively. In general, these results suggest a quite good accuracy and precision of our force measurements. Theoretically, the vdW forces between a polymer repeating unit and substrates are estimated with a typical molecule-surface physisorption distance (0.32–0.38 nm, see the ESM for details) [44]. Good agreement between the theoretical and experimental results confirms that the desorption force measured in high vacuum can be attributed to vdW forces, see Fig. 4(b) for details.

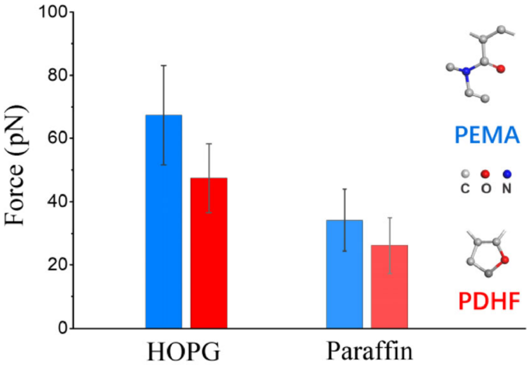

Figure 3 Mean plateau height of PEMA (blue) and PDHF (red) measured in high vacuum on HOPG and paraffin, respectively. Inset: The structures of the repeating units of the two polymers (the H atoms are omitted). The number of events is 500 for PEMA and 440 for PDHF on each substrate, respectively.

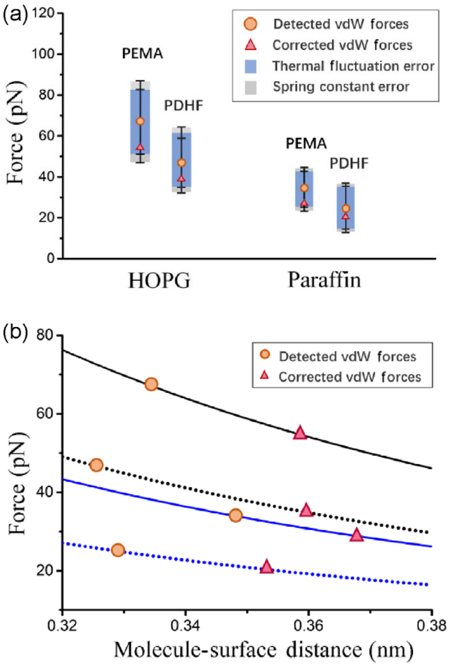

Figure 4 (a) Error analysis of the force measurements. The mean detected vdW forces (desorption forces) between a PEMA repeating unit and different substrates are shown by yellow circles. The corrected mean vdW forces by eliminating the systematic error (+20%) are shown by red triangles. The random errors induced by thermal fluctuation and spring constant calibration are shown by blue and grey columns, respectively. (b) Theoretical results of the vdW forces in the range of a typical physisorption distance (0.32–0.38 nm). Black and blue lines represent the HOPG and paraffin substrates, respectively; solid and dotted lines represent PEMA and PDHF, respectively.

Poly(2,3-dihydrofuran) (PDHF) is used as another target molecule in the force measurements. Statistical analysis shows that the single-chain desorption forces of PDHF chain obtained on HOPG and paraffin substrates in high vacuum are 47.4 ± 10.8 and 26.1 ± 8.9 pN (38.0 ± 8.6 and 20.9 ± 7.1 pN, the vdW forces of a single repeating unit after correction) respectively, which are lower than those of PEMA on the same substrates (Fig. 3 and Fig. S6 in the ESM). This result can be associated with the different size (number of atoms) of polymer repeating units because of the additivity of vdW forces. Since the size of PDHF repeating unit is smaller than that of PEMA, the vdW forces exerting on a PDHF repeating unit should be smaller than that of PEMA. Theoretical results show that the vdW forces of a PDHF repeating unit on HOPG and paraffin substrates are 28.5–47.0 and 16.2–26.7 pN respectively, which are in good agreement with the experimental results (see the ESM for details). Thus, we can conclude that the lower vdW forces than that of PEMA can be associated with the smaller size of the PDHF repeating unit.

A quartz slide is used as the substrate to further study the polymer desorption behavior in high vacuum. Since quartz is polar, PEMA may form some strong adsorption anchor points on the quartz surface [45], which will lead to a much larger rupture force upon stretching after the desorption plateau. Two types of F–E curves are obtained on the quartz substrate in high vacuum: (i) the F–E curve with only a long plateau, and (ii) the F–E curve with a long plateau, followed by an elastic stretching behavior, see Fig. 5(a). The elastic behavior of the chain after the plateau can be described well by an elastic model of a single polymer chain (QM-FRC model, see the ESM for details), suggesting that a single-chain event is observed [16, 45]. The plateau heights of the two types of F–E curves are identical (42.7 ± 13.7 pN, Fig. S7 in the ESM), indicating that both the plateaus in the F–E curves in Fig. 5(a) can be attributed to the single-chain desorption from the substrate. Moreover, the corrected

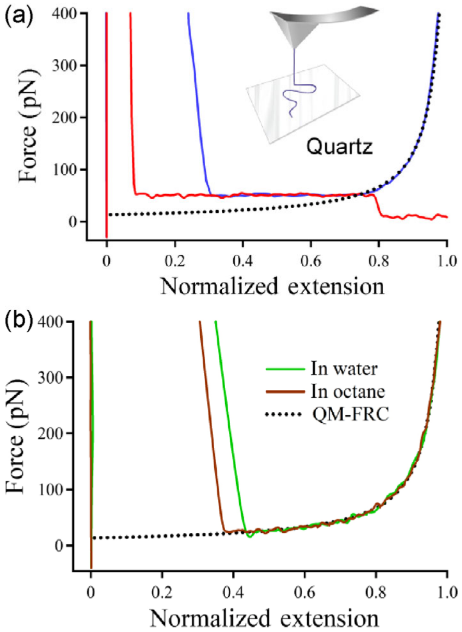

Figure 5 (a) Two types of F–E curves of PEMA obtained on the quartz substrate in high vacuum. (b) Normalized F–E curves of PEMA obtained on the quartz substrate in water (green) and octane (brown), respectively. The QM-FRC fitting curve with l_b = 0.154 nm (dotted line) is shown as a reference in (a) and (b).

vdW forces on quartz substrate (34.2 ± 11.0 pN) is in good agreement with the theoretical value (24.8–40.9 pN, see the ESM for details). These results support that all of the long plateaus shown in Figs. 1 and 5(a) and Fig. S6 are single-chain events.

In contrast to high vacuum, no plateau is observed in the F–E curves obtained in liquid environments. The F–E curves of PEMA on quartz obtained in water (or octane) can be superposed well with the QM-FRC fitting curve in the whole force region (Fig. 5(b) and Fig. S8 in the ESM). These results indicate that the single PEMA chain shows a pure elastic behavior in a liquid environment. In addition, all F–E curves obtained on the HOPG or paraffin substrates in liquid environments show no plateau; only noise signals can be observed (Fig. S9 in the ESM). Theoretical results also show that the vdW forces are several pN or even less in a liquid environment (see the ESM for details). All these results indicate that the vdW forces between PEMA and the substrate are too weak to be detected in liquid environments, i.e., vacuum environment is the precondition for vdW forces detection at the single-molecule level.

The pulling angle of the polymer chain may be an important parameter for the force measurements [46]. In this study, because both of the vdW forces and the measured force are vertical force vectors, the measured force is always equal to the vdW forces, which is independent of the pulling angle of the polymer chain, see Fig. S10 in the ESM for details.

In this study, all the force measurements are carried out with various stretching velocity. The mean desorption forces are almost constant when the stretching velocity is changed from 1 to 10 μm/s, see Fig. S11 in the ESM. Recently, Butt et al. found that the vdW forces between an AFM tip and a nonpolar surface are almost independent on the loading rate when it is below 10^5 nN/s (equivalent to a stretching velocity of ~ 170 μm/s for the AFM tip used in this study) [13], which consists with our results. These results indicate that our force measurements are carried out in a quasi-equilibrium condition [47].

On the basis of the experimental results in this study, the strength of the vdW forces in high vacuum between a polymer repeating unit and the substrate are estimated to be in the range of 0.7–2.0 kcal/mol. These values are slightly lower than or similar to that of π-π interactions (~ 2 kcal/mol for benzene dimer) [48], much lower than that of a typical hydrogen bond (4–15 kcal/mol) [49] or a typical coordination bond (21 kcal/mol for Cu(II)–N bond) [50] and far lower than that of a covalent bond (85 kcal/mol for C–C bond) or ionic interactions (183 kcal/mol for NaCl) [50, 51]. It is worth noting that the vdW forces in a non-vacuum environment (such as a liquid environment) will be even weaker, which make it the weakest non-covalent interactions in most cases.

Although the vdW forces have been measured at the single-molecule level in this study, many questions of vdW forces remain unsolved. Among others, two of them are listed below. 1) There are three components that contribute to the total vdW forces: the induction force, the orientation force and the dispersion force. To date, it is still difficult to quantify the exact contribution of each component. 2) The descriptions of vdW forces at both the macroscopic and the atomic scale are satisfying. However, it is difficult to describe the vdW forces at the molecular scale.

4 Conclusion

In summary, by using high vacuum SMFS, the vdW forces between a polymer chain and a solid surface are directly detected. In high vacuum, the mean vdW forces between a PEMA repeating unit and the solid substrate, i.e., HOPG and paraffin, are ~ 54 and ~ 27 pN, respectively. For PDHF, lower vdW forces are detected (~ 38 and ~ 21 pN on HOPG and paraffin, respectively) due to the smaller size of repeating unit than that of PEMA. These experimental results are in good agreement with those estimated in theory. In a liquid environment, however, the vdW forces are estimated to be several pN or even less, which are difficult to be detected by AFM. It is greatly anticipated that this approach can be applied to directly detect other noncovalent interactions (such as hydrogen bond and π-π stacking) at the single-molecule level in the future.

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