

Imaging, polymerization, and reconstruction of polystyrene films with a scanning tunneling microscope

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(Received 6 March 1997; accepted 10 March 1997)

Polystyrene microparticles can be investigated by using a scanning tunneling microscope. The observed images show the hydrogen atoms on the phenyl groups and the extended polymer chains without entanglement. After a sustained tip scanning, some of the polystyrene surfaces develop a highly ordered structure. Furthermore, the polymerization of styrene monomers can be initiated by the tip field, to form nanometer-scale polystyrene films on graphite substrates, in air at room temperature. The yield was verified by time-of-flight secondary ion-mass spectroscopy. © 1997 American Vacuum Society. [S0734-211X(97)01504-7]

I. INTRODUCTION

A scanning tunneling microscope (STM)¹ can give atomic resolution imaging of solid surfaces which have, in principle, sufficient electrical conductivity. Otherwise an atomic force microscope (AFM)² is preferable. However, in recent years, it has been found that some very thin polymer films, e.g., polyethylene,^{3,4} poly(1-butene),⁵ polybutadiene,⁶ poly(ethylene oxide),⁷ and single-molecule, single crystal of isotactic polystyrene⁸ can be imaged by STM. For poly(methyl methacrylate), polydiphenyl-siloxane, and conventional polystyrene,⁹ surface morphology can be shown without molecular details. There is still a lack of clear understanding of the mechanism, however, in the case of polystyrene, the image resolution apparently depends upon physical and chemical states of the polymers. This article reports our studies on surfaces of polystyrene microparticles (PM). Their structures can be imaged with high resolution and reconstructed under sustained operation of a STM.

Besides the imaging function, the electric field of the STM tip under normal operating conditions has drawn our attention. The tip-sample distance is only on the order of 0.1 nm, therefore, even though the voltage applied between them is very low (<1 V), the electrostatic field produced is extremely high. This field has already induced the tunneling current for STM imaging,¹⁰ and proved to be a good means for submicron processing and/or atom manipulation.¹¹ This article examines some additional effects, e.g., surface polymerization and surface reconstruction. It is remarkable that a high-resolution, real-time observation is possible during the evolution of a surface. This is unique and thus makes the STM a multifunctional tool.

II. IMAGING OF POLYSTYRENE MICROPARTICLE SURFACES

The conventional atactic polystyrene with entangled polymer chains has never been seen by atom-resolved STM, yet the single molecule, single crystal of isotactic polystyrene can give a rough STM image. Very recently we have applied

STM to the investigation of surfaces of PM prepared by microemulsion free-radical polymerization,¹² where each particle contains only one or a few high molecular weight polymer chains which are strictly constrained in a very limited space (about 20 nm in diameter). The PM has been found to have different properties from ordinary atactic polystyrene.¹³⁻¹⁵ In our case, the molecular weight of the PM is about 1×10^6 .¹⁵

Highly oriented pyrolytic graphite (HOPG) was selected as the substrate because it is clean, inert, conductive, and defect-free in a relatively large area. Moreover, since the surface structure of HOPG is universally known, the STM image obtained cannot be confused with the substrate. After mixing PM with de-ionized water by ultrasonic stirring, a drop of the aqueous suspension was deposited on a substrate of freshly cleaved HOPG, then dried naturally at room temperature for a week. A film of PM was formed on HOPG. Scanning electron microscopy (SEM) showed that film surfaces, although rugged, were fully covered with PM.

Our STM is a combination of hardware CSTM-9000 made by the Institute of Chemistry, CAS, and a software written by ourselves. The software has the ability to permit fast data acquisition, fast image processing, and allows four different images to be displayed simultaneously for an effective comparison of surface structural changes. The STM tips were made of Pt-Ir. All images were obtained in air under ambient conditions. Experimental results can be summarized as follows.

(1) The PM surface had different modes of coagulation. In most regions of the surface, the tip current was not stable and the background noise level was very high, hence no STM image could be obtained. However, at least in some regions, the surface could be imaged clearly. Figures 1(a) and 1(b) were two images obtained from a region with different magnification. The STM images sometimes varied from region to region, however, no entangled polymer chains were ever observed.

(2) In high-resolution STM images, generally there are two or three bright spots assembled together to construct groups of spots [Fig. 2(a)]. In a typical group of two spots, the measured distance between them is about 2.5 Å. In a

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group of three spots, usually the middle spot is the brightest one, and the maximal distance between two terminal spots can reach 4.3 Å. We proposed that these bright spots might be the STM images of hydrogen atoms on the upward rim of phenyl groups. The phenyls are sitting vertically on the polystyrene surface, hence the hydrogen atoms are higher than other atoms and thus give brighter spots.^{16,17} This statement was further substantiated as follows. Assuming that the structure of a phenyl group is nearly identical to that of a benzene molecule,¹⁸ where the C–C distance is 1.395 Å and C–H distance is 1.08 Å, we can calculate the horizontal distances between the upward H atoms for three different modes of phenyl groups sitting vertically on the surface, as shown in Fig. 2(b). The computed results, d_A , the maximal distance between two terminal spots of a three-spot group, and d_C , the distance between two bright spots of a two-spot group, are 4.30 and 2.48 Å, respectively. When the phenyl group is not sitting symmetrically to the normal of the surface, the distance d_B should be shorter than d_A but longer than d_C . In this case usually one spot is very faint. Therefore, we only measured d_A and d_C as the criterion of H sites. The results are 4.3 and 2.5 Å, respectively, which is in good agreement with the computed values.

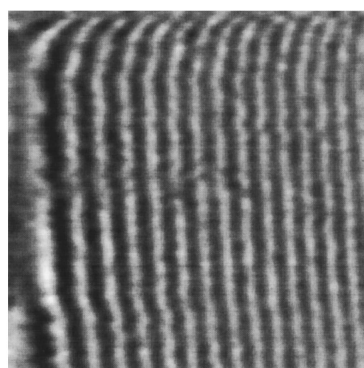
(3) Since the phenyl groups are sitting vertically, we cannot see their cyclic structures directly. However, the alignment of the spot groups gives a definite orientation, from which the projection of the phenyl groups on the surface, and

then the orientation of the phenyl plane, can be decided. The ability to determine the orientation of phenyl plane promises great importance in studying the interaction between the phenyl groups.

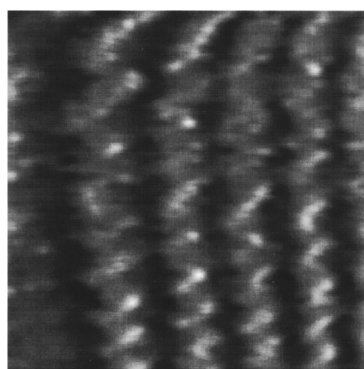
III. STACKING OF PHENYL GROUPS

Noncovalent interaction between aromatic units plays a major role in determining the properties and the behavior of molecules. Mitchel and Windle¹⁹ suggested the existence of the phenyl stacks in polystyrene glasses according to the measurement of the wide-angle X-ray scattering, yet it has never been seen. Here a direct observation of the stacking has been realized for the first time.

Figure 3(a) shows that on the PM surface many large, elongated spots are arranged in well defined chains. As mentioned previously, these large spots which consist of two or three smaller ones correspond to phenyl groups that are vertically sitting in parallel. This arrangement can be compared to a stack of coins standing on their rims and leaning against one another, in which each coin represents a phenyl group. We believe we have seen the stacking of phenyl groups.¹⁹ It is noticeable that the phenyls stacked with a direction parallel to the axis of the polymer chains; however, this direction is not perpendicular to the phenyl plane but at an angle of about 65°, as shown in Fig. 3(b). This is similar to the proposed “most stable” parallel-displaced (PD) structure^{20,21} for benzene dimers by *ab initio* calculations. In the case of stacking, since more than two phenyls are involved, the stacks appear as the multiple PD structure. Because each

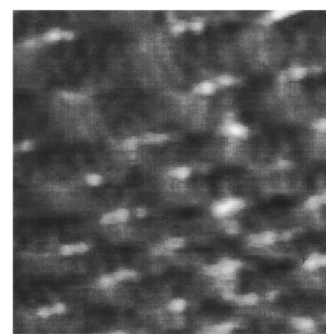


(a)

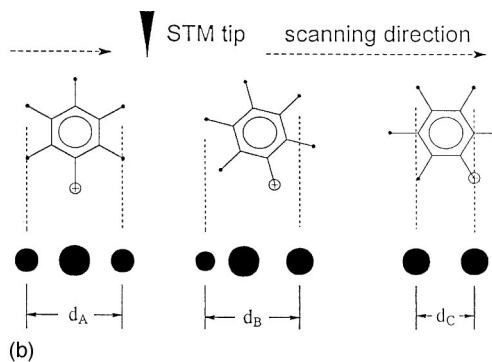


(b)

FIG. 1. STM images of a polystyrene surface. (a) 10.5 nm×10.5 nm; (b) 4.0 nm×4.0 nm.



(a)



(b)

FIG. 2. (a) High resolution STM image of polystyrene surface, 3.7 nm×3.7 nm. (b) The models for explanation of three typical images of hydrogen atom groups. In this schematic drawing, a bigger spot means brighter.

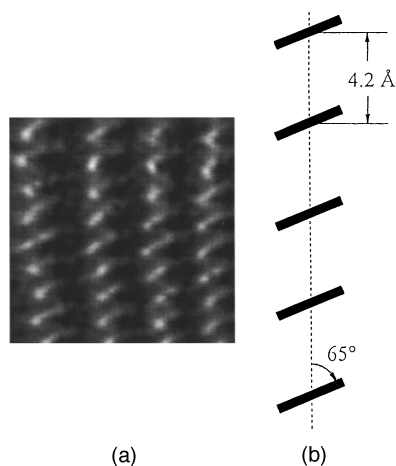


FIG. 3. (a) An STM image of phenyl stacks, $3.7 \text{ nm} \times 3.7 \text{ nm}$. (b) A model of the multiple PD structure for the stacking of phenyls.

phenyl group participates in two PD structures and the phenyls are bound on the polymer chain, the distance between two neighboring phenyls (4.2 \AA) is slightly larger than that in a benzene dimer (3.9 \AA).²¹ This kind of stacking may greatly affect the conformation and properties of the polymer.

IV. WAGGING MOTION OF POLYMER CHAINS AND RECONSTRUCTION

In our STM, the information obtained from two directions of tip scanning, i.e., from left to right (L-R) and from right to left (R-L), can be separately collected, and two images may be plotted. In the case of PM, it is found that the STM images on the same surface area dramatically depend on different tip scanning directions, L-R and R-L, as shown in Figs. 4(a) and 4(b), respectively. It implies that the segments of polymer chains can be dragged by the STM tip at the scanning direction, and squeezed to the end terminal of every scan. Obviously they are essentially symmetrical but not identical because the chains are not inherently perpendicular to the scanning direction of the STM tip.

The dragging effect has been ignored when metals, alloys, and oxides are imaged, because the STM tip cannot drag these atoms or molecules under ordinary operating conditions of a STM. For instance, when a bare HOPG is imaged, no dragging effect can be seen. The dragging effect for polymers is not surprising. The effect of drag of the AFM tip has been reported and even molecules can be pulled out by the atomic force.²² Since STM has a very intense electric field, we proposed that the effect may be more dramatic. In the case of polymers like polystyrene, the polymer chains, especially the phenyl groups, are highly polarizable and thus can be easily polarized under the tip field. Consequently, an electrostatic attractive force should exist between the STM tip and the chains. While the tip is moving to-and-fro, the polymer chains are dragged accordingly to cause a wagging motion.

As a direct result of the wagging, under some circumstances the scanning electric field can induce the ordering

surface reconstruction. Figure 5 showed that the surface structure can be varied with time under a sustained tip scanning. At the very beginning [Fig. 5(a)], on the first received STM image, only small spots can be seen. After scanning 2 min, the image [Fig. 5(b)] showed that instead of small ones, numerous larger and longer bright spots were observed. As mentioned previously, these might represent the phenyl groups. To continue the scan makes the images clearer and more orderly. Finally, after 30–40 min, a stable reconstructed surface was available, as shown in Fig. 5(c). The created surface has a closely packed structure. The crystal-like surface suggests the existence of phenyl stacking. It implies that the phenyl groups are not only on the same polymer chain but also on the neighboring chains stack. The arrangements of phenyls in the stacks tends to interlock neighboring chains and accordingly results in the crystal-like structure.

Generally speaking, the successive wagging motion of chains caused by the to-and-fro scanning field gives an opportunity for every phenyl group to arrange according to minimum potential energy requirements, hence it gives the periodic structure. This result also implies that an intense scanning electric field can be used for surface modification.

V. THE INLAYLIKE SELF-ASSEMBLY OF POLYMER CHAINS

We have also investigated the PM swelled with a small amount of benzene. The solution that contained nonsoluble

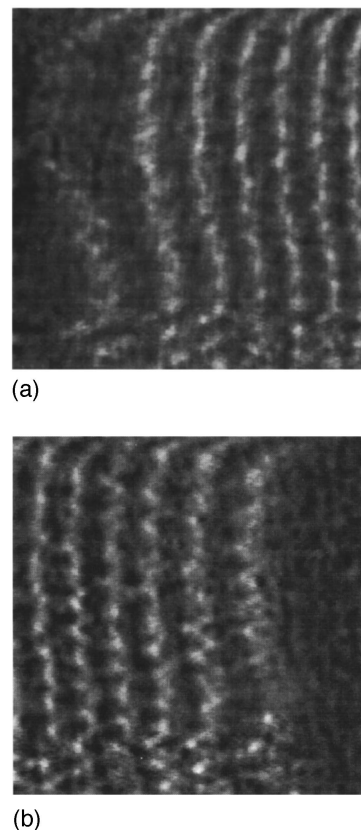
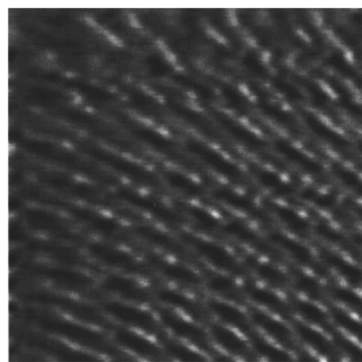
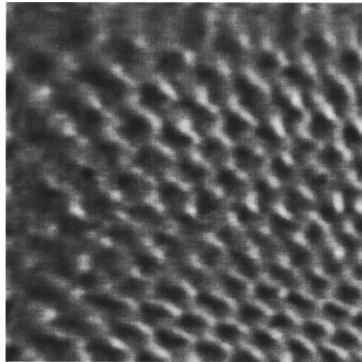


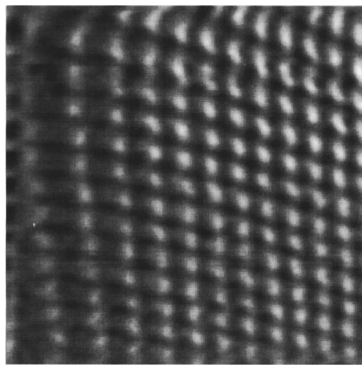
FIG. 4. STM images from the same region of polystyrene surface but with different scanning directions, $5.3 \text{ nm} \times 5.3 \text{ nm}$: (a) L-R; (b) R-L.



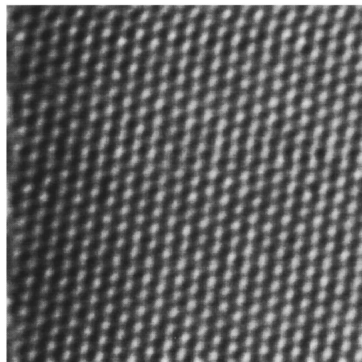
(a)



(b)

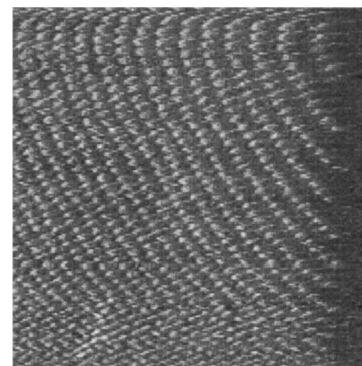


(c)

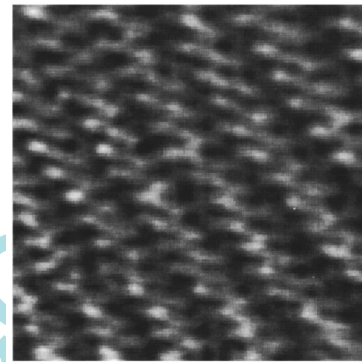


(d)

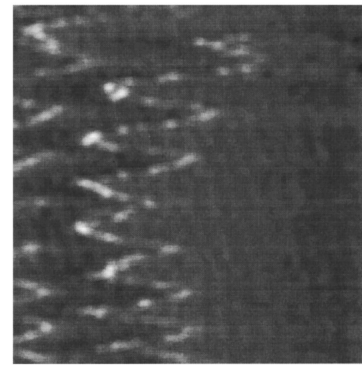
FIG. 5. STM images of the surface reconstruction, $5.3 \text{ nm} \times 5.3 \text{ nm}$: (a) the first received; (b) 2 min later, (c) the final, 0.5 h later. An HOPG surface structure (d) of the same size under the same operating conditions, is used for comparison.



(a)



(b)



(c)

FIG. 6. STM images of swelled polystyrene surface: (a) $19.3 \text{ nm} \times 19.3 \text{ nm}$, (b) $7.5 \text{ nm} \times 7.5 \text{ nm}$, (c) $5.3 \text{ nm} \times 5.3 \text{ nm}$.

particles was deposited on a HOPG surface. After drying, the STM images also revealed different modes of surface coagulation. An image with a relatively larger scale is presented in Fig. 6(a). The bright spots arranged as a chainlike structure might be the extended polymer chains. Further decreasing the scanning area for a better resolution, the fine structure can be seen, as shown in Fig. 6(b), where the polymer chains self-assembled as an inlaylike form. The image with the best resolution is shown in Fig. 6(c), where the inlaylike self-assembly seems more distinct. But, since the chains are dragged by the STM tip and squeezed onto one side of the image, only two chains can be seen in this scanned area.

From Figs. 6(b) and 6(c), we can see that the shape of polymer chains is similar to helixes. The measured pitch of

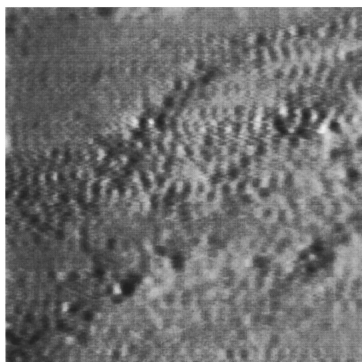


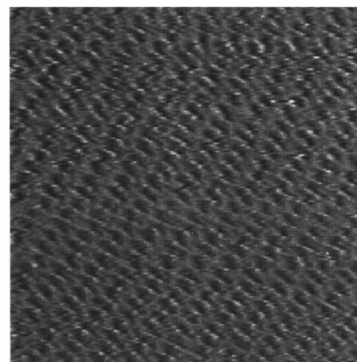
FIG. 7. STM image of the region which was directly under the intense electric field, 10.5 nm×10.5 nm.

the helix is about 0.6 nm, which is in good agreement with the measured value for c axis in a crystalline cell of isotactic polystyrene by x-ray diffraction.²³ This is interesting, but no satisfactory explanation is available now.

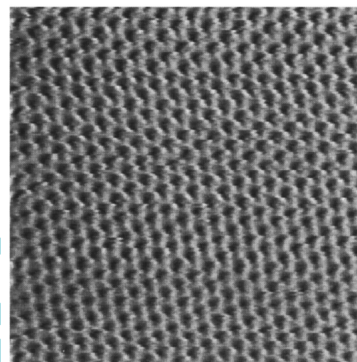
VI. FIELD-INITIATED POLYMERIZATION OF STYRENE

Considering that the STM tip can provide an extremely intense electrostatic field (10^9 – 10^{10} V/m), it may be used for some other purposes. Under optimal conditions, no matter how strong this field, the energy of tunneling electrons is relatively low (0.1–1 eV), by which no effect of electron bombardment should be considered. All the effects which happened, if any, should be due to the field itself. Therefore, this is a very good condition to verify pure field effects, and STM itself might be the unique instrument to provide microscopic inspection of these effects. The purpose of this work is to investigate whether any reaction will happen to some monomers under such a field.

A thin film was deposited by one drop of distilled styrene (liquid) on an HOPG substrate. The styrene began to evaporate instantaneously, then a very thin film was formed on HOPG. The sample was put into the STM sample chamber in air at room temperature. No initiator or catalyst was added. With a bias of +0.1 to +1.0 V, a Pt/Ir tip was arranged to be close to the sample for operation with conventional constant-current mode. At the very beginning, the tip current was unstable, and the background noise level was very high. Nothing could be observed. But after a couple of minutes, the tunneling current became stable. The STM gradually presented a rugged topographical image, as shown in Fig. 7. When the STM tip was moved to a new neighboring region, the first received STM image showed some flat and uniform surfaces with slightly ordered structures, as shown in Fig. 8(a). When the tip was continuously scanning, the figure became more and more orderly, and finally the surface presented a crystal-like structure, as shown in Fig. 8(b). It implies that the scanned area behaves as a “crystal seed,” and the crystalline structure can be automatically self-extended under suitable conditions.



(a)



(b)

FIG. 8. STM images of a reconstructing polystyrene film, 5.3 nm×5.3 nm: (a) initial image, (b) final image (after sustained scanning for 6 min).

We further discovered that the initiation of polymerization was not dependent on scanning at all. If the tip stayed at any fixed point for 2–5 min with an applied bias voltage, the result was just the same. For confirmation of the product, it was analyzed by a time-of-flight type secondary-ion mass spectrometer (TOF-SIMS). The instrument used in our investigation is a TFS-2000 MPI produced by Charles–Evans and Associates Co. A gallium liquid metal ion source delivers a Ga^+ ion current of 60 pA at 15 keV. Compared with the existing data of static SIMS,²⁴ we found that our product shows all the known characteristic fragments of polystyrene, i.e., negative ion peaks with mass number 37 (C_3H^-), 49 (C_4H^-), 62 (C_5H^-), 73 (C_6H^-); positive-ion peaks of 51 (C_4H_3^+), 63 (C_5H_3^+), 77 (C_6H_5^+), 91 (C_7H_7^+), and relatively weak but important signals of 107, 115, 128, 152, 165, 178, 193, 207, 221, and 281. After analysis the sample was kept in vacuum environment under room temperature for 23 h, and then re-analyzed by TOF-SIMS. The resulting mass peaks were very reproducible.

VII. CONCLUSION

Structures of PM prepared by the microemulsion method differ from conventional atactic polystyrene. The surfaces of PM can be imaged by STM with high resolution. The STM images revealed the existence of the orderly stacked phenyls and polymer chains which is impossible for ordinary polystyrene. The extended polymer chains can be dragged by the

STM tip. Furthermore, the intense scanning field can induce the ordered surface reconstruction. The hydrogen atoms on the phenyl groups are distinguished by atomic resolution imaging, and accordingly the orientation of the phenyl plane can be determined. In some cases, the phenyl groups are found to be stacking as the parallel-displaced (PD) structure.^{20,21} This experimental observation supports the results of *ab initio* calculations for benzene dimers. The inlay-like self-assembly of polystyrene chains is of value in studying the aggregation of polymers. Together with other experimental results, our observation may provide a deeper insight into the PM microstructures.

It was proved that styrene monomers can be directly polymerized to form a thin polystyrene film under an intense electric field, in air at room temperature. Disregarding tip scanning, the active center can be an area or simply a point. However, only after a sustained scanning of field will the polystyrene film on a single-crystal surface have a highly ordered reconstructed structure. This process can be regarded as the growth of epitaxial polymer film on a crystalline substrate.^{25,26} Our experiments show that STM can be a unique versatile instrument to initiate polymerization, provide microscopic imaging, and induce surface reconstruction.

ACKNOWLEDGMENTS

The authors thank R. Shen, T. Y. Yu, and Y. M. Lu for helpful discussions. They also appreciate X. L. Lu for providing the PM sample and Y. F. Chen for his outstanding work on STM instrumentation. This work is partially supported by the Chinese Natural Science Foundation (CNSF) and the Shanghai Science Foundation.

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