

# Imaging of Hydrogen Atoms and Stacks of Phenyl Groups on the Surface of Polystyrene Microparticles by Scanning Tunneling Microscopy

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## ABSTRACT

Polystyrene microparticles prepared by microemulsion free-radical polymerization have been investigated using a scanning tunneling microscope. It has been found that the polymer chains are extended without entanglement in some regions of the polymer surface. The hydrogen atoms on the upward rim of the phenyl groups can be distinguished by atom-resolved imaging. The phenyl groups in the same chain can stack up as a parallel-displaced structure, similar to that predicted for benzene dimers. The existence of the orderly stacked polymer chains and phenyl groups may be due to the fact that the polymerization is constrained in a very limited space.

## INTRODUCTION

The ability to view macromolecules on an atomic scale promises great progress in understanding the details of their structures. Polystyrene microparticles (PM) prepared by microemulsion free-radical polymerization [1] have been found to have properties different from those of ordinary atactic polystyrene, for example, glass transition temperature [2–5]. However, the structure of the PM still remains unknown. In recent years, scanning tunneling microscope (STM) [6] has made possible

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the imaging of some generally nonconducting polymers [7–11]. Therefore, we have applied STM for investigating PM. In this paper we report that hydrogen atoms and stacks of phenyl groups (phenyls) can be observed by STM.

## EXPERIMENTAL RESULTS AND DISCUSSION

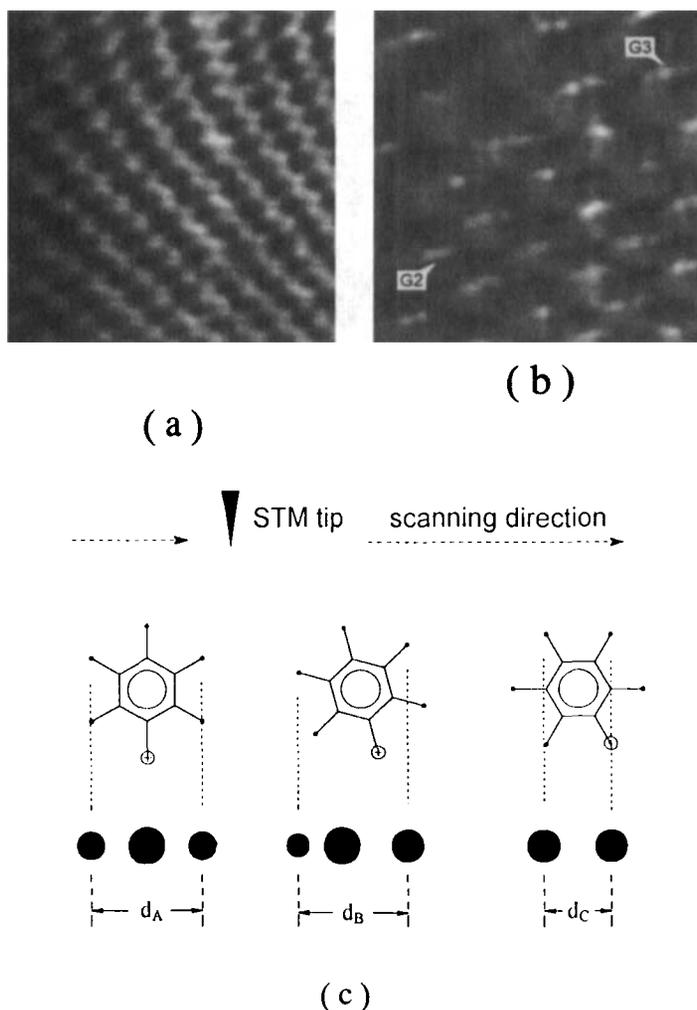
Highly oriented pyrolytic graphite (HOPG) was selected as the substrate because it is clean, inert, conductive, and defect-free in relatively large areas. Moreover, since the surface structure is universally known, the sample images obtained by STM cannot be confused with the substrate. The PM [5] used was newly prepared (molecular weight ca.  $1 \times 10^6$ ). After having been completely washed, deionized water was added to make an aqueous suspension by ultrasonic stirring. Then it was deposited on a freshly cleaved HOPG and dried naturally at room temperature. The dried film could be examined directly by a scanning electron microscope (SEM) without any metallic coating, showing that the HOPG surface was almost fully covered with rugged PM film, the thickness of which was estimated at 50–500 nm.

The STM instrument used was a CSTM-9000 from the Institute of Chemistry, Chinese Academy of Sciences (CAS), whereas the software for data acquisition and processing was written by the present authors. All imaging studies were carried out with Pt–Ir tips in air at room temperature.

The STM was used to investigate the PM surfaces at random. In some regions of the surface, extended polymer chains without entanglement were observed, as shown in Fig. 1(a). An image with a higher resolution, presented in Fig. 1(b), shows that groups of spots are generally formed by two or three bright spots. In a group of three spots (G3), usually the middle spot is the brightest one, and the maximal distance between two terminal spots ( $d_A$ ) can reach 4.3 Å. In a typical group of two spots (G2), the measured distance between them ( $d_C$ ) is about 2.5 Å. We suggest that each group of spots corresponds to the hydrogen atoms on the upward rim of a phenyl group which is sitting vertically on the surface. Since the hydrogen atoms are higher than other atoms, the STM are sensitive to them [12,13]. If we assume that the structure of a phenyl group is identical to that of a benzene molecule ( $R_{CC} = 1.395$  Å,  $R_{CH} = 1.08$  Å) [14], the three different modes of spot groups in Fig. 1(b) are in good agreement with the models shown in Fig. 1(c), where the calculated  $d_A = 4.30$  Å,  $d_B < 4.30$  Å, and  $d_C = 2.48$  Å. In some locations of Fig. 1(b), however, the spot groups are out of shape or not clear enough. This might be due to rotation [15] and/or wagging of phenyls.

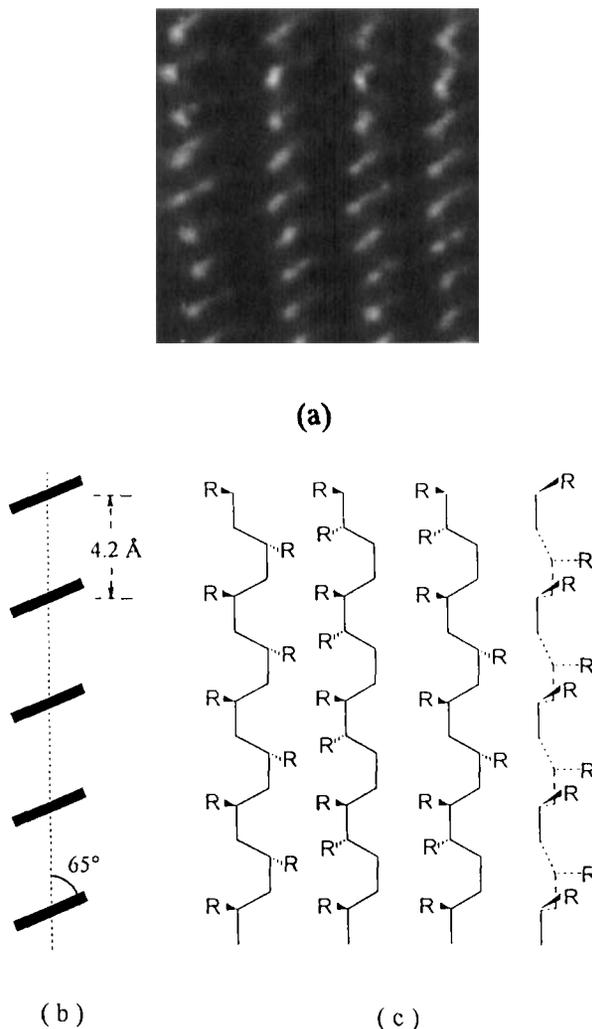
Since the phenyls are sitting vertically, we cannot see their cyclic structure as is typically seen for benzene [16] and naphthalene [17] on metal surfaces. However, the alignment of the spot groups gives a definite orientation, from which the projection of the phenyls on the surface, and thus orientation of the phenyl plane, can be decided.

Figure 2(a) is a STM image obtained in another region. An array of many large, elongated spots in well-defined chains is shown, where some of the spots are composed of two or three smaller spots corresponding again to hydrogen atoms on the phenyls. However, the length of some of the large spots, particularly those in the left part of Fig. 2(a), can be larger than 4.3 Å. This might be due to the motion of the phenyls caused by the scanning tip. The distance between two neighboring chains is near 10 Å. Hence the interaction between phenyls on different chains could



**FIG. 1.** STM images of the PM surface. Constant current mode. The tunneling current was 0.88 nA and the bias voltage was 0.500 V (tip positive). (a) 7.5 nm  $\times$  7.5 nm; (b) 3.7 nm  $\times$  3.7 nm; (c) models for explanation of three typical images of hydrogen atom groups. For example, G2 is a group of two spots and G3 is a group of three spots where the middle spot is obviously the brightest. In these schematic drawings, a bigger spot indicates a brighter one.

be neglected. On the same chain, the phenyls are parallel and the distance between two neighboring phenyls is around 4.2 Å. We suggest we are observing the stacking of the phenyls [18]. It is noticeable that the phenyl planes are not perpendicular to the direction of the stacking, which is parallel to the axis of the polymer chains, but at an angle of ca. 65°. This is similar to the proposed “most stable” parallel-displaced (PD) structure [19,20] of benzene dimers. Since more than two phenyls are involved in stacking, it appears as the multiple PD structure, as shown in Fig.



**FIG. 2.** STM image of another region on the PM surface. Constant current mode. The tunneling current was 0.88 nA and the bias voltage was 0.500 V (tip positive). (a) 3.7 nm  $\times$  3.7 nm; (b) a model of the multiple PD structure for the stacks of phenyls; (c) four of the possible structures for the polystyrene chain segments (R = phenyl group), according to the image in (a).

2(b). This kind of stacking may greatly affect the polymer's conformation and properties.

On the basis of Fig. 2(a), the polymer chain skeleton might adopt a unique conformation in which the skeletal carbon atoms are nearly sitting on the same plane, as shown in Fig. 2(c). Since only the upward oriented phenyls can be observed, while the downward phenyls cannot, the chain segments may have many possible structures, for instance, the four presented in Fig. 2(c). These unusual structures can explain the STM image. Unfortunately, it is difficult to determine

which one is the real structure of the chain segments. The mechanism by which the unusual structures are formed is not yet clear. One possible explanation is that, under the constraint of very limited space, the styrene monomers might stack in an orderly fashion in some parts within micromicellae of surfactant. Hence they can be polymerized according to proper selection rules. As a result, the polymer chains in some regions may have similar structures, and they can be closely stacked in order.

Finally, we should state that only the extended polymer chains without entanglement could be imaged clearly and repeatedly. In most regions of the film surface, however, the STM cannot obtain clear images, because, most probably, entangled chains exit in these regions. Some weak crystal-like x-ray diffraction peaks from these samples [5] might indicate the orderly stacked regions.

## CONCLUSION

In summary, we have used the STM to image the PM [5] prepared by micro-emulsion free-radical polymerization. In some regions of the polymer surface, the STM images reveal orderly stacked phenyls and polymer chains, which is generally impossible for ordinary polystyrene. The unusual structures and coagulation may be one of the reasons why the PM are very different from ordinary polystyrene in properties. We also find that the phenyls stack up as the multiple PD structure. This experimental observation supports the results from *ab initio* calculations for benzene dimers [19,20]. Our observations might be a meaningful step toward the studies of polymer structures as well as the interaction between organic groups.

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