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SHORT COMMUNICATION

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Observation of nanoparticles and film formation by scanning tunneling microscopy: methyl methacrylate/butyl methacrylate nanoparticles prepared by microemulsion polymerization

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Abstract Latexes as dispersions of poly(methyl methacrylate-*co*-butyl methacrylate) copolymeric nanoparticles within water were produced by microemulsion polymerization of the respective comonomers. Polymer yield, number-average and weight-average molecular weights, polydispersity index, and the glass-transition temperature of the copolymer produced were 50%, 8.8×10^4, 2.54×10^5, 2.87, and 45 °C. Scanning tunneling microscopy (STM) images of the latex nanoparticles and film formation on highly oriented pyrolitic graphite (HOPG) were obtained with a 2 V sample bias and a tunneling current of 20 pA. The STM pictures revealed that the particle size was 18 ± 3 nm. There was no film formation in the case of dehydration at room temperature. There was some coalescence of particles when the HOPG surface was preheated at 55 °C, while complete film formation was achieved when the latexes were annealed at 55 °C in an oven for about 10 min.

Key words Scanning tunneling microscopy · Latex · Nanoparticles · Film formation

Introduction

Water-based latex formulations, in which polymeric microspheres are dispersed within an aqueous medium, have been utilized in a wide variety of applications in coating and adhesive technologies, the biomedical field, and the information industry and microelectronics. In many of these applications, for example, coatings and adhesives, latexes form thin polymer films on a substrate surface. The properties (mechanical, optical, transport, etc.) of the final film should be tailor-made according to the application. When the latex is cast onto a substrate, upon dehydration of the dispersion, the polymeric particles approach each other and eventually stick and, subsequently, fuse to each other by interdiffusion of the polymer chains and form continuous clear films by complete welting [1–3].

Recently, atomic force microscopy (AFM) has provided coating researchers with a new direction to analyze latex particles (morphology and size) and also film formation mechanisms [4–19]. Alternatively, scanning tunneling microscopy (STM) can also give high-resolution imaging of surfaces and structures on the surfaces, which have, in principle, efficient electrical conductivity. In recent years, it has been found that some very thin polymer films can also be investigated by STM [20–27]. In this study, we attempted to visualize latex particles and also film formation process by STM. Latexes as dispersions of poly(methyl methacrylate-*co*-butyl methacrylate) [poly(MMA/BMA)] copolymeric nanoparticles within water were produced by microemulsion polymerization. We report the STM analysis of these nanoparticles and their film formation abilities.

Materials and methods

The monomers MMA and BMA (Fluka, USA) were treated with an aqueous solution of NaOH (10% by weight) to remove the inhibitor. The surfactant cetyltrimethylammonium bromide (CTAB) (Fluka, USA) and the initiator potassium persulfate (Aldrich, USA) were used as received. The dispersion medium was distilled/deionized water. Microemulsion polymerizations to obtain the latex containing poly(MMA/BMA) nanoparticles were carried out in a ternary oil-in-water system. The mixture containing proper amounts of the comonomers (MMA and BMA) was added to the aqueous solution of CTAB in a 100-ml glass reactor which was agitated at room temperature by means of a magnetic stirrer for about 10 min. It was then stored at 4 °C for about 24 h to reach equilibrium. Prior to polymerization, initiator was added to the solution and nitrogen gas was flowed through the medium for about 1–2 min to remove dissolved oxygen. The reactor was then placed in a shaker in a temperature-controlled bath and polymerization was realized at a constant temperature of 60 °C for 24 h. Note that prior to the polymerization the medium was a transparent liquid, while after polymerization the latex obtained was bluish and clear. Washing the latex particles with methanol and water several times cleaned the latex (removed the surfactant). The total monomer contents and the initial concentrations of the surfactant and initiator were 6.33%, 9.3% (by weight), and 2.5 mM (based on water). The latex used in this study was prepared by using a MMA/BMA ratio of 1/3 (by weight).

The polymerization yield was obtained by extraction of copolymer from the latex particles by chloroform and by weighing the solid phase after complete removal of the unconverted monomers by controlled drying. The molecular weights of the polymers were determined by gel permeation chromatography using a Shimadzu 10A liquid chromatography system equipped with a RID 10A detector (Shimadzu, Japan). The column used was a Shimadzu GPC 804 and the eluant was chloroform. The flow rate was maintained at 1.0 ml/min. Polystyrene standards (Pressure Chemica, Pa., USA) 5 g/L in chloroform) were used for the calibration. The high-resolution ^{1}H-NMR spectrum of the copolymer was recorded in $CDCl_3$ on a 500 MHz NMR spectrophotometer (Brucker, USA). The glass-transition temperature (T_g) of the copolymer produced was measured using a Shimadzu model DSC-50 differential scanning calorimeter (Shimadzu, Japan) and 5 mg samples at a scan rate of 10 °C/min from 25–300 °C followed by rapid cooling.

The scanning tunneling microscope was constructed in our laboratory [28]. It consists of two main modules. The scanner part is constructed with a piezo tube (PZT) (EBL no. 3 PZT-5H, Staveley Sensors, Conn.) glued to an aluminium body. Electrical connections to the PZT are through a special connector. The coarse positioner is a magnetically driven slider which is fastened to the scanner and the whole system is mounted on a vibration isolation stage.

For STM imaging of the latex particles, the latex samples (5 μl containing 0.1 mg particles/ml) were deposited onto freshly cleaved highly oriented pyrolitic graphite (HOPG). The samples were dried at room temperature. Then, the STM images were taken with a 2V sample bias and a tunneling current of 20 pA. Etched tips of Pt/Ir (4:1) wires (0.5 mm in diameter, Digital Instruments, Santa Barbara, Calif.) were used. Prior to use the tips were washed in acetone. The color was added using PhotoShop v3.0 (Adobe Systems, Calif.) to enhance the details. For film formation experiments, the HOPG samples were brought to a temperature of 55 °C in an oven. The latex samples were placed on these HPOG surfaces, and the whole system was brought to room temperature prior to STM imaging (in about 5 min), which was performed under the same conditions as given previously. In the last group of experiments, the dispersion was put on the HOPG surface equilibrated at 55 °C and the whole system was placed in the oven. The HOPG samples were taken from the oven after 5, 10, or 15 min and were brought to room temperature for STM imaging.

Results and discussion

We produced several latexes containing acrylate-based copolymeric nanoparticles by microemulsion polymerization by changing the polymerization recipe and conditions. We selected the poly(MMA/BMA, 1/3) copolymeric particles for demonstration of film formation using STM. The properties of the latex obtained using the recipe and polymerization conditions given in the previous section are presented in Table 1.

As shown the polymerization yield is about 50%, the average molecular weights are quite high, and T_g is about 45 °C, which are typical in these types of microemulsion polymerizations [29–31]. From these values one expects that even if the T_g is higher than room temperature, this latex can form a film at room temperature due to the high monomer content, which is most probably left in the particles (the swollen particles, swollen with its comonomers). However, the average molecular weights are quite high; thus, the film formation is expected to be slow at room temperature. Therefore, in this study, just for demonstration, we heated the HPOG substrate to a temperature of 55 °C for film formation in a shorter time.

HOPG was selected as the substrate because it is clean, inert, conductive, and free of defects over a large area. Moreover, since the surface of HOPG can be observed well with STM, the substances can be clearly identified.

Upon dehydration of the dispersion at room temperature, the nanoparticles on the HOPG surface were directly imaged in air. Some representative STM images are given in Fig. 1. Figure 1a shows a low-magnification STM image of the nanoparticles with a scan area of 2 × 2 μm. This image reveals the nanoparticles are quite spherical and well dispersed (no agglomeration) on the graphite surface and there is no sign of film formation. A more detailed three-dimensional STM image of the nanoparticles is shown in Fig. 1b with a scan area of 0.36 × 0.36 μm. The height and size of the nanoparticles were measured by taking the line profiles as exemplified in Fig. 3c. This profile was taken over two particles which are touching each other, but which are not starting to fuse (see the curves given at the bottom of Fig. 1c). From the line profiles we estimated the average particle size as 18 ± 3 nm.

In order to observe the initial state of the interaction of the latex particles, we first heated the substrate (i.e., HOPG) to 55 °C and then dropped the latex (5 μl) on its

Table 1 Properties of the poly(methyl methacrylate-*co*-butyl methacrylate) copolymer (1:3 ratio) obtained by microemulsion polymerization

Polymerization yield (%)[a]	50
Number-average molecular weight[b]	8.8×10^4
Weight-average molecular weight[b]	2.5×10^5
Polydispersity index[b]	2.9
Glass-transition temperature[c]	45

[a] [(Comonomers used – copolymer obtained)/comonomers used] × 100

[b] Obtained by gel permeation chromatography

[c] Obtained by differential scanning calorimetry

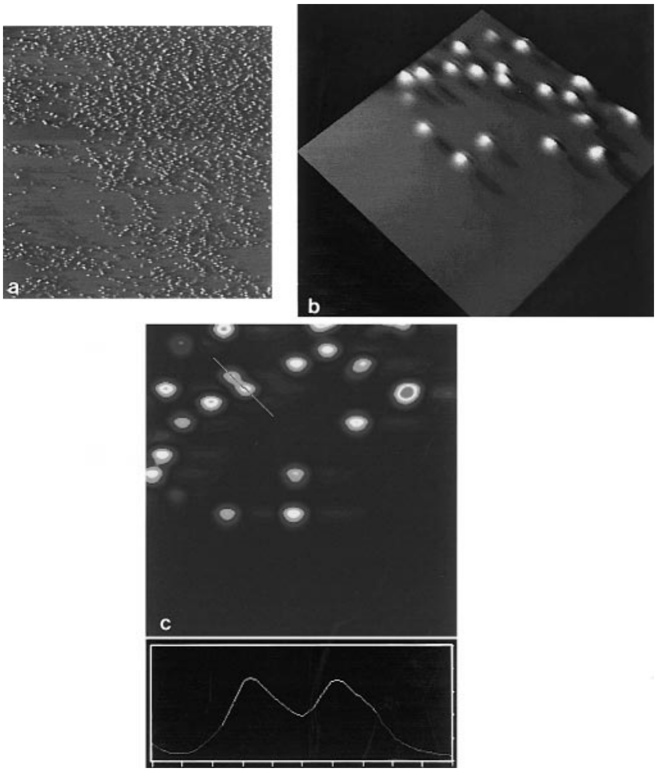

Fig. 1a–c Representative scanning tunneling microscopy (*STM*) images of the poly(methyl methacrylate-*co*-butyl methacrylate) [*poly(MMA/BMA)*] nanoparticles on a. highly oriented pyrolitic graphite (*HOPG*) surface, which was at room temperature. **a** Scan area: 2 × 2 μm (two-dimensional, colored); **b** scan area: 0.36 × 0.36 μm (three-dimensional, colored); **c** scan area: 0.36 × 0.36 μm (two-dimensional, colored)

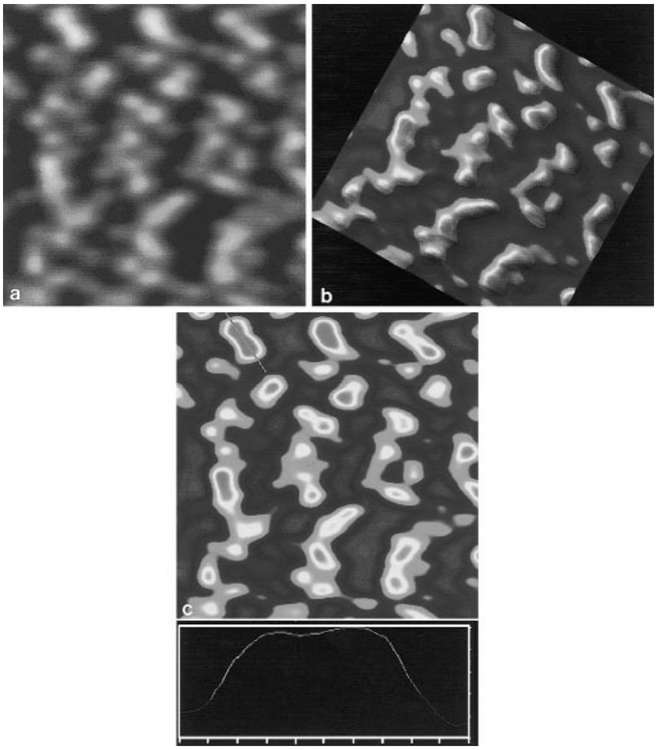

Fig. 2a–c Representative STM images of the poly(MMA/BMA) nanoparticles on a HOPG surface, which was first at 55 °C, but which was rapidly brought to room temperature. **a** Scan area: 2 × 2 μm (two-dimensional, colored); **b** scan area: 0.36 × 0.36 μm (three-dimensional, colored); **c** scan area: 0.36 × 0.36 μm (two-dimensional, colored)

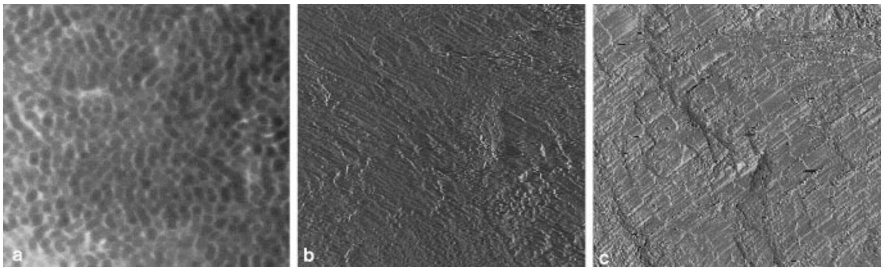

Fig. 3a–c Representative STM images of the poly(MMA/BMA) nanoparticles and film formation on a HOPG surface, which was maintained at 55 °C for different periods of time. Scan area: 0.36 × 0.36 μm (two-dimensional). **a** Annealing time: 5 min; **b** annealing time: 10 min; **c** annealing time: 15 min

surface. During the cooling period, which was only about 5 min, water was also evaporated. Because the initial temperature was over the T_g, the polymer phases in the particles were able to start interparticle fusion as shown in Fig. 2. Two or more particles were already in contact with each other upon drying. The line profile given in Fig. 2c reveals that the particles were not only in contact, but that they had already fused with each other. Since the temperature decreased rapidly below the T_g of the copolymer, even to room temperature, there was no continuous film formation. Note that we took STM images of these samples again after about 24 h at room temperature, but we did not see any sign of further flocculation or film formation.

Therefore, we designed the third step of the study, in which the latex sample was placed on the HOPG surface equilibrated at 55 °C and was immediately put in the oven (at a constant temperature of 55 °C. The samples were taken at selected intervals (5, 10, or 15 min) and cooled rapidly to room temperature prior to STM imaging. Figure 3a shows that all the particles are already contacting and that they even formed something like a porous surface film, but that they had certainly not fused completely after 5 min annealing in the oven. However, the continuous films were clearly observable (no sign of individual particles left) after 10 and 15 min annealing.

Conclusion

This study shows for the first time that STM imaging can be used to measure the particle size of latex nanoparticles and also film formation process, similarly to the AFM technique; however, it should be noted that with these novel techniques we can only analyze a two-dimensional system, the substrate surface. Film formation is a three-dimensional system and we do not know if the two-dimensional result can be extrapolated directly to a three-dimensional system, such as porosity and pore structure in the bulk, etc; however, our and further studies using the modified forms of these techniques would certainly bring more color to the analysis of related processes.

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