The Observation of Crystalline Structures of Evaporated 8-arm Star Polystyrene in Methylcyclohexane

Nithya Leela Venkataraman

Physics Department, The College of Wooster, Wooster, Ohio 44691

April 30, 2003

The purpose of this experiment was to observe the structures of evaporated 8-arm polystyrene in methylcyclohexane using an optical microscope and an atomic force microscopy. Streetscape structures located on the slides of evaporated 8-arm polystyrene and methylcyclohexane were observed under the AFM to analyze the topography of the material. The streetscape structures resulted from trenches that were 300nm deep and 900nm wide. The length of one of the protruding branches of the streetscape structures was 10 microns.

INTRODUCTION

The star polymer that is being observed is 8-arm star polystyrene in the solvent, methylcyclohexane. The solution of star polystyrene and methylcyclohexane evaporated from a homogenous (one-phase) state.

When in solution, the branches or arms of a molecule of star polystyrene have a tendency to become flimsy and entangled with its own arms or with the arms of other molecules of star polystyrene. Hence, when observed in solution, several molecules of star polystyrene will be found clustered together or balled up within the molecule's own arms. The radius of a molecule of star polymer when entangled in its own arms and clustered into a ball is known as the radius of gyration.

A 5 mm cell containing an evaporated solution of 8-arm star polystyrene and methylcyclohexane was observed. After evaporation, the solution was exposed to air and kept at room temperature. An unexpected development of crystalline features took place inside the cell. Growth with respect to time was observed. The solution had formed a clear gel like material against the sides and the bottom of the glass cell. Over time, the edges of the gel, where the material was in contact with the glass, had grown a thick, solid band and had several, unique, crystalline characteristics seen under an optical microscope at different magnifications. The purpose of this experiment is to observe the similar growth process and the unique characteristics using an optical microscope and an Atomic Force Microscopy (AFM).

The optical microscope is helpful in recognizing and locating unique crystalline characteristics at 10-1000 micron scale size. The optical microscope has three magnifications of 5, 10, and 40, and three plates, a white light plate, a cross polarized plate, and a quarter wave plate. The white light plate allows to naturally view of the material. The cross polarized plate indicates whether the material that is being observed is optically active.

The Atomic Force Microscopy, also known as the AFM, is a valuable tool to understand and observe the topography of materials with great resolution. The AFM has a tiny tip that scans the surface of the materials. In tapping mode, the tip moves up and down or taps across the x-y plane of the surface locating elevated regions and depressions in the material and measuring the heights and depths of the region. The AFM allows the surface of materials to be observed at a nanometer scale size.

EXPERIMENT

To create samples on slides, a mixture of star polystyrene and methylcyclohexane was created. This involved taking 0.025±0.010 grams of star polystyrene, with molecular weight of 228,000, and adding it to a beaker with 0.52±0.05g of methylcyclohexane present. At first, the solid star polystyrene and the methylcyclohexane did not mix, therefore the solution needed to be heated. The beaker was placed in a tray of water, and then onto a heater where the solution was heated slowly, and stirred to mix the contents. The microscope slides along with a few cover slips were cleaned using acetone. Once the solution was completely mixed, some of the solution was drawn out using a pipet, and one drop of the solution was placed on a few slides and a cover slip was added to a couple of slides. The slides were placed on a tray and then heated under a vacuum at 50°C for an hour to evaporate the solution. The slides were then removed from the vacuum and then kept open at room temperature. After a couple of weeks, the slides were examined using an optical microscope with an attached camera. Pictures were taken of the different samples. Any structures of resembling that of the 5mm cell were observed and recorded under the tapping mode of the Atomic Force Microscopy.

A Nikon OPTIPHOT2-POL optical microscope with an attachable camera was used to observe and characterize the structures inside the 5mm cell and the slides. First the cell was observed under the optical microscope at a magnification of 5 under the cross polarized plate. Once, a unique structure was observed, the structure was focused on and snapshot of the feature would be taken. Then the plate would be changed to the quarter wave plate, where a snapshot of the image would be taken. Next, the side, location, and description of the feature would be recorded. This procedure would be repeated every observation. Then, the description and the changes from the last observation would be recorded.

One of the produced slides that had developed structures was scanned under the AFM. Once the tip approached the surface, the tip would begin to scan and produced an image of the area scanned. The scan sizes that were used in this experiment were 50μm and 10μm. The scan rate was often decreased to reduce oscillation and was rarely increased to scan faster. In this experiment, the scan rate was held at 0.998 Hz. The integral gain and proportional gain were changed to reduce the amount of oscillation of the tip shown in the image being produced. The integral and proportional gain stayed approximately 1.000 and 2.000, respectively.

ANALYSIS AND INTERPRETATION

From observations using an optical microscope, the structures of the slides were very primitive. Only one structure similar to the structures in the 5mm cell was observed, which were that of the streetscape structures. The structures are very unique and have a repetitive pattern. There appears to be a cluster of many small branches, and as you move away from the cluster, there are several long lines with very few small branches protruding from them. Another unique feature was an unexplainable straight line, right through every center of the cluster of branches.

One of the small branches was measured in length to compare that to the length of 8-arm star polystyrene. The equation

$$\frac{M_{w_1}}{M_{w_2}} = m \qquad [1]$$

was used to determine the number of monomers per molecule of the polystyrene, where M_{w2} was the molecular weight of styrene. A molecular weight of 104g was used for styrene[1]. Then the end to end length was determined using the equation

$$\frac{1}{4}(m \times l_s) = l_p \qquad [2]$$

where l_s is the length of styrene. The end-to-end length of 8-arm polystyrene with a total molecular weight of 282,000 was estimated to be 0.10 microns.

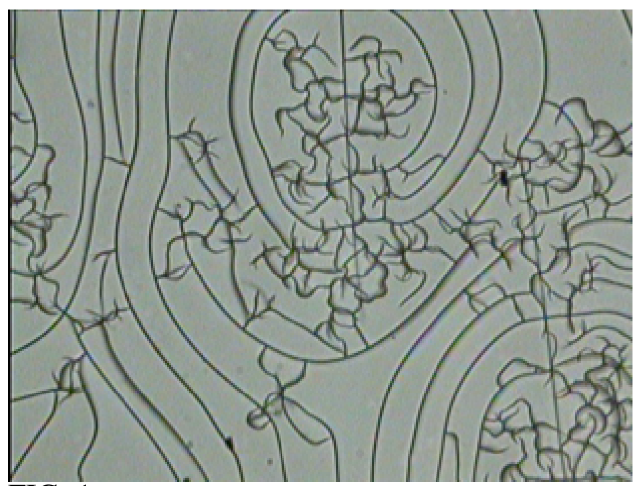

FIG. 1. A snapshot of the streetscape structure located in the 5mm cell. This picture was taken using an optical microscope at a magnification of 40.

The small-branched structures in Figure 1 were measured using a microscopic slide scale. The length of one of the branches found in Figure 1 was measured out to be approximately 0.01 millimeters or 10 microns, which indicated that these branches were composed of many 8-arm star polystyrene molecules.

The radius of gyration for the polymer was approximated using the equation[2]

$$S^2 = 4.1 \times 10^{-18} M_w \text{ (cm}^3\text{)} \qquad [3]$$

for a 6-arm star polystyrene, where M_w is the molecular weight of the polystyrene. The value came out to 1.1×10^{-6} cm^3. Since the branches found in Figure 1 were significantly larger than the calculated value for a branch of 8-arm star polystyrene, the radius of gyration wouldn't be significant in this situation.

The slide that contained a similar streetscape structure was then observed. The slide contains 8-arm polystyrene with a different molecular weight of 228,000. The area shown in Figure 2 was the area chosen to be observed under the AFM. The area had several small-branched structures similar to that in Figure 1. Unfortunately, the area did not have the repetitive pattern of clusters of small-branched structures that were found in Figure 1. Although, the structures were not identical to that inside of the 5mm cell, the branched structures from the slide were observed under the AFM to gain a better understanding of the streetscape structures.

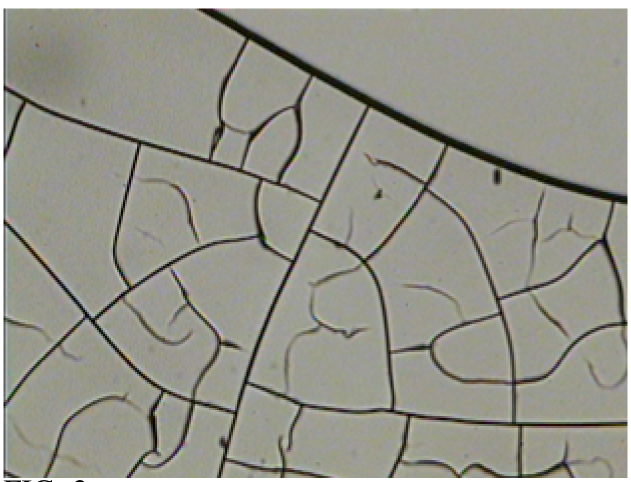

FIG. 2. This is a snapshot of the streetscape structure on a slide. This picture was taken using an optical microscope at a magnification of 40.

The streetscape structures shown in Figure 2 were scanned, once at a scan size of 50 microns and the other at a scan size of 10 microns. For the scan of 50 microns, the scan rate was held at 0.998 hertz, and the integral gain and proportional gain was adjusted to 1.047 and 1.997, respectively. The data scale was set to 2.000 microns. Figure 3 shows an image of the streetscape structure at a 3 dimensional perspective. This snapshot was captured when the scan size was set to 50 microns. From the three dimensional view of the sample, the streetscapes were distinguished as trenches in the surface.

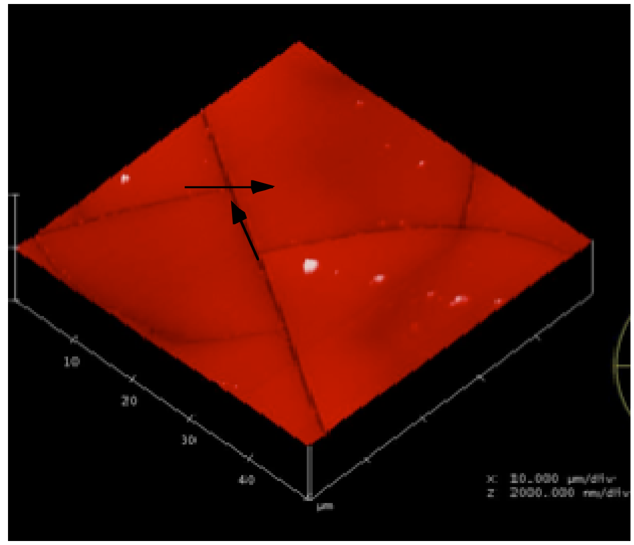

FIG. 3: This is a 3 dimensional view of the streetscape structure scanned by the AFM. From this view of the structure, the streetscapes structures can be distinguished as trenches in the surface of the material. The arrow pointing through the trench is the direction at which section analysis along the bottom was taken. The arrow pointing across the trench is the direction at which the depth and width were observed.

Figure 4 shows a section analysis on the depth of a trench. The surface is very level, and then there is a sudden drop indicating the presence of a trench. The depth of the trench was measured and came out to approximately 330 nanometers.

The width of the trench was also measured. The trenches have a wide opening and then slowly close in to a tip. The width of the trench came out to approximately 900 nanometers.

A section analysis was done along the bottom of the trench, as well. From the data that was collected, the bottom of the trench is not level and the depth is inconsistent. The unleveled bottom suggests that the crack formed due to the limited area to expand. This was also observed in the contents of the 5mm cell.

Unfortunately, due to the few similarities of the streetscape structures on slide compared to that contained in the 5mm cell, it is unknown how similar the streetscape structures were alike. Therefore, the observations made by the AFM that the structures were trenches could not be applied quantitatively to the structures found in the 5mm cell.

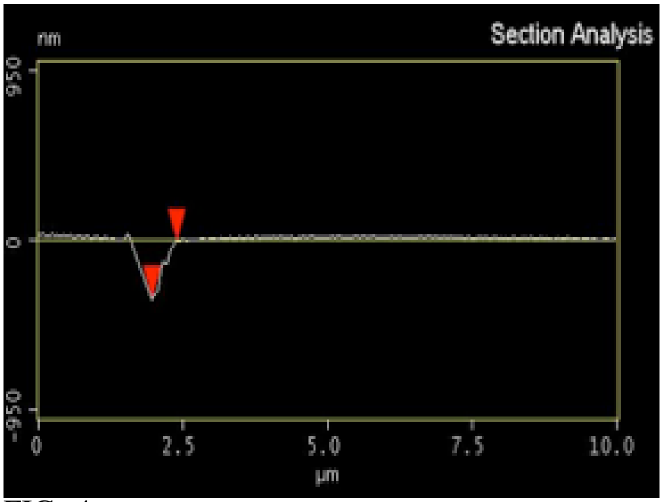

FIG. 4: A section analysis on one of the trenches. This section analysis is measuring the depth of the trench.

Calculations were made to compare the length of one of the protruding branches with the length of the 8-arm star polystyrene. The length of the 8-arm star polystyrene with a molecular weight of 282,400 came out to be 0.10 microns. The length of one of the protruding branches was 10 microns. The significant difference in length concluded that that producing branch was not individual 8-arm star polystyrene.

The streetscape structure on the microscope slide was observed under the AFM. From the data collected by the AFM, the streetscape structures were trenches or cracks found in the surface of the material. The trenches were approximately 900 nanometers wide, and 300 nanometers deep.’

[1]O’Neal, Maryadele J. *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biological*, 13th Edition; Merck Research Laboratories; New Jersey, 2001; pp. 8942
[2]Okumoto, Mitsuhiro, “Excluded-Volume Effects in Star Polymer Solutions: Six-Arm Star Polystyrene in Cyclohexane near the Temperature”, *Macromolecules*. 1999