Unique Morphology of Surface Grown Aggregates of BBL Ladder Polymer as Probed by the Atomic Force Microscope

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Poly[7-oxo-7H,10H-benz(d,e)imidazo(4',5':5,6)-benzimidazo(2,1-a)isoquinoline-, 4:10,11-tetrayl)-10-carbonyl] (BBL)[1] is one of the few conjugated ladder polymers. Its chemical structure shown in Figure 1 exhibits a double stranded, coplanar conjugated structure along the backbone. Outstanding thermal and chemical stability as well as high mechanical strength[1~3] can be attributed to the unique extended and coplanar structure of BBL ladder polymer. The extended π-conjugation is also responsible for the unusual electronic and optical phenomena found in BBL.[4~7] The polymer is soluble only in strong acid such as methane sulfonic acid (MSA), and highly ordered fibers and films are processed from the acidic solutions.

X-ray fiber pattern indicates that the polymer chains form an axially disordered two-dimensional crystalline structure in solid state. An orthorhombic unit cell with cell parameters, a=7.87 b=3.37 c=11.97 Å, has been proposed by Song *et al.*[8] One of the unique structural order of this ladder polymer, particularly in thin films, is the self-assembled anisotropic layered structure. The molecular plane or crystallographic a-axis is oriented perpendicular to the film surface and the chain and b-axis parallel to the film surface.[8] Similar anisotropic packing order has also been observed in other rigid-rod polymer such as the poly (p-phenylene benzobisthiazole) (PBT).[9,10] Structural similarity between the two polymers is that both polymers consist of aromatic and hetero-cyclic compounds and maintain collinearity along the backbone. It was suggested[8,9] that the unique chain orientation found in films of these polymers is attributed to the collinear and flat molecular plane of the polymer backbone, allowing the ladder or rod-like molecules to nucleate and grow in a preferred direction (b-axis direction) associated with the π-π electron interaction between the chains.

In this communication, we report the unusual morphologies of the BBL polymer aggregates studied by the atomic force microscope (AFM), which supports our previous supposition of forming the unique chain orientation in films. In particular, the aggregates were prepared by dispersing a dilute polymer solution in MSA on the surface of water.

BBL polymer used in this study was provided by the Materials Laboratory in Wright Patterson Air Force Base. The intrinsic viscosity of the polymer was 23.5 dlg^{-1}. A small drop of dilute polymer solution in methane sulfonic acid (MSA) was added on the water surface. The coagulation process differed depending on the solution strength. The solution below the 0.1 wt. % concentration spreads instantly and forms many thin islands of polymer aggregates floating on the water surface (Figure 2-B). When 0.1 wt. % concentration, the solution first nucleates a single large thick island and in subsequent a number of thin fibrils of 100 (m wide grow radially out from the island edge (Figure 2-A). It is interesting to observe that the aggregates are afloat on the water surface, although the densities of both BBL and MSA are far greater than 1.0 g/cc. At higher solution concentrations, the aggregates no longer grow on the water surface and one large aggregate precipitates out in the water. Schematics of coagulation processes from 0.1 and 0.05 wt.

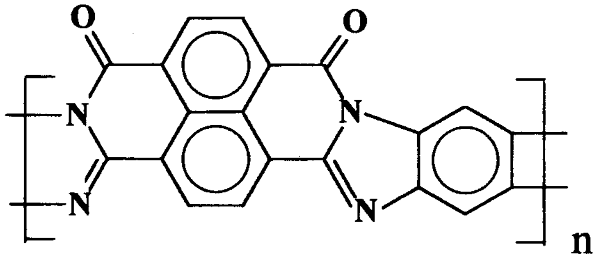

Figure 1. Chemical structure of BBL.

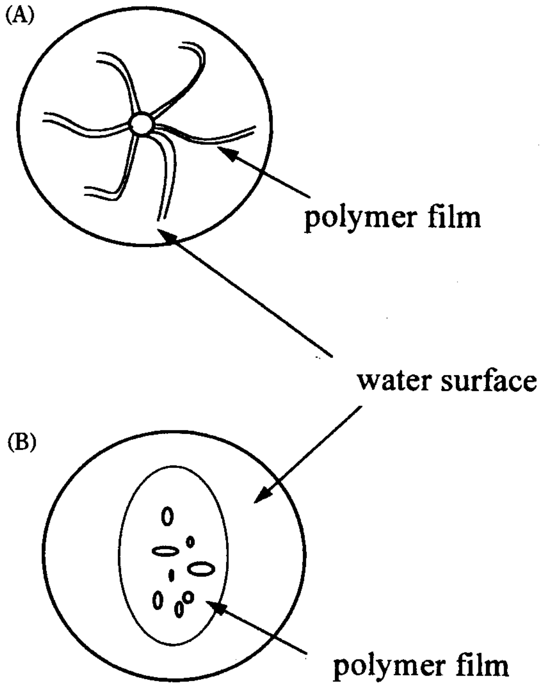

Figure 2. Schematics of film formation on the water surface: 0.1 wt. % solution concentration (A) and 0.05 wt. % solution concentration (B).

% concentrations are depicted in Figure 2-A and -B, respectively. In this report, we only discuss the morphologies of aggregates grown from 0.05 wt. % solution. The samples prepared from 0.1 wt. % and other concentrations are still under investigation. For the AFM examination, the aggregates were transferred on the slide glass surface and then dried in a vaccum oven at an elevated temperature (50 °C). The AFM was a Park Scientific Instruments (PSI) Autoprobe CP and scanning was done by the contact mode.

Figure 3 shows a morphology of the thin polymer aggregates grown from the 0.05 wt. % solution and observed under the atomic force microscope. The micrograph indicates that the polymer aggregates are composed of well defined grains of a spear-head shaped morphology. It is rather surprising to observe the extremely well defined grains because the morphology was formed, in particular, under a very rapidly precipitating condition. The unique morphology has never been observed previously in other polymer precipitates from solution. Detailed grain shape was analyzed by the height profiles of the micrographs shown in Figure 3. As indicated by the horizontal (H) and vertical (V) height profiles, the grains are on the average 300-400 nm long and 100 nm wide. The thickness of the grains is about 10 nm. The height profiles of the micrograph also reveal that the surface of the grain in the direction of long axis is flat with a sharp edge. On the other hand, the grain surface along the short axis is rather round and the edge is not as sharp as those along the long axis. The differences noted in the height profiles along the two directions suggest that the polymer chains are oriented, probably with the chain axis along the long axis of each grain. The number of chains stacked in the long axis direction to yield a grain size of 300-400 nm is not certain, since the experimental data regarding the molecular weight and the intrinsic viscosity is not available at the present time. Other molecular ordering to be determined in the grain is along the direction of short axis as well as along the grain thickness direction. As briefly discussed in the previous section, our study results[7] of thin films demonstrated that the crystallographic a-axis is oriented perpendicular to the film thickness, *i.e.* the large molecular plane of BBL polymer chain is standing perpendicular to the film surface. This unusual self-assembled packing was attributed to the one-dimensional growth of polymer molecules in the direction of π-π electron overlap, leading to a large flat structure. The spear-head shaped flat grain observed in this study clearly demonstrates the anisotropic growth of the chains and it can be speculated that in each grain the chain axis is oriented along the long axis of the grain, b-axis is oriented parallel to the short axis, and a-axis perpendicular to the flat grain surface. Proposed molecular orientation in each grain is depicted in Figure 4. It is not certain, however, that each grain possesses a single crystalline order or a mono-domain with an axial shift between chains as has been noted in X-ray fiber patterns of PBT and BBL. Origin of the two dimensional crystalline order observed in the fibers is not clear. It might be due to the shear force imposed on the polymer molecules upon spinning or the minimum energy related phenomenon associated with the charge transfer interaction between the chains. Determination of the exact molecular packing in individual grains will offer clues for this question and for the chain orientation in the grain. An electron diffraction study of the individual grain is currently under investigation.

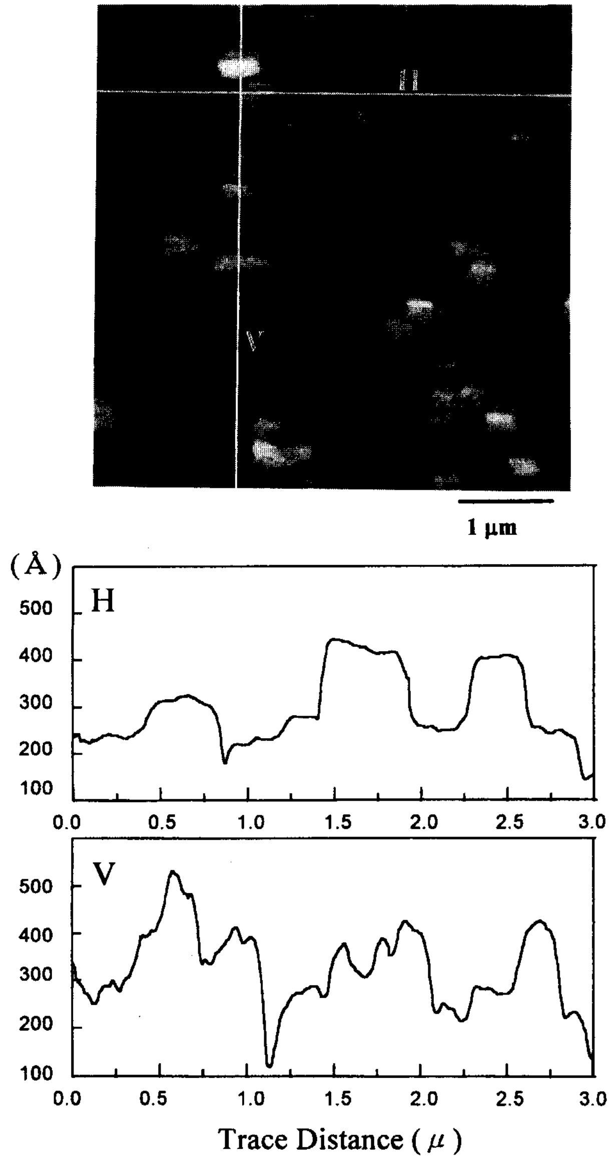

Figure 3. AFM micrograph of water surface grown BBL aggregates from 0.05 wt. % solution in MSA and height profiles in the horizontal (H) and vertical (V) direction.

A micrograph shown in Figure 5-A reveals another remarkable morphology that the individual grains organized themselves in a very ordered manner to form many columns stacked to one another. It is noted that all the

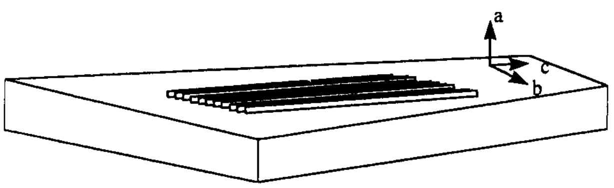

Figure 4. Schematics illustrating molecular orientation in individual grains.

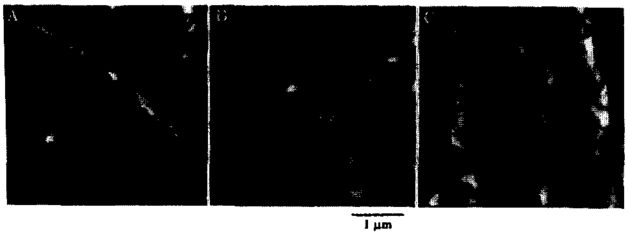

Figure 5. AFM micrographs showing ordering of BBL grains into columns. The grain heads are aligned perpendicular to the column axis (A), tilted to the column axis (B) and parallel to the column axis (C).

spear tips are facing the same direction, transverse to the column axis, demonstrating that self-ordering of the grains is associated with a certain preferred strong interaction between the individual grains. Figure 5-B exhibits a different super structure that the columns formed by the grains are not as regular as those found in Figure 5-A. The grain heads are pointing a direction with some tilt angle relative to the column axis. The rotation of grains relative to the column axis might be attributed to the solvent flow during precipitation on water surface. A similar effect is further noted in the AFM micrograph shown in Figure 5-C. The spear-head shaped grains are also forming columns but the grain heads are now aligned parallel to the column axis. The columns are approximately 100 nm wide. The three different super structures noted in the AFM micrographs (5-A, B, and C) can represent the structures formed under the various levels of shear flow. The morphology found in Figure 5-C could be the case of film formation under the greatest shear flow among the three samples. Fibers and films of high orientation are known to consist of fibrils or micro-fibrils as a sub-structural unit and the presence of columns in Figure 5 could represent the formation of fibrils in fibers and films of high orientation.

In summary, very thin layers of BBL polymer aggregates were prepared by adding a drop of a dilute polymer solution (0.05 wt. %) of MSA on the water surface. Thin layers of aggregates were formed and float on the surface of the water. The surface morphology of the aggregates examined by the AFM revealed that the polymer formed well defined large flat grains, exhibiting a spear-head morphology. The appearance of flat grains confirmed our previous suggestion[8,9] to account for the unique orientation of the polymer molecules in rigid-rod and ladder polymer thin films. The grains are on the average 300-400 nm long, 100 nm wide and 10 nm thick. The height profiles of the grains suggested that the BBL chains are oriented with the crystallographic c-axis parallel to the grain long axis, and the b and a-axis along the short axis and the thickness direction, respectively. The micrographs also revealed self-ordering of the grains, resulting in a super structure of well ordered columns stacked to one another. The orientation of the grain heads relative to the column axis differed from place to place and was interpreted as a result of the solvent flow during precipitation. A preliminary study suggests that the aggregation behaviors differed depending on the solution concentration, hence yielding different morphologies. Polymer aggregates prepared from various solution concentrations are now under investigation.

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