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Novel Morphology of Vertically Aligned Polyacetylene Film

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Liquid crystal polymerization method was modified in order to prepare a vertically aligned polyacetylene film. As a result, a film with a very curious morphology was formed. The film was composed of two layers. The layer on the solvent side was a vertically oriented fibril structure, whereas the layer on the acetylene gas side was a randomly oriented fibril structure. The modified method is a very promising one for visualizing the polymer growth process, and the present work clearly demonstrates that a polyacetylene chain grows in the liquid crystal solvent.

We have previously proposed a liquid crystal polymerization method for aligning polyacetylene molecules.[1,2] Because the main purpose of this method is to increase the electrical conductivity of the film, particular attention was paid to orientation parallel to the film surface.[3-7] Although the liquid crystal polymerization method gives an oriented film without a stretching procedure, basic questions on the polymerization mechanism in a liquid crystal solvent remain unanswered. For example, because the morphology of a horizontally aligned film is often complex, we still do not know whether a polymer chain grows in the liquid crystalline solvent or on the solvent surface. We therefore modified the liquid crystal polymerization in order to prepare a vertically aligned polyacetylene film. Tsuji et al. have also attempted to use a similar polymerization procedure to produce a vertically aligned film, but a clear morphology was not observed.[8] According to our experience, washing and drying processes are essential for obtaining a polyacetylene film's actual morphology, so these processes were improved in the present work. As a result, a film with a very curious morphology was obtained. The modified method clearly demonstrates that a polyacetylene chain grows in the liquid crystal solvent.

The same procedures described in our previous paper were used to polymerize acetylene.[1] Briefly, polymerization conditions were as follows: the liquid crystal solvent was an equimolar mixture of 4-(trans-4-n-propylcyclohexyl)-ethoxybenzene (E. Merck, ZLI-1476) and 4-(trans-4-n-propylcyclohexyl)-butoxybenzene (E. Merck, ZLI-1477); the temperature was 18 ^{o}C ; the Al Et 3 / Ti(OBu)4 ratio was 2; the catalyst concentration was 0.05 mol / l of Ti(OBu)4; and the initial pressure of acetylene was 600 mmHg. To prepare an oriented film vertical to the film surface, we modified the method for aligning the liquid crystal as shown in Fig. 1. The permanent magnet was placed so that its magnetic field becomes vertical, and the reaction flask containing the liquid crystal solvent was laid down in the magnet. The flask was 50 mm in diameter, and the magnetic field was 0.2 T between a 60 mm gap.[9] The thickness of the liquid crystal layer was at most 10 mm. After polymerization for 2 hours, the polyacetylene film formed on the liquid crystal surface was washed with toluene and a hydrochloric acid solution (90 vol% methanol) under nitrogen gas. A freeze-drying method was then used

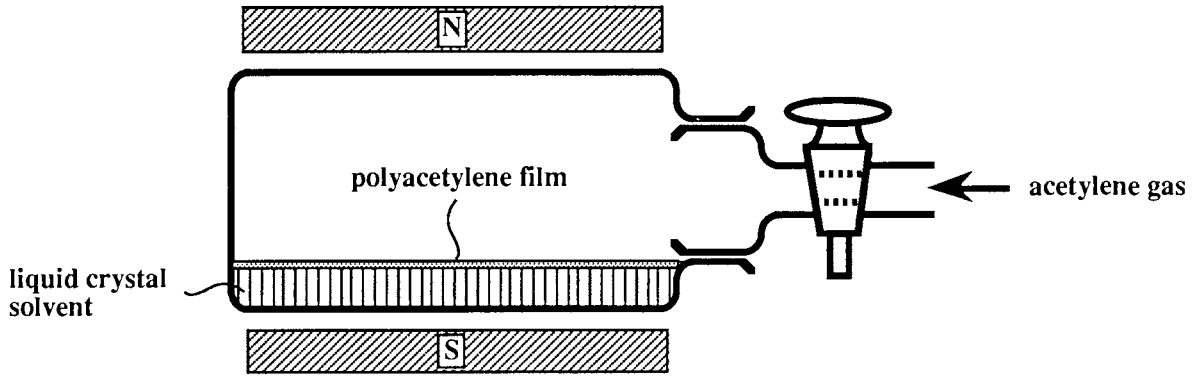

Fig. 1. Apparatus used in the preparation of vertically aligned polyacetylene film.

to preserve the film's initial morphology: the washing solvent was exchanged for benzene, which was sublimed in-vacuo at 0 °C.[10] The film was 30 mm x 90 mm and about 0.3 mm thick. Morphological observation was performed using a Hitachi S-800 type scanning electron microscope with an electron beam energy of 5 keV. To observe the actual film morphology, the iodine-doped polyacetylene film without a metal coating was used.[11]

The cross section of the freeze-dried polyacetylene film (shown in Fig. 2a.) reveals a very curious morphology. The film consists of two layers. The layer on the solvent side is oriented and has a loosely packed fibril structure, whereas the layer on the acetylene gas side is densely packed. The oriented layer is over 200 μm

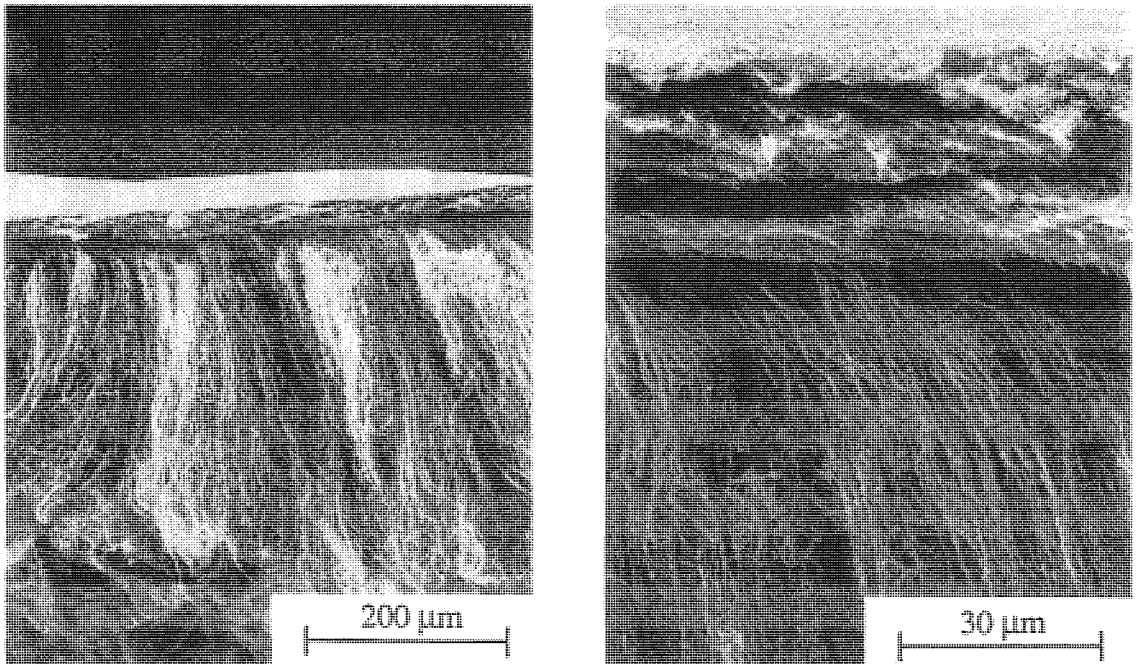

Fig. 2. Scanning electron micrographs of a freeze-dried polyacetylene film.

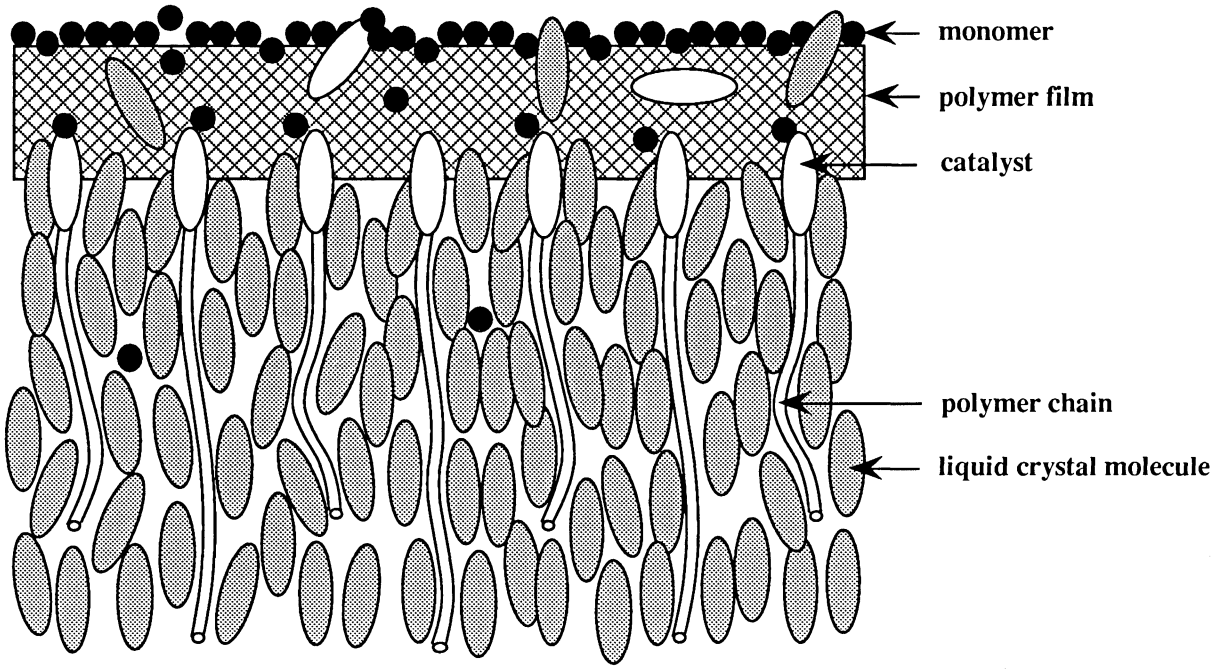

Fig. 3. Illustration of polyacetylene growth process in a liquid crystal solvent.

thick and the densely packed layer is 30 μm thick. As shown in Fig. 2b, the densely packed layer also consists of fibrils, but they are randomly oriented. The presence of long fibrils in the oriented layer clearly indicates that polyacetylene chains grow in the liquid crystal solvent. The thickness of the oriented layer increases with increasing polymerization time, and a thick film might be a sample suitable for investigating the intrafibrillar transport properties. The random layer appears to have grown in isotropic solvent, which was probably formed because enough heat released during the initial polymerization on the liquid crystal surface to transform the liquid crystal phase into the isotropic phase. It should thus be possible to control the thickness of the random layer by adjusting the polymerization conditions, especially the initial pressure of the acetylene gas. In an extreme case, only the vertically oriented fibril layer would be obtained. The conductivity of a horizontally aligned film has been reported to depend on the film thickness,[12] and this might be explained by the double layered fibril structure reported here.

Liquid crystal polymerization is not only a method for increasing the electrical conductivity of a polyacetylene, but is also a promising approach to exploring the polymer growth process. The morphology of a vertically aligned polyacetylene film can be interpreted in terms of the polyacetylene film growth. As shown in Fig. 3, after a densely packed polyacetylene film was formed on the liquid crystal surface, acetylene monomers diffused slowly into the liquid crystal layer through a densely packed film until, finally, a loosely packed oriented fibril structure was organized. These phenomena remind us of the organization of living systems.

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