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POLYMERIZATION OF ACETYLENE IN LIQUID CRYSTAL SOLVENT

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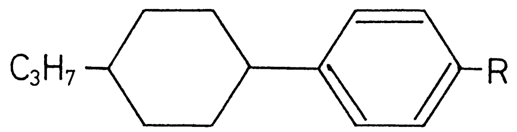
Highly oriented polyacetylene was synthesized using nematic liquid crystals as polymerization solvent

Polyacetylene (PA) has attracted much interest since it becomes a conductive polymer on doping. As reported by Ito, et al.[1] samples exhibt the morphology of an aggregation of randomly oriented fibrils. If PA consisting of well oriented fibrils could be obtained, its conductivity should be enhanced. Moreover, measurement of anisotropic properties becomes possible. With this in mind, Meyer[2] synthesized PA using a shear flow method to obtain partially oriented PA. Woerner, et al.[3] obtained an oriented film of PA by polymerizing acetylene on the surface of a biphenyl crystal. In the present work, we examined the polymerization of acetylene by using liquid crystals (LCs) as polymerization solvent. As a result, highly oriented PA film was obtained due to LC orientation.

The LC used was an equimolar mixture of 4-(trans-4-n-propylcyclohexyl)-ethoxybenzene (1, E. Merck, ZLI-1476) and 4-(trans-4-n-propylcyclohexyl)-butoxybenzene (2, E. Merck, ZLI-1477). These were chosen for their chemical stability in the



1 $R=OC_2H_5$
2 $R=OC_4H_9$

presence of Ziegler-Natta catalyst. The solid-nematic LC transition temperature of this mixture was 20 °C and the nematic LC-isotropic liquid transition temperature was 34 °C. Solidification did not occur until 0 °C under supercooling conditions. Therefore, we could use this mixture in the temperature range between 0 and 34 °C. The catalyst solution was prepared by dissolving 100 µl of $Ti(OC_4H_9)_4$ and 85 µl of $Al(C_2H_5)_3$ in 5 ml of the LC mixture (molar ratio, Al/Ti=3). At this concentration (50 mmol/l in Ti), the nematic LC-isotropic liquid transition temperature was lowered to 28 °C. In this study, flow of the catalyst solution was used to control orientation. Nematic LCs readily attain maximum orientation in the direction of flow.[4,5]

After 2 ml of the catalyst solution was transferred into a Schlenk flask, the flask was connected to a vacuum line and degassed. The catalyst solution was coated onto the glass wall of the flask by rotating it. After returning the flask to its original upright position, 500 Torr of acetylene gas was introduced into the flask at room temperature (18 °C). At this time, the coated solution flowed down (due to gravity) and orientation of the LC mixture was obtained. Formation of a PA film was observed immediately after introduction of acetylene gas. The film was washed with toluene under nitrogen gas and dried by blowing nitrogen gas on it. The PA formed was a thin purple film. Scanning electron microgragh (SEM) examination of the PA film showed the high degree of fibril orientation (Fig. 1). This orientation corresponded to the direction of flow. At present, the reason for such a fibril orientation is not clear. However, it is reasonable to consider that the fibrillar crystals grew together in the same direction due to an alignment effect of the LC molecules.

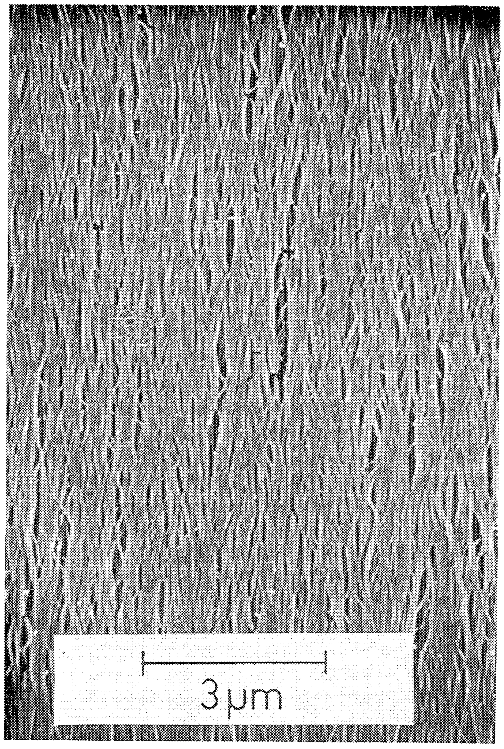


Fig. 1. Scanning electron micrograph of the PA film obtained in liquid crystal solvent.

The present method allows synthesis of highly oriented film with large areas. This makes electrical and optical measurements possible and such experiments are currently in progress.

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