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Vertically aligned helical polyacetylene synthesized in chiral nematic liquid crystal under magnetic field

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Abstract

Polyacetylene films with vertically aligned fibril morphology were synthesized in homeotropic nematic LC (N-LC) solvent, by using a magnetic field of 5 T as an external perturbation. Next, helical polyacetylene films with vertically aligned and screwed fibril morphology were synthesized in macroscopically aligned chiral nematic LC (N*-LC) under magnetic field. Scanning electron micrograph (SEM) indicated that the lengths of fibrils from the substrate were 5–20 μm, depending on polymerization time, acetylene pressure and catalyst concentration.

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Keywords: Vertically aligned polyacetylene; Homeotropic liquid crystal; Magnetic field; Chiral nematic liquid crystal

1. Introduction

Polyacetylene is the most representative conducting polymer because of its simple linear conjugated molecular structure and intrinsic high electrical conductivity [1]. Morphology of polyacetylene film is determined during the polymerization owing to its insolubility and infusibility. Recently, we synthesized helical polyacetylene film in chiral nematic liquid crystal (N*-LC) [2–4]. Now it is desired to prepare macroscopically aligned helical polyacetylene film to draw intrinsic electromagnetic properties such as induced solenoid magnetism. Note that although there is a choice for synthesizing horizontally [5,6] or vertically [7–9] aligned polyacetylene film, only the latter is focused in this study. The former is to be subjected elsewhere.

Previously, we synthesized vertically aligned polyacetylene film in homeotropic LC [9]. The homeotropic LC was prepared by adding a so-called orientation dopant into nematic LC, where the orientation dopant is composed of two mesogenic cores linked with hexamethylene spacer. Although the orientation dopant technique gave us very convenient and easy way to achieve the homeotropic alignment of LC, it prevented us to obtain highly homogeneous vertical aligned fibrils. This is because the effect of the orientation dopant in N-LC is sensitively affected by changes of temperature and pressure during acetylene polymerization.

In this study, therefore, we employed an alternative method for construction of the homeotropic LC phase. Namely, we applied a magnetic field of 5 T, as an external perturbation [6], to the vertical direction of the polyacetylene film (parallel to film thickness), as shown in Fig. 1. Under such an external force field, N-LC and

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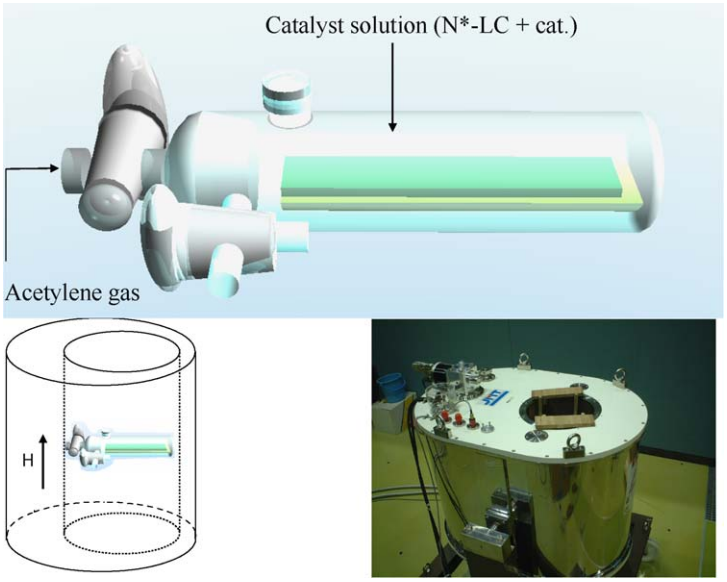


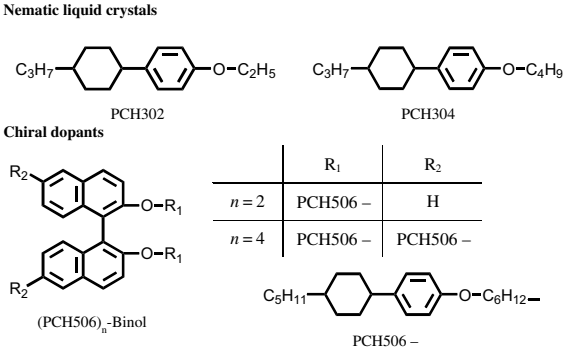
Fig. 1. Apparatus for acetylene polymerization in N- and N*-LC solvents under vertically applied magnetic field.

N*-LC were vertically aligned. These reaction fields were used to synthesize macroscopically vertical aligned polyacetylene and helical polyacetylene films, respectively.

2. Experimental

2.1. Preparation of N*-LC

N*-LC were prepared by adding a small amount of chiral dopant (0.5–1 mol%) into equi-molar mixture of two kinds of N-LCs, 4-(*trans*-4-*n*-propylcyclohexyl)ethoxybenzene [PCH302] and 4-(*trans*-4-*n*-propylcyclohexyl)butoxybenzene [PCH304]. As chiral dopants were used the binaphthyl derivatives, (*R*)- or (*S*)-(PCH506)$_n$-Binol ($n = 2, 4$), where the binaphthyl rings have substitutions of phenylcyclohexyl (PCH) moieties at 2, 2′ positions ($n = 2$), and 2, 2′, 6, and 6′ positions ($n = 4$), respectively (Scheme 1).



Scheme 1. N-LCs and chiral dopants.

These di-and tetra-substituted binaphthyl derivatives were well miscible in N-LC of PCH320 and PCH304, and exhibited large twisting powers owing their axial chirality. Helical pitches of N*-LCs were measured using the Cano–Grandjean method [10]. The N*-LCs including the di- and tetra-substituted binaphthyl derivatives showed helical pitches of 5 μm (1 mol%) and 1.5 μm (0.5 mol%), respectively. This indicates that the tetra-substituted binaphthyl derivative has a larger twisting power than the di-substituted one.

2.2. Polymerization of acetylene

The equi-molar mixture of two kinds of N-LCs was used as solvents for Ziegler–Natta catalyst consisting of Ti(O–*n*-Bu)$_4$ and Et_3Al. Typical concentration of the catalyst was 30 mmol/l of Ti(O–*n*-Bu)$_4$ and the ratio of [Al]/[Ti] was 4.0. The catalyst solution was aged at room temperature for 30 min and was added using a syringe into a flat-bottoms container inside a Schlenk flask. We applied magnetic field of 5 T vertical to the flat-bottom container for an hour (see, Fig. 1). By continuing the application of magnetic field, we introduced acetylene gas into the flask. The initial acetylene pressure was about 40 Torr and the polymerization time was about 5 min. After polymerization, polyacetylene film was carefully stripped off from the container and washed with purified toluene several times and then with methanol solution of hydrochloric acid (1 mol/l) and THF. The film was dried through vacuum pumping on Teflon sheet and stored in a freezer at 20 °C. Besides, we used N*-LC as a solvent. Polymerizations using N*-LC were carried out using the same procedure as in the case of N-LC.