Vertically Aligned Carbon Film Synthesized from Magnetically Oriented Polyacetylene using Morphology Retaining Carbonization

Munju Goh* and Yong Mun Choi

Carbon Convergence Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST) Eunhari san 101, Bongdong-eup, Wanju-gun, Jeonbuk 565-905, Korea

Article Info

Received 8 August 2012

Accepted 5 September 2012

*Corresponding Author

E-mail: goh@kist.re.kr

Tel: +82-63-219-8141

Open Access

DOI: <http://dx.doi.org/10.5714/CL.2012.13.4.226>

This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

<http://carbonlett.org>

pISSN: 1976-4251

eISSN: 2233-4998

Copyright © Korean Carbon Society

Abstract

Polyacetylene (PA) films with vertically aligned fibril morphology were synthesized in homeotropic nematic liquid crystal (N-LC) solvent by using a magnetic field of 5 Tesla as an external perturbation. Scanning electron microscope (SEM) photographs indicated that the lengths of fibrils from the substrate were 5–35 μm , depending on polymerization time. Carbonization was carried out using iodine-doped PA film and a morphology-retaining carbonization method. From the SEM results, we confirmed that the vertical morphology of the PA remains unchanged even after carbonization at 800°C. The weight loss of the films due to carbonization at 800°C is about 20% of the weight of the film before iodine doping. It is expected that vertically aligned carbon might be a precursor for preparing vertical graphite materials, which materials could be useful for electrochemical energy storage and cell electrodes.

Key words: carbon, polyacetylene, liquid crystal, iodine, morphology-retaining carbonization

1. Introduction

Polyacetylene (PA) is the most representative conducting polymer because of its simple linear conjugated molecular structure and intrinsic high electrical conductivity [1]. The polymerization procedure reported by Shirakawa and coworkers yields a randomly oriented fibril morphology [2]. However, the morphology of PA can be neither changed nor modified after the polymerization, because PA is infusible and insoluble in organic solvents. In order to solve this problem, liquid crystals (LC) have been adapted as an anisotropic reaction solvent for controlling the morphology of PA during acetylene polymerization. In fact, highly oriented PA films were obtained under a gravity flow [3] or magnetic field [4] of catalyst solution in which a nematic LC (N-LC) was used instead of common solvents such as toluene and cumene. Furthermore, higher-ordered helical PA (H-PA) was synthesized in a chiral nematic LC (N*-LC) reaction field [5].

Carbon films are interesting materials because of their special physicochemical and mechanical properties. They have been used in various applications, such as electrochemical energy storage, cell electrodes, and gas absorbent materials. Freestanding carbon thin film, which has a peculiar nanofibril structure, is expected to afford novel electrical properties. However, it has been considered difficult to prepare a freestanding carbon thin film through the carbonization of an organic polymer film. This is because carbonization at high temperatures causes thermal decomposition and volatilization of hydrocarbon gases, destroying the morphology of the original film. Above all, the low carbon atom contents of organic polymers would lower the carbonization yield. On the other hand, because of their high carbon atom content and sp^2 -hybridized carbon, conjugated polymers have received a lot of attention as carbonization precursors. As shown in Scheme 1, many kinds of conjugated polymers or sp^2 -hybridized carbon materials can draw on a graphene sheet. Recently, car-

Scheme 1. Conjugated polymers and sp^2 -hybridized carbon materials drawn on graphene sheet. (a) trans-polyacetylene, (b) cis-polyacetylene, (c) poly(p-phenylene), (d) poly(p-phenylenevinylene), (e) polyacene, (f) pyrene, (g) perylene.

bon and graphitic films have been successfully prepared from iodine-doped PA film using morphology-retaining carbonization with high carbonization yield [6,7].

For practical use, vertically oriented carbon materials are required. This condition is well understood in the case of carbon nanotubes; for applications in areas such as field emission and nanoelectronics, it is necessary to grow vertically oriented carbon nanotubes [8]. If vertically aligned PA film was synthesized, we can make vertically aligned carbon materials by using a morphology-retaining carbonization method. Recently we synthesized vertically aligned PA in homeotropic LC solvent. Homeotropic N-LC was prepared by adding a so-called orientation dopant into the N-LC; in this process the orientation dopant is composed of two mesogenic cores linked with a hexamethylene spacer [9]. Although the orientation dopant technique gives us a very convenient and easy way to achieve the homeotropic alignment of LC, it prevents us from obtaining highly homogeneous vertically aligned fibrils. This is because the effect of the orientation dopant in fluid N-LC is sensitively affected by changes of temperature and pressure during acetylene polymerization. Therefore, we employed an alternative method for construction of the homeotropic LC phase. Namely, by using a magnetic field of 5 Tesla as an external perturbation, a PA film with vertically aligned fibril morphology was synthesized in homeotropic N-LC solvent. Furthermore, the synthesis of the vertically aligned carbon film was examined with iodine-doped PA film as a carbonization precursor by using morphology-retaining carbonization. This could be a step toward obtaining hierarchically morphology controlled carbon and graphite materials.

2. Methods

N-LCs of phenylcyclohexane derivatives, 4-(*trans*-4-*n*-propylcyclohexyl)ethoxybenzene (PCH302) and 4-(*trans*-4-*n*-propylcyclohexyl)butoxybenzene (PCH304) were synthesized according to the methods listed in previous reports (Table 1) [5]. The host N-LC was prepared by mixing equimolar amounts of two N-LCs of PCH302 and PCH304, as shown in Table 1. It should be noted that although each component (PCH302 or PCH304) shows a LC

Table 1. Molecular structures of N-LCs and mixing ratios of host N-LC

N-LCs	$C_2H_5O-C_6H_4-C_6H_4-C_3H_7$ PCH302	$C_4H_9O-C_6H_4-C_6H_4-C_3H_7$ PCH304
Host N-LC	PCH302 : PCH304 = 100 : 100 (in mol ratio)	

N-LC: nematic liquid crystal.

Fig. 1. Apparatus for acetylene polymerization in liquid crystal (LC) solvent under vertically applied magnetic field.

phase, the LC temperature region is very narrow, i.e., less than 1 to 2°C. This is not suitable for acetylene polymerization, irrespective of N-LC reaction field, because the exothermal heat evoked during the acetylene polymerization would raise the temperature inside the Schlenk flask and easily change the LC phase into an isotropic one. Hence, we prepared an LC mixture by mixing the two equimolar N-LCs. In the N-LC mixture, the nematic to isotropic temperature, T_{N-I} , and the crystalline to nematic temperature, T_{C-N} , might be raised and lowered, respectively. In fact, the mixture exhibited an LC phase in the region from 20 to 35°C.

N-LC was used as a solvent for the Ziegler-Natta catalyst, which consists of $Ti(O-n-Bu)_4$ and $AlEt_3$. The concentration of [Ti] was 30 mM; the mole ratio of the co-catalyst to the catalyst [Al]/[Ti] was 4.0. The catalyst solution was aged for 30 min at room temperature; it was then completely degassed through a vacuum line and was transferred to a flat-bottomed container inside a Schlenk flask. The Schlenk flask was placed in a superconducting-magnet so that the solution in the container could be kept horizontal. A 5 Tesla magnetic field (JASTEC) was employed, and temperature was kept at 18 to 20°C during the application of the magnetic field and the polymerization, in order to maintain the LC phase. A vertical magnetic field was applied to the N-LC for 30 min. Then, acetylene gas was introduced into the Schlenk flask. The initial acetylene pressure was about 40 torr and the polymerization time was about 5 min. The apparatus for acetylene polymerization under vertically applied magnetic field is shown in Fig. 1. After polymerization, the PA film was carefully stripped from the container, washed with purified toluene several times and, subsequently, washed with a methanol solution of hydrochloric acid (1N) and tetrahydrofuran. The films were dried through vacuum pumping on a Teflon sheet and stored in a freezer at -20°C. Morphologies of the PA films were observed using an

scanning electron microscope (SEM) of type DS-130 (TOPCON). Before measurements of SEM, the PA films were coated with Pt-Pd alloy using an ion coater of type IB-5 (EIKO). The coating thickness was evaluated and found to be ca. 10 nm. The SEM operation was performed under an acceleration voltage of 10 kV. Note that the helical pitch and the spiral morphology of the H-PA were maintained during the Pt-Pd alloy coating and the SEM observation, because of its infusibility.

3. Results and Discussion

Fig. 2 shows SEM photographs of the PA film synthesized in N-LC. Vertically aligned fibril morphology was observed. The fibrils (whose diameters are 70–200 nm) are grown in parallel to the direction of the magnetic field. The fibril length was in the range of 5–35 μm , depending on the polymerization time.

Fig. 2. Scanning electron microscope photographs of vertically aligned polyacetylene film synthesized in nematic liquid crystal reaction field with vertically applied magnetic field of 5 Tesla.

Fig. 3. Schematic representation of homeotropic nematic liquid crystal (N-LC) with external magnetic force and vertically aligned polyacetylene film.

LC molecules with positive or negative anisotropy in diamagnetic susceptibility were aligned parallel or perpendicular to the direction of the magnetic field, respectively [10]. In this work, owing to the positive anisotropy in diamagnetic susceptibility of the phenyl moiety of the LCs (PCH302 and PCH304), the LC molecules tend to be aligned parallel to the direction of magnetic field. Moreover, it has been reported that the PCH derivatives can be aligned by a magnetic field of 10 000 gauss (1 Tesla) [4]. Therefore, the magnetic field of 5 Tesla is strong enough to change the multi-domain to the mono-domain structure N-LC one, namely aligned N-LC. It is thought that the disorder of the fibrils comes from the fluctuation of the LC solvent by the generation of exothermic heat during acetylene polymerization.

Fig. 3 provides a schematic representation of the synthesis of a vertically aligned PA film using a magnetic field. The N-LC containing the catalyst vertically aligns from a multi-domain to a mono-domain structure under a vertical magnetic field, giving rise to an anisotropic reaction field. The PA grows along with the longitudinal direction of the LC molecules. Therefore, interfacial acetylene polymerization in the anisotropic reaction field prepared with the aligned N-LC reaction field gives a vertically aligned PA film. The aligned PA film has aligned bundles of fibrils that are free from entanglement.

Iodine doping was performed by exposing iodine gas to the PA film at room temperature for 24 h in a glass vessel. The atomic ratio of doped iodine to carbon in the PA film (I/C) was 0.26–0.30%. The doped PA film was placed between graphite plates ($80 \times 80 \times 2$ mm) and was inserted into an electric furnace (KDF75, Denken). The doped PA film was then carbonized at 800°C for 1 h under argon gas atmosphere. The hydrogen content of the carbon film after carbonization was less than 1.0 wt%. The carbonization yield of the carbon film is about 70–90% of the weight of the PA film. Fig. 4 provides SEM images of the vertically aligned carbon films prepared by carbonization of iodine-doped PA film. Interestingly, the vertically aligned morphology of the PA film was maintained after carbonization. The fibril length of the carbon film was controlled at 10–35 μm by changing the acetylene polymerization time from 30 min to 6 h. The maximum value of electrical conductivity of the vertically aligned carbon film was 200 S/cm.

Fig. 4. Scanning electron microscope photographs of vertically aligned carbon films prepared using iodine-doped polyacetylene film, which synthesized in magnetically oriented nematic liquid crystal reaction field. (a) Top view and (b, c, d) quarter view.

4. Conclusions

Vertically aligned PA film was synthesized in a homeotropic N-LC. A homeotropic N-LC of the mono-domain structure was constructed with a magnetic field of 5 Tesla. The fibrils of PA grow parallel to the magnetic field. We successfully demonstrated the synthesis of vertically aligned carbon film using a vertical PA film as a carbonization precursor, with a high carbonization yield of 70–90%. A more detailed carbonization mechanism using iodine doping was discussed in another report [6,7]. It is expected that, by virtue of their electrical conductivity, surface area, porosity, and gas permeability, these vertically aligned carbon materials might be useful for many applications in such areas as electrochemical energy storage, cell electrodes, and gas absorbent materials.

Acknowledgements

The authors acknowledge Professor Kazuo Akagi, Department of Polymer Chemistry, Kyoto University, for his valuable advice. This work was supported by a grant from the Korea Institute of Science and Technology (KIST) institutional program.

References

- [1] Shirakawa H, Louis EJ, MacDiarmid AG, Chiang CK, Heeger AJ. Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, $(\text{CH})_x$. *J Chem Soc Chem Commun*, 578 (1977). <http://dx.doi.org/10.1039/C39770000578>.
- [2] Shirakawa H, Ikeda S. Infrared spectra of poly(acetylene). *Polym J*, **2**, 231 (1970). <http://dx.doi.org/10.1295/polymj.2.231>.
- [3] Araya K, Mukoh A, Narahara T, Shirakawa H. Synthesis of highly-oriented polyacetylene film in a liquid crystal solvent. *Synth Met*, **14**, 199 (1986). [http://dx.doi.org/10.1016/0379-6779\(86\)90184-0](http://dx.doi.org/10.1016/0379-6779(86)90184-0).
- [4] Akagi K, Katayama S, Ito M, Shirakawa H, Araya K. Direct synthesis of aligned cis-rich polyacetylene films using low-temperature nematic liquid crystals. *Synth Met*, **28**, D51 (1989). [http://dx.doi.org/10.1016/0379-6779\(89\)90673-5](http://dx.doi.org/10.1016/0379-6779(89)90673-5).
- [5] Akagi K, Piao G, Kaneko S, Sakamaki K, Shirakawa H, Kyotani M. Helical polyacetylene synthesized with a chiral nematic reaction field. *Science*, **282**, 1683 (1998). <http://dx.doi.org/10.1126/science.282.5394.1683>.
- [6] Kyotani M, Matsushita S, Nagai T, Matsui Y, Shimomura M, Kaito A, Akagi K. Helical carbon and graphite films prepared from iodine-doped helical polyacetylene film using morphology-retaining carbonization. *J Am Chem Soc*, **130**, 10880 (2008). <http://dx.doi.org/10.1021/ja803865e>.
- [7] Goh M, Matsushita S, Akagi K. From helical polyacetylene to helical graphite: synthesis in the chiral nematic liquid crystal field and morphology-retaining carbonisation. *Chem Soc Rev*, **39**, 2466 (2010). <http://dx.doi.org/10.1039/b907990b>.
- [8] Jung YJ, Wei B, Vajtai R, Ajayan PM, Homma Y, Prabhakaran K, Orino T. Mechanism of selective growth of carbon nanotubes on SiO_2/Si patterns. *Nano Lett*, **3**, 561 (2003). <http://dx.doi.org/10.1021/nl034075n>.
- [9] Shirakawa H, Otaka T, Piao G, Akagi K, Kyotani M. Synthesis of vertically aligned polyacetylene thin films in homeotropic liquid crystal solvents. *Synth Met*, **117**, 1 (2001). [http://dx.doi.org/10.1016/S0379-6779\(00\)00530-0](http://dx.doi.org/10.1016/S0379-6779(00)00530-0).
- [10] Goh M, Matsushita T, Satake H, Mutsumasa K, Akagi K. Macroscopically aligned helical polyacetylene synthesized in magnetically oriented chiral nematic liquid crystal field. *Macromolecules*, **43**, 5943 (2010). <http://dx.doi.org/10.1021/ma1009726>.