

Macroscopically Aligned Helical Polyacetylene Synthesized in Magnetically Oriented Chiral Nematic Liquid Crystal Field

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Received May 3, 2010; Revised Manuscript Received May 26, 2010

ABSTRACT: We have succeeded in synthesizing macroscopically aligned helical polyacetylene (H-PA) by using magnetically oriented chiral nematic liquid crystal (N*-LC) with monodomain structure. The N*-LC with monodomain structure was prepared by applying a magnetic field as an external perturbation to a N*-LC with polydomain structure. Because of the positive anisotropy of the diamagnetic susceptibility of N*-LC, the helical axis of the N*-LC was oriented perpendicular to the direction of the applied magnetic field. The monodomain N*-LC enabled us to synthesize macroscopically aligned H-PA. The bundles of fibrils were aligned parallel to the direction of the magnetic field and perpendicular to the axis of the N*-LC. It is anticipated that the macroscopically aligned H-PA film might be available for novel organic electromagnetic materials and also for the promising precursor of aligned helical graphite by using the morphology-retaining carbonization method.

Introduction

Since the discovery of polyacetylene thin film,¹ conjugated polymers have attracted significant interest due to their profound potential to produce light-emitting diodes,² photovoltaics,³ secondary batteries,⁴ and artificial muscles⁵ in addition to their ability to serve as biosensor materials.⁶ According to the progress of research on conjugated polymers, development of novel conjugated polymers and their precise structure control are quite important not only for improvement of the conventional properties but also for discovery of the new useful functions and applications.⁷ Recently, there have been increasing interests in helical conjugated polymers because of their unique properties.^{8–10} So far, the helical conjugated polymers have been synthesized with chiral agents¹¹ and soft templates^{12,13} and by directly inserting chiroptical moieties into the conjugated backbone.^{7b,14} In particular, an asymmetric reaction field constructed using a chiral nematic liquid crystal (N*-LC) has been observed to be useful for providing π -conjugated polymers with super-hierarchical helical structures.^{7c,15,16} Helical polyacetylene (H-PA) synthesized in the N*-LC has a spiral morphology that consists of helical bundles of fibrils, and it has shown a high electrical conductivity on the order of 10^3 S/cm after iodine doping, despite its helically twisted π -conjugated chain.^{7c,15} Moreover, the hierarchical helical structures (i.e., screw direction of the polyacetylene chain, fibril bundle, and spiral morphology) are rigorously controlled by changing the screw degree or direction of the N*-LC reaction field. H-PA is expected to be used as a prototypical molecular solenoid due to its helical structure and high electrical conductivity,^{7c,10,15,17} however, the polydomain spiral morphology of H-PA makes it difficult to evaluate an induced magnetism because the solenoid magnetism that emerges in the bundle of fibrils may cancel out (see Supporting Information). More specifically, the opposite magnetic poles in the solenoid magnetism could encounter one another, resulting in a cancellation of the magnetism.

Therefore, the H-PA needs to be aligned with retaining the helically twisted structure of the fibrils in order to avoid the induced magnetic field from canceling itself out. However, there has been no report for the synthesis of macroscopically aligned helical conjugated polymer with maintaining the helical structure.

The helical structure of H-PA is well controlled by the N*-LC reaction field. This means that the construction of macroscopically aligned N*-LC with a monodomain structure is a prerequisite for preparing aligned H-PA.^{17,18} It should be emphasized here that once H-PA is prepared, it cannot be fabricated or easily aligned; although there are some reports relating to the alignment of conjugated polymers bearing liquid crystalline substituents,^{7b,14a,19} the unsubstituted conjugated polymers represented by PA are infusible and insoluble in organic solvents. Hence, a direct synthesis of aligned H-PA via acetylene polymerization in macroscopically aligned and monodomain structured N*-LC is necessary.

It should be noted that the N-LC shows a spontaneous orientation due to an excluded volume effect in a domain, where an averaged orientation-direction called “a director” is defined. The N-LC also forms a helically screwed structure in the domain to give the N*-LC when mixed with chiral dopants. These behaviors are attributed to self-assembling abilities of LC molecules. However, the director in each domain of the N*-LC is still randomly oriented. This causes a polydomain structure, but not a monodomain one necessary for macroscopically aligned N*-LC reaction field. The formation of the monodomain structure requires a usage of external force such as electric field, magnetic field, or gravity flow technique.^{20–23} Namely, the construction of the monodomain type N*-LC reaction field needs not only the self-assembling ability of the LC molecules but also the artificial procedure based on the external force. From the viewpoint of safety in acetylene polymerization, the magnetic field is more preferred than the electric field.¹⁸ However, the detailed orientation behavior of the N*-LC in magnetic field remains unclear and has to be disclosed before carrying out the polymerization in the monodomain N*-LC.

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induced by a D-1 with (*R*)- and (*S*)-configurations were found to have right- and left-handed screw structures, respectively.¹⁵

The N*-LC was placed between a microscope slide glass and a cover glass. The sample was fixed in a superconducting magnet (JASTEC) so that the N*-LC could be kept horizontal. The orientational behavior of N*-LCs under an applied magnetic field was examined by changing the applied magnetic field from 0 to 10 T. During applying the magnetic field horizontally to the N*-LC, temperature was kept at 18–20 °C in order to maintain the N*-LC phase. After application of magnetic field for 10 min, the sample was subjected for the measurement of the POM. The microscope observation was carried out under crossed Nicols by using a Nikon ECLIPSE E 400 POL polarizing optical microscope equipped with a Nikon COOLPIX 950 digital camera.

Figure 1 depicts the changes in N*-LC optical texture as a function of magnetic field using a POM photograph. Before applying the magnetic field, the N*-LCs showed a spiral morphology of polydomain, wherein each domain exhibited a fingerprint texture consisting of spiral striae (Figure 1a). The interdistance between these striae, which corresponds to half of the N*-LC helical pitch, was measured to be 2.5 μm . Note that the helical axis of the N*-LC is perpendicular to the striae. When the magnetic field was increased from 1 to 2 T, the spiral striae were deformed into ellipse forms, while the polydomain structure was maintained (Figure 1b). When the magnetic field was increased to more than 5 T, the striae gradually aligned parallel to the direction of the magnetic field, and the polydomain was merged into one another, resulting in a monodomain (Figure 1c). Figure 1c indicates that the helical axis of the N*-LC is aligned perpendicular to the applied magnetic field. These results were rationalized with a previous report that the helical axes of N*-LCs with positive²¹ and negative anisotropies in diamagnetic susceptibility^{22,23} oriented perpendicular and parallel to the direction of the magnetic field, respectively. The nematic LC used as a host has a phenylcyclohexyl (PCH) moiety as a mesogenic core. Owing to the positive anisotropy of the PCH moiety in diamagnetic susceptibility, i.e., $\chi_a = \chi_{\parallel} - \chi_{\perp} > 0$ ($\chi_{\parallel} < 0$, $\chi_{\perp} < 0$), the helical axes of the N*-LC tend to orient perpendicular to the direction of an applied magnetic field.²⁵ The N*-LC monodomain structure was maintained in an applied magnetic field from 3 to 5 T; however, the N*-LC changed into N-LC at applied magnetic fields greater than 6 T, as shown in Figure 1d. It is anticipated that the helix of the N*-LC with positive anisotropy of diamagnetic susceptibility is unwound in an applied magnetic field with a critical magnetic strength (H_c).²¹ This result indicates that an applied magnetic field from 3 to 5 T is strong enough to convert polydomain N*-LC into monodomain N*-LC, but not strong enough to change N*-LC into N-LC. In other words, although the monodomain N*-LC is intrinsically metastable under magnetically forced environment, it should be feasible for the macroscopically aligned asymmetric reaction field for acetylene polymerization so far as the optimal conditions such as a magnetic field from 3 to 5 T is employed.

We prepared an asymmetric reaction field by adding a Ziegler–Natta catalyst consisting of $\text{Ti}(\text{O}-n\text{-Bu})_4$ and AlEt_3 to a N*-LC with a helical pitch of 5 μm . The concentration of [Ti] was 50 mM, and the mole ratio of the cocatalyst to catalyst [Al]/[Ti] was 4.0. After the aging of the catalyst for 30 min at room temperature, the catalyst solution was completely degassed through a vacuum line. Before the polymerization of acetylene gas, we observed the orientation behavior of asymmetric reaction field with the magnetic field of 5 T for application time of 10 min.

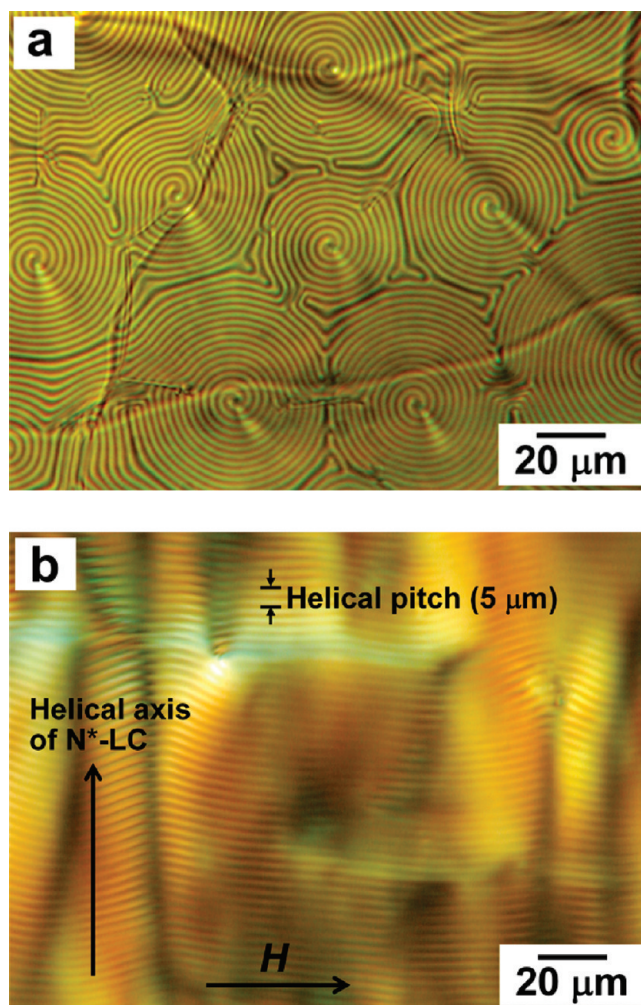


Figure 2. POM photographs of N*-LCs including Ziegler–Natta catalyst before (a) and after (b) the application of magnetic field of 5 T.

Figure 2a,b depicts POM photographs of the prepared asymmetric reaction field. Even in the presence of catalyst, the polydomain N*-LC phase (Figure 2a) changed into a monodomain structure (Figure 2b) after the application of a 5 T magnetic field. Meanwhile, the interdistance between the striae corresponding to a half helical pitch (2.5 μm) of N*-LC remained unchanged. An asymmetric reaction field with a 5 T magnetic field-induced monodomain structure was used as a reaction field for acetylene polymerization.

2. Polymerization of Acetylene in Magnetic Field. The solution including N*-LC and Ziegler–Natta catalyst was transferred using a syringe into a flat-bottomed container which was located inside a Schlenk flask. The Schlenk flask was fixed in the superconducting magnet so that the solution in the container could be kept horizontal. The apparatus used in the acetylene polymerization in the magnetic field is shown in the Supporting Information. The magnetic field of 5 T was employed, and temperature was kept at 18–20 °C during the polymerization in order to maintain the N*-LC phase. After application of the magnetic field to the N*-LC for 120 min, acetylene gas was introduced into the Schlenk flask. Noted that although the N*-LC well oriented under the magnetic field of 5 T within 10 min (see Figure 2b), the H-PA synthesized in this condition showed a partly aligned morphology like an ellipse form (see Figure S3 in the Supporting Information). This is because the acetylene polymerization for H-PA film uses the flat-bottomed container

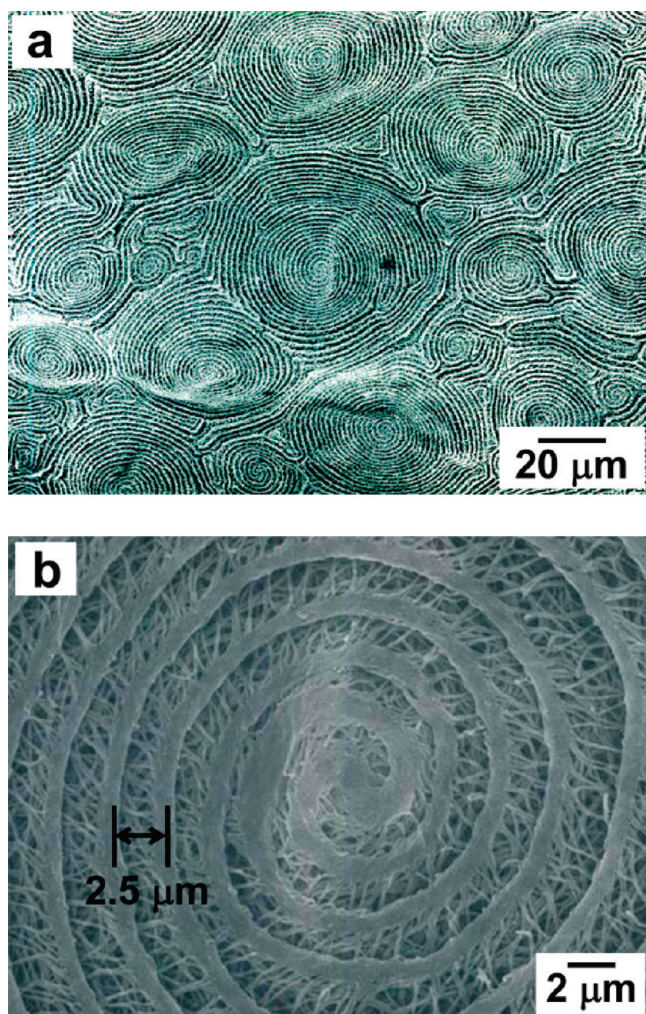


Figure 3. SEM photographs of H-PA synthesized in polydomain N*-LC without magnetic field. The photograph of (b) is the magnified one of (a).

with a size of 2.5 cm \times 20.0 cm (see Supporting Information), and hence it needs much quantity (5 g) of N*-LC as a polymerization solvent than the case of POM observation. Thus, the application time of magnetic field must be sufficiently long for complete orientation of N*-LC. Actually, we applied the magnetic field of 5 T for 120 min for the synthesis of macroscopically aligned H-PA. The initial acetylene pressure was about 30 Torr. The polymerization was stopped when the pressure decreased by 5 Torr. The H-PA film thus obtained was washed with purified toluene, methanol solution containing 1 N hydrochloric acid, and THF in turns, dried through a vacuum line on a Teflon sheet for 2 h, and stored in a deep freezer at -20°C .

The morphologies of the H-PA films synthesized in N*-LC without (Figure 3) and with (Figure 4) an applied magnetic field were examined by a scanning electron microscope (SEM). Representative spiral morphology was observed in the H-PA film that was synthesized without an applied magnetic field (Figure 3). The morphology of the spirals is the same as the polydomain structure of the asymmetric reaction field (Figure 2a).

In contrast, Figure 4 depicts the macroscopically aligned morphologies of the H-PA with screwed bundles of fibrils. The screwed bundles were aligned parallel to the direction of the magnetic field. In the macroscopically aligned H-PA film, the PA chains are self-assembled to form a helical fibril.

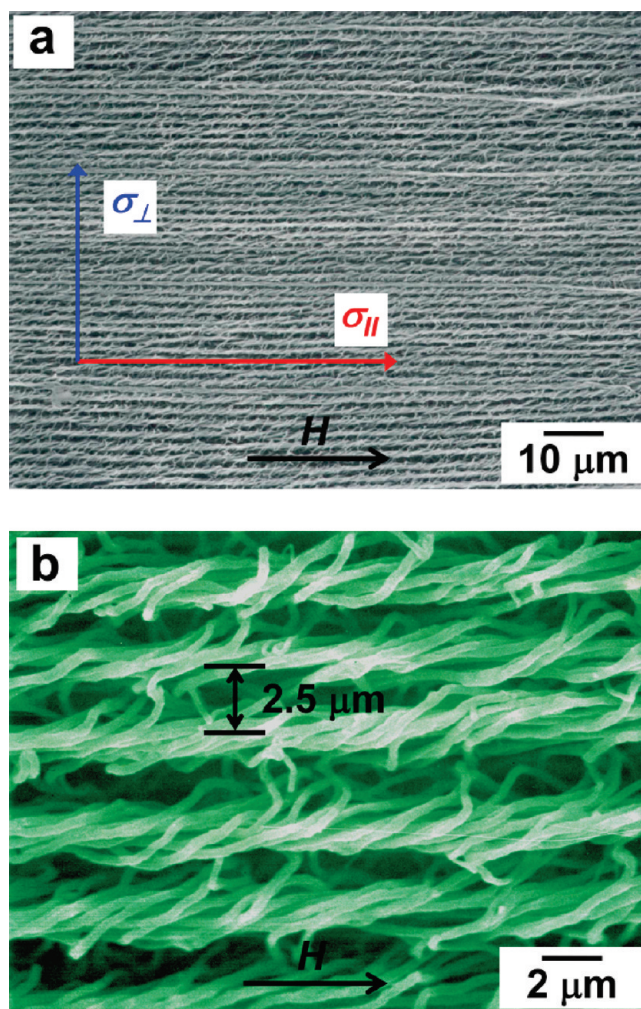


Figure 4. SEM photographs of H-PA synthesized in monodomain N*-LC with magnetic field of 5 T for 2 h. The photograph of (b) is the magnified one of (a).

The helical fibrils are furthermore gathered to form a bundle of fibrils. It has been elucidated hitherto that the interdistance (a) between the fibril bundles of the H-PA is correlated with half of the helical pitch (p) of the N*-LC, i.e., $a = p/2$.^{7c,15} More specifically, this means that the interdistance of the fibril bundles can be used as an index to evaluate not only the helicity of the H-PA but also that of the N*-LC used as a solvent. Interestingly, there is no notable difference in the interdistance ($a = 2.5\ \mu\text{m}$) of the fibril bundles between the H-PAs synthesized without and with applied magnetic field (Figures 3 and 4). This is the same situation as in the halves of the helical pitches of the N*-LC (see Figure 2). These results should be attributed to the following two facts. One is that each N*-LC domain consists of a lot of LC molecules, and it behaves as if a supermolecular assembly which can be affected by the magnetic force enough to conquer a thermal fluctuation (Figure 5).²⁵ Another is that the morphology of H-PA is strictly determined by that of the N*-LC used as a reaction field. It is found that the fibril bundles of the H-PA are aligned parallel to the direction of the applied magnetic field and perpendicular to the helical axis of the N*-LC (Figures 4 and 5).

Electrical conductivities parallel and perpendicular to the orientation direction of the H-PA film after iodine doping were measured using the four-probe method. The maximum measured parallel and perpendicular conductivities were

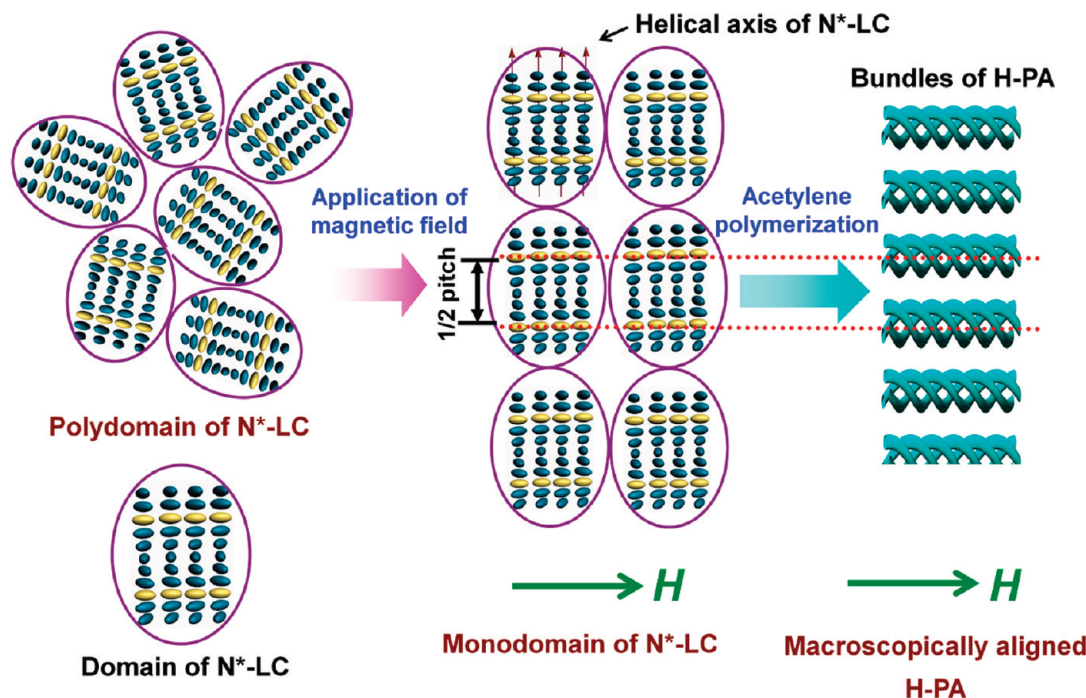


Figure 5. Schematic illustration of polydomain N*-LC, monodomain N*-LC, and macroscopically aligned H-PA synthesized in the oriented N*-LC.

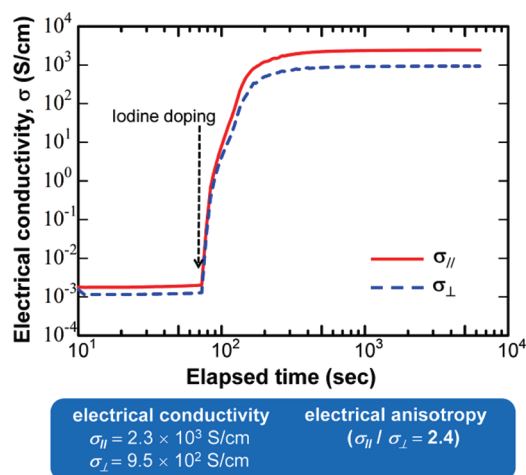


Figure 6. Changes of electrical conductivities of aligned H-PA during iodine doping. $\sigma_{||}$ and σ_{\perp} represent the electrical conductivities parallel and perpendicular to the aligned direction of H-PA, respectively.

2.3×10^3 and 9.5×10^2 S/cm, respectively. Electrical anisotropy, which is defined as a ratio of parallel and perpendicular conductivities, was calculated to be about 2.4 (see Figure 6). This value is one-sixth of that of the aligned PA film synthesized in achiral N-LC under a gravity flow of catalyst solution.²⁶ The small electrical anisotropy can be rationalized with the fact that the bundle of the fibrils connect to neighboring fibrils via microfibrils (see Figure 4)

Conclusion

An orientation behavior of highly twisted N*-LC under magnetic field of 5 T was elucidated. A monodomain N*-LC was constructed by applying a magnetic field as an external perturbation to a polydomain N*-LC. Because of the positive anisotropy of the diamagnetic susceptibility of the N*-LC, the helical axis of the N*-LC was oriented perpendicular to the direction of the applied magnetic field. The monodomain N*-LC

is found to be metastable and hence changes into N-LC with unwinding its helix, when a magnetic field greater than 6 T is applied. Nevertheless, the monodomain N*-LC is feasible for the macroscopically oriented asymmetric reaction field so far as the optimal conditions such as a magnetic field of 3–5 T is employed. Actually, the monodomain N*-LC including a certain amount of catalyst enabled us to synthesize macroscopically aligned H-PA. The bundles of fibrils of the H-PA were aligned parallel to the direction of the magnetic field and perpendicular to the helical axis of the N*-LC.

It is anticipated that the macroscopically aligned H-PA film might be available for organic materials with induced solenoid magnetism and also for a precursor of aligned helical graphite that can be prepared by the morphology-retaining carbonization method.^{7c,27} Besides, the magnetically aligned N*-LC should be a versatile reaction field to produce a variety of helical conducting polymers with macroscopic alignment.

Acknowledgment. This work was supported by a Grant-in-Aid for Science Research (S) (No. 20225007) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and partly supported by Ogasawara Foundation for Science and Technology of Japan.

Supporting Information Available: Apparatus used for the acetylene polymerization under magnetic field; SEM photograph of H-PA synthesized with applying magnetic field of 5 T for 10 min. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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