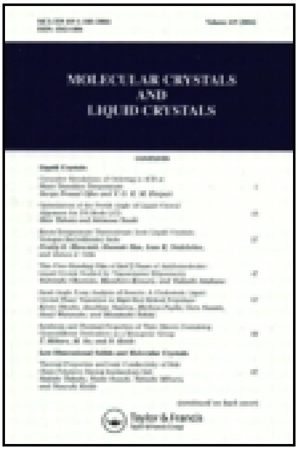

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Orientational Behavior of Nematic Liquid Crystals Containing a Soluble Ziegler-Natta Catalyst Under Magnetic Field

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We have investigated orientational behaviors of nematic liquid crystals of phenylcyclohexane derivatives and their solutions of $Ti(OBu)_4$—$AlEt_3$ catalyst under a magnetic field by means of optical transmission measurements. Magnetic field required to achieve an ultimate orientation of the liquid crystal is found to be 1 kG, which is shifted to 10 kG upon dissolving the catalyst with a concentration of 0.89 vol% into the liquid crystal, although the onset of orientation is observed around 0.4 kG in both cases. Through a numerical evaluation of free energy associated with magnetically forced orientation, a molecular assembly of liquid crystals aggregated in a domain with size of 1–2 μm is stressed to behave as a "supermolecule," accounting for global feature of orientational behavior of the liquid crystal under the magnetic field. Roles of macroscopic and microscopic alignments of the liquid crystals in synthesis of as-grown aligned polyacetylene films are discussed from a view point of anisotropic reaction field.

INTRODUCTION

It is well known that liquid crystal has a long range orientational order of molecules in spite of absence of a long range translational order with respect to center of gravity.[1,2] By virtue of its ordered liquidity, the liquid crystal is expected to serve as a medium which provides an anisotropic reaction field for chemically interacting systems.[3]

Recently, we have developed a novel polymerization method for highly oriented polyacetylene film by using nematic liquid crystal as a polymerization solvent for soluble Ziegler-Natta catalysts.[4–8] In order to align the liquid crystal more homogeneously than the flow method,[4–6] we have employed a magnetic force as an external perturbation (which is called **magnetic field method**).[7] Polyacetylene films thus obtained exhibited an extraordinarily high electrical conductivity with notable optical and electrical anisotropies. This is rationalized to be due to highly oriented fibrillar morphology generated by the macroscopically aligned nematic phase.[7,8] In addition, polyacetylene films prepared in the liquid crystal solvent without the magnetic force (which is called **quiescent method**[5,8]) are found to have microscopically aligned fibrils which may also reflect the reaction field of the liquid crystal. These fascinating results have promoted us to elucidate orientational behavior of the liquid crystal.

The primary aim of the present study is to provide a deeper understanding for the acetylene polymerization in the nematic liquid crystal solvent by focusing on an orientational behavior of the liquid crystal in the magnetic field.

EXPERIMENTAL

Thermotropically nematic liquid crystals of phenylcyclohexane derivatives, $R—C_6H_{10}—C_6H_4—R'$ (R = alkyl and R' = alkoxy group) were adopted since they are inert and stable towards a soluble Ziegler-Natta catalyst, $Ti(OBu)_4—AlEt_3$, and also the same as those used so far.[4-8] In practice, an equimolar mixture of 4-(trans-4-*n*-propylcyclohexyl)-ethoxybenzene ($R = C_3H_7$, $R' = OC_2H_5$: PCH302) and 4-(trans-4-*n*-propylcyclohexyl)-butoxybenzene ($R = C_3H_7$, $R' = OC_4H_9$: PCH304) was used without further purification except for degassing prior to use. Rod shape molecular structures of PCH302 and PCH304 are described in Figure 1. Triethylaluminum, $AlEt_3$, was used without further purification. Tetra-*n*-butoxytitanium, $Ti(OBu)_4$, was distilled under argon gas prior to use.

Two kinds of samples were prepared for the measurement: One is the equimolar mixture of PCH302 and PCH304 (Sample 1); another is the liquid crystal mixture containing $Ti(OBu)_4—AlEt_3$ catalyst (Sample 2), in which concentration of $Ti(OBu)_4$ is 0.01 mol/l and a ratio of $AlEt_3$ to $Ti(OBu)_4$ is 4.0, yielding a volume concentration of 0.89 vol.% for the catalyst. It has been already confirmed that the liquid crystal containing the catalyst with such a concentration maintains the nematic phase in temperature region of 5–25°C.[4-8]

An apparatus used for optical transmittance measurement is shown in Figure 2. Glass cell for the liquid crystal sample was located between two poles of electrical magnet (JEOL JM-FE3A). Two polarizers were placed above and below the glass cell so that each polarization direction was 45° to magnetic lines (hence to orientation direction of the liquid crystal), and at the same time polarization angle

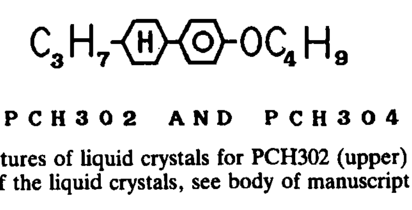

FIGURE 1 Molecular structures of liquid crystals for PCH302 (upper) and PCH304 (below). As to the abbreviation for names of the liquid crystals, see body of manuscript.

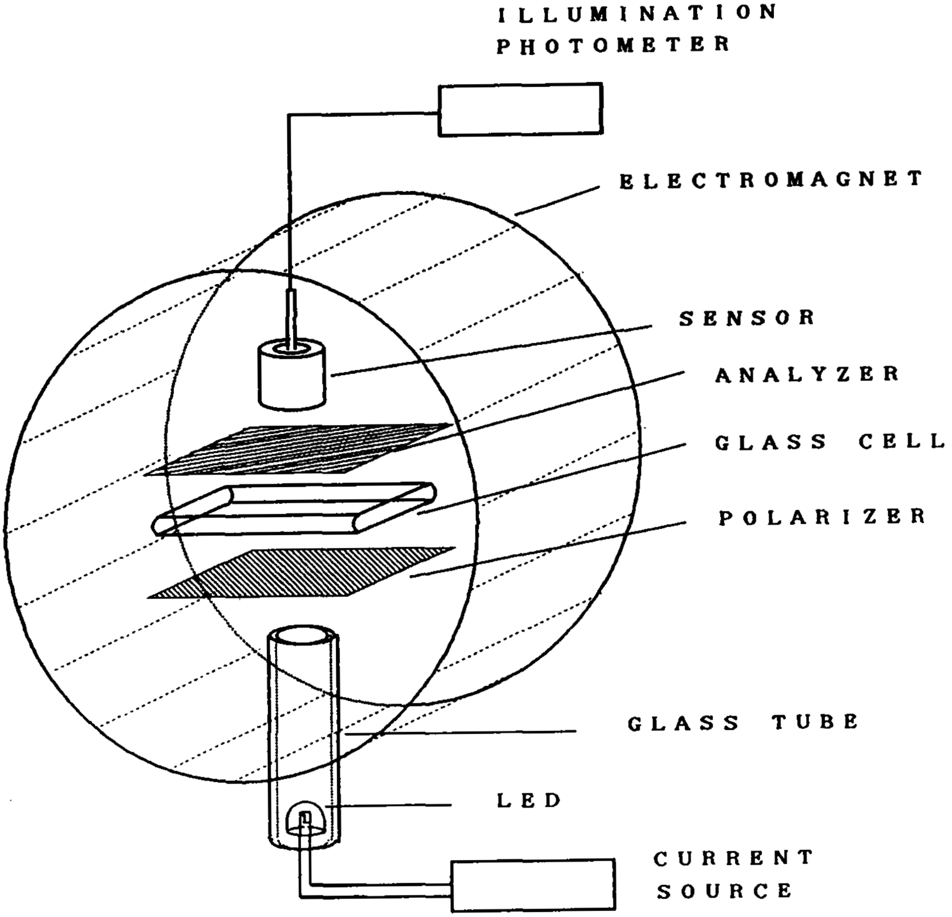

FIGURE 2 Schematic illustration of apparatus for measuring transmittance of light propagating through nematic liquid crystal system in a magnetic field.

between the two polarizers were fixed at 90°. As a source of monochromatic light was used a red light emitting diode (LED). Intensity of incident beam on the sample was kept constant throughout the measurement by using a constant current source (ADVANTEST TR-6141). In order that metallic parts of the light source might not be affected by the magnetic field, the light source was detached by a distance of ca. 30 cm from the magnet by setting a glass tube between the magnet and the light source. The glass tube was covered with aluminum foil in order that the light might not be scattered during passage through the glass tube. Transmitted light was detected by a light sensor connected with an illumination photometer (United Detector Technology #111A). Note that in case of measurement for the catalyst-containing liquid crystal (Sample 2), a Schlenk type glass cell connected with Teflon stopcock, as illustrated in Figure 3, was used instead of the above mentioned glass cell. Thus the catalyst dissolved in the liquid crystal was able to

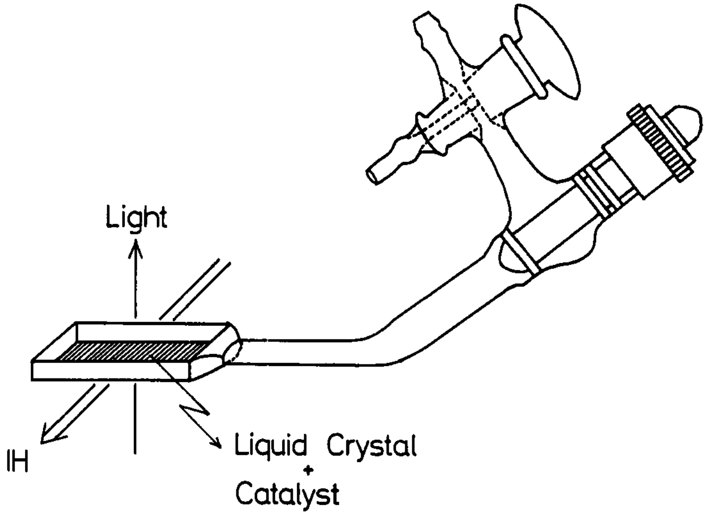

FIGURE 3 Glass cell for sample of the liquid crystal solution of $Ti(OBu)_4$–$AlEt_3$ catalyst.

be avoided for oxidation owing to treatments under inert argon gas filled in the cell.

RESULTS AND DISCUSSION

In order to grasp an orientational behavior of the liquid crystal perturbed by magnetic force, we measured an intensity of the light transmitted through the liquid crystal under magnetic field. Measurements were carried out at 12–13°C, where nematic phase of the liquid crystal was sufficiently maintained. In order to minimize a so-called wall effect in the orientational behavior of the liquid crystal, which will be discussed later, appropriate amount of the liquid crystal was taken into the cell so that the liquid crystal might not be in contact with an upper wall of the cell. Thus sample thickness through which the light was transmitted was 670–700 μm, common to Samples 1 and 2.

Figures 4 and 5 show changes of intensities of the lights transmitted through Samples 1 and 2, respectively, as a function of magnetic field strength. As found in Figure 4, the liquid crystal becomes oriented around 0.4 kG of magnetic field and then attains a maximum orientation at 1 kG, resulting in a plateau in the range of 1 to 15 kG. It can be therefore argued that threshold of magnetic field for an ultimate orientation of the present liquid crystal is 1 kG. On the other hand, as shown in Figure 5, the catalyst-containing liquid crystal also becomes oriented around 0.4 kG and shows an abrupt increase in orientation up to 1 kG. This may allow us to regard the magnetic field of 1 kG also as an essential threshold for macroscopic alignment in this case, although the orientation at 10 kG is undoubtedly an ultimate one. This argument is supported from our preliminary experimental

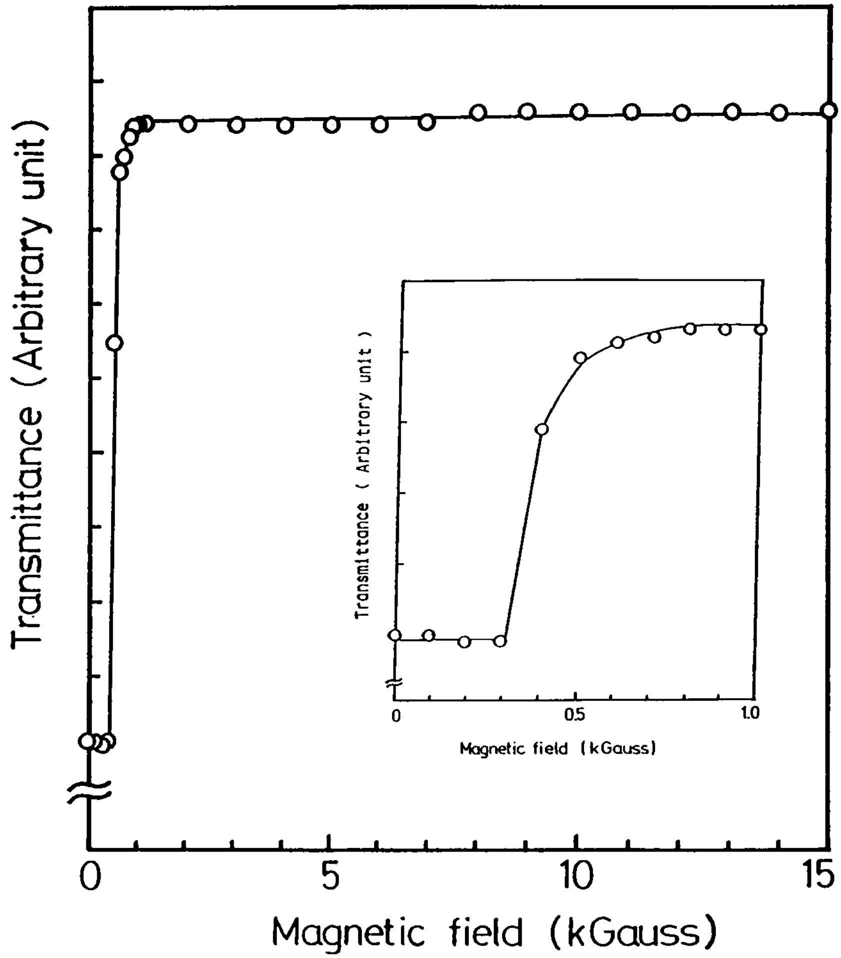

FIGURE 4 Dependence of orientation of the liquid crystal on magnetic field. The liquid crystal is an equimolar mixture of PCH302 and PCH304.

facts that acetylene polymerizations by means of the magnetic field method using Sample 2 as a catalyst solution yield aligned polyacetylene films under magnetic field of more than 2.0 kG, although degree of alignment of the films is slightly inferior to those of films prepared at 10–14 kG. The increase of magnetic field intensity from 1.0 to 2.0 kG required for achievement of macroscopic alignment of the liquid crystal in the practical synthesis of polyacetylene may be attributed to both an incorporation of acetylene monomer being a second heterogeneous species towards the liquid crystal alignment and enhanced thermal motions of the liquid crystal molecules associated with an exothermic acetylene polymerization.

Difference between orientational behaviors described in Figures 4 and 5 is easily attributed to the existence of the catalyst with a viscosity as a heterogeneous species which should suppress an orientational motion as well as a translational motion of

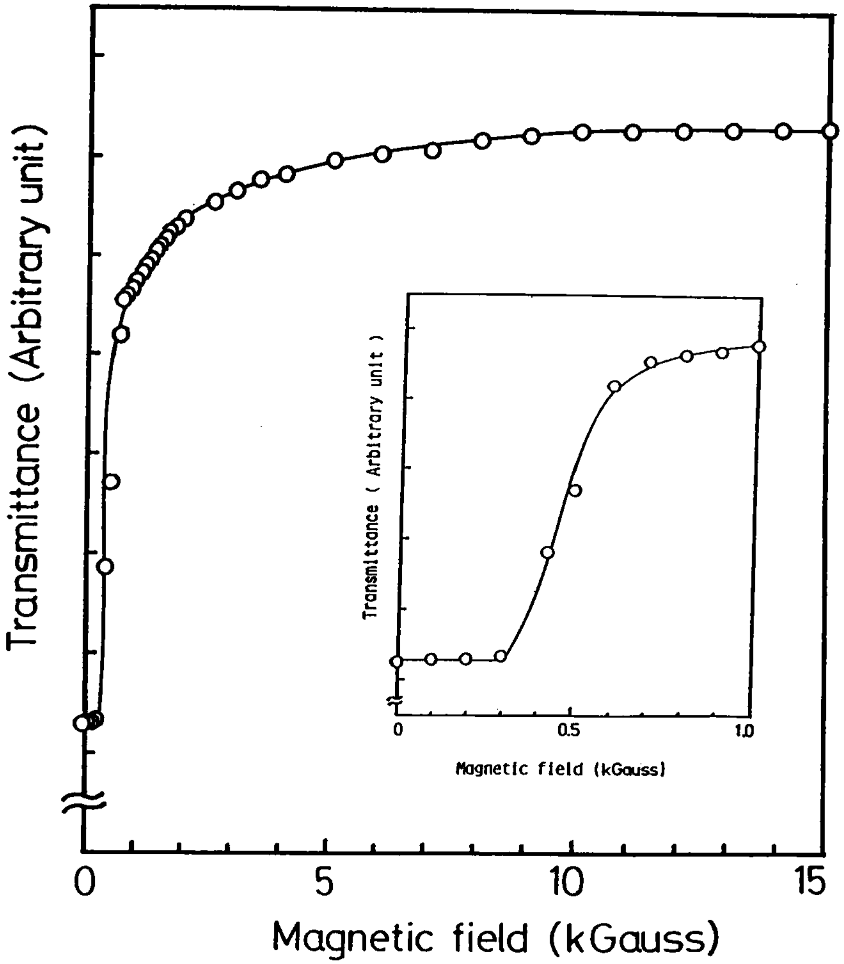

FIGURE 5 Dependence of orientation of the liquid crystal solution of $Ti(OBu)_4$–$AlEt_3$ catalyst on magnetic field.

the liquid crystal, requiring a higher magnetic field for the macroscopic alignment with an ultimate orientation. Nevertheless, a similar profile in changes of optical transmittance, particularly the onset of orientation around 0.4 kG, implies that the assembly of the liquid crystal is not drastically interfered by the catalyst contamination with the concentration of 0.89 vol.%

It must be examined at this stage whether the sample thickness (670–700 μm) is sufficiently large enough to neglect boundary effects and deformations due to curvature strains.[2,9–11] For this aim, it may be useful, for instance, to compare the sample thickness with a magnetic coherence length which represents a thickness of the deformation layer near the boundary, let us say the wall of the cell. Suppose that |n is an orientational unit vector of the liquid crystal called director defined in physically infinitesimal region (unit volume) and that $\chi_{\parallel}$ and $\chi_{\perp}$ are diamagnetic susceptibilities of the liquid crystal parallel and perpendicular to the director. When the liquid crystal is in contact with the surface of the glass wall with occupying a half space, the magnetic coherence length,[2,9] ξ, is given as a function of magnetic field, H,

$$\xi(\mathrm{H}) = (k_{22}/\chi_a)^{1/2}\,\mathrm{H}^{-1},$$

where k_{22} is Frank elastic constant due to the deformation of twist modulus,[10] and χ_a is a anisotropic susceptibility defined as $\chi_{\parallel}-\chi_{\perp}$. It is obvious that the magnetic coherence length is inversely proportional to the magnetic field. That is, assuming that k_{22} is an order of 10^{-6} dyne[2,12] and χ_a an order of 10^{-7} CGS Gauss unit, ξ is estimated to be 80, 32, and 3 μm for 0.4, 1.0, and 10 kG of H, respectively. This means that the magnetically forced orientation cannot be regarded as homogeneous near the cell wall, especially when the magnetic field is below 0.4 kG, although this argument, strictly speaking, holds only when the surface of the cell wall is treated by a particular method to impose a perpendicular orientation on it to the magnetic field.[9] Actually, since the cell used here does not have such an artificial treatment, the deformation region near the surface should be much less than 80 μm even in the magnetic field of 0.4 kG, leading to a validity of the sample thickness in the present optical transmission measurement.

Now let us discuss in more detail the orientational behavior of the liquid crystal under the magnetic field. Free energy per unit volume, F, due to the magnetic field, **H**, is given as follows,[2]

$$\mathrm{F} = -\frac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2, \qquad (1)$$

in which **n** is the director defined above. Liquid crystal including benzene ring in molecular skeleton is known to have a positive anisotropy ($\chi_a = \chi_{\parallel} - \chi_{\perp} > 0$) in diamagnetic susceptibility, since $\chi_{\perp}$ is larger than $\chi_{\parallel}$. It follows that when the director is parallel to the direction of the magnetic field, the free energy becomes minimum, yielding the most stable state. Adopting the value of 1 kG determined as the threshold of H and also $\chi_a = 10^{-7}$ CGS Gauss unit, the free energy per unit volume is numerically evaluated,

$$\mathrm{F} = -\frac{1}{2}\chi_a\,\mathrm{H}^2 = 0.05\ \mathrm{erg/cm^3}. \qquad (2)$$

It is straightforward to obtain a number of molecule per unit volume, N, by assuming that molecular weight of liquid crystal, M, is 260 which being an average of those of PCH302 (m.w. = 246) and PCH304 (m.w. = 274) liquid crystals and density, ρ, of the liquid crystal is 0.9 g/cm³,

$$\mathrm{N} = \mathrm{N_A}\,\rho\,/\,\mathrm{M} = 2.07 \times 10^{21}\ \mathrm{molecules/cm^3}, \qquad (3)$$

where N_A is Avogadro number. Hence the free energy per molecule, $F_{mol.}$, is obtained as follows,

$$F_{mol.} = |F| / N = 2.42 \times 10^{-23} \text{ erg.} \tag{4}$$

In practice, the orientation of the liquid crystal can be achieved only when the stabilization given by interaction between the liquid crystal and the magnetic field overwhelms a destabilization due to a thermal motion of the liquid crystal molecule. The thermal motion of molecule, k_BT, at temperature of 13°C (T = 286 K) is

$$k_BT = 3.95 \times 10^{-14} \text{ erg,} \tag{5}$$

where k_B is Boltzmann constant. It is clear that the thermally motioning energy is much greater than the free energy per molecule ($F_{mol.} << k_BT$), leading to no occurrence of the magnetically forced orientation. This is in conflict with the experimental fact described above. The discrepancy can be settled by taking account of a domain, macroscopic entity, characteristic to the liquid crystal. That is, if molecular assembly forming the domain can behave as a "supermolecule" and it is so large as to include 10^{10} molecules, the free energy given in Equation 4 must be multiplied by 10^{10} times. As a consequence,

$$F_{mol.} = 2.42 \times 10^{-13} \text{ erg.} \tag{6}$$

This value is sufficiently larger than k_BT ($F_{mol.} > k_BT$), enabling the magnetically forced orientation to conquer the disorder by the thermal motion. At this stage, each domain is aligned parallel to the direction of the magnetic field to result in a macroscopic orientation which is called "monodomain."[2,12]

On the other hand, when a value of 0.4 kG is adopted instead of 1 kG for H in Equation 2, $F_{mol.}$ is calculated to be 3.86×10^{-14} erg, very close to the value of k_BT. This may provide us with a prediction that the magnetic field of 0.4 kG should give an onset of the magnetically forced orientation, being in good agreement with the experimental result (see Figure 2).

Next we focus on the domain itself of the liquid crystal. Using Equation 6, the domain including 10^{10} molecules is understood to correspond to a volume of 4.8×10^{-12} cm^3. When the domain is regarded as a cube, a side of the cube is ca. 1.7 μm; when it is as a sphere, a diameter of the sphere is ca. 2.1 μm.

It is worthy to remember that the fibrils of polyacetylene films synthesized in the present liquid crystals used as solvent without the magnetic force (quiescent method) are locally oriented in microscopic region of several μm, although the films themselves show neither optical nor electrical anisotropy.[5,8] Surprisingly, such a size of region well corresponds to the domain concerned here. This may allow us to remark that the local orientation of the fibrils is attributed to a spontaneous orientation of the nematic liquid crystals in each domain. In this case, since the director representing an orientational vector defined in the domain is permitted to take any direction due to an absence of external force, the liquid crystal can be regarded as a "multi-domain" to show no macroscopic alignment. This causes to the isotropic nature in optical and electrical properties of the polyacetylene films prepared by the quiescent method using this sort of liquid crystal as a polymerization solvent.

Conclusion

Orientational behaviors of nematic liquid crystals of phenylcyclohexane derivatives and their nematic solution of $Ti(OBu)_4-AlEt_3$ catalyst under a magnetic field are investigated by means of optical transmission measurements. It is confirmed the magnetically forced orientation of the liquid crystals is achieved through a mechanism of the conversion from the multi-domain into the mono-domain, resulting in a macroscopically aligned reaction field indispensable for highly aligned polyacetylene films.

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