

## Direct Synthesis of Oriented *trans*-Polyacetylene Films

Seiji Shibahara,\* Motoi Yamane,  
Ken Ishikawa, and Hideo Takezoe

Department of Organic and Polymeric Materials,  
Tokyo Institute of Technology, 2-12-1, O-okayama,  
Meguro-ku, Tokyo 152-8552, Japan

Received November 13, 1997

Revised Manuscript Received March 24, 1998

**Introduction.** Polyacetylene, as a highly conductive conjugated polymer, has been the subject of extensive research because of its high conductivity and simple structure as a model compound of the one-dimensional system. A variety of routes have been reported for the synthesis of polyacetylene films.<sup>1–7</sup> Until now, conductivities close to copper have been reported by Naarmann and Theophilou<sup>2</sup> and Tsukamoto et al.<sup>3</sup> The optical spectra of these polyacetylene films showed a broad absorption/reflection peak at about 1.9 eV. The peak energy hardly changed among films, which suggested that the optical spectra of these films were intrinsic to the *trans*-polyacetylene.<sup>8</sup> However, some authors insisted that these spectral features came from inhomogeneous broadening.<sup>9,10</sup>

Recently, we succeeded in synthesizing *trans*-polyacetylene films directly without the heating process for isomerization of as-grown *cis*-polyacetylene films.<sup>11,12</sup> The reflection spectrum of directly synthesized film has a peak at about 1.5 eV, which shifts to a lower energy side than that of the ordinary thermoisomerized film. This peak shift means that directly synthesized *trans*-polyacetylene film has longer averaged conjugation length than that of the ordinary films. Moreover, electron spin resonance (ESR) spectra show that directly synthesized films have a lower density of defects than ordinary films.<sup>13,14</sup> The directly synthesized *trans*-polyacetylene has the potential to present new intrinsic optical properties of *trans*-polyacetylene.

Since *trans*-polyacetylene is a quasi one-dimensional system that shows highly anisotropic transport and optical properties, the use of oriented films is essential to studying polyacetylene. Preparation of oriented films by stretching of as-prepared films can induce defects and breaks the fibrils.<sup>15</sup> Therefore preparation of oriented films without stretching is also important. For that purpose, the liquid crystal polymerization method is useful.

Liquid crystal polymerization method has enabled us to prepare oriented polyacetylene film directly through an anisotropic reaction field, which is produced by macroscopically oriented nematic liquid crystals used as the polymerization solvent for a Ziegler–Natta catalyst.<sup>15–19</sup> Therein, the gravity flow technique or magnetic field employed as an external force is essential for the macroscopic orientation of liquid crystals. The magnetic field method enabled us to obtain higher oriented films than the gravity flow method.<sup>16</sup> Akagi et al. synthesized *cis*-rich oriented polyacetylene films using the magnetic field liquid crystal polymerization method.<sup>17</sup> The doped film showed high electrical conductivity:  $1.6 \times 10^4 \text{ S cm}^{-1}$  along the oriented direction. Moreover, Coustel et al. combined the gravitation flow and a strong magnetic field.<sup>15</sup> The electrical

conductivity of the doped film was  $2.0 \times 10^4 \text{ S cm}^{-1}$  along the oriented direction. They obtained highly oriented films composed of fibrils longer and thicker than those of Shirakawa-polyacetylene.<sup>1</sup> Thus the application of a strong magnetic field leads not only to highly oriented films but also to very long and thick fibrils.

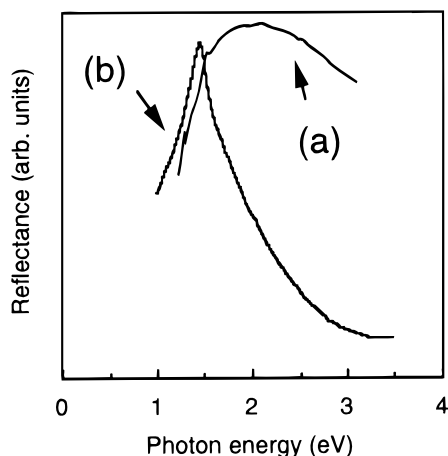
As mentioned above, great efforts have been done on the synthesis of highly conductive films. Even now no attention has been paid to synthesize oriented *trans*-polyacetylene films directly, since *trans*-rich as-grown films show lower electric conductivity after doping compared with that of *cis*-rich as-grown polyacetylene films.

On the other hand, preparation of oriented *trans*-polyacetylene films without thermal treatment and stretching prevents defects and breaking fibrils. Therefore, these films are suitable for studying polyacetylene as a model of a one-dimensional system. In this paper, we will present direct polymerization of oriented *trans*-polyacetylene films and their optical properties.

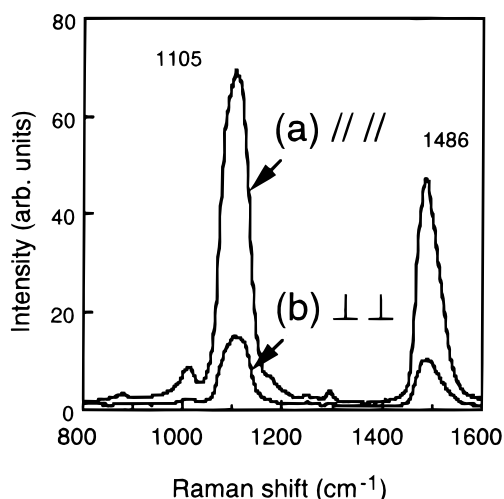
**Experimental Section.** To obtain the oriented *trans*-polyacetylene films, we modified the liquid crystal polymerization method<sup>19</sup> to control the polymerization conditions adequate for the synthesis of *trans*-polyacetylene films, i.e., initial acetylene gas pressure and an Al/Ti ratio.<sup>20,21</sup> The catalyst consists of 0.02–0.04 mol/L Ti(OBu)<sub>4</sub>, and the ratio of AlEt<sub>3</sub> to Ti(OBu)<sub>4</sub> was 4.0. An equimolar mixture of 4-(*trans*-4-*n*-propylcyclohexyl)-ethoxybenzene and 4-(*trans*-4-*n*-propylcyclohexyl)-butoxybenzene supplied by Merck Japan was used as the solvent for the catalyst. The catalyst solution was aged for 2 h in a vacuum of 0.1 Pa at room temperature. A drop of the catalyst that passed through a microfilter (FUJI PHOTO FILM, FLSP 45 1.3CMD) was deposited and spread out on quartz or KBr substrates (20 × 8 mm<sup>2</sup> rectangular). The deposited catalyst was bulk. Polymerization proceeded at the liquid crystal catalyst and the gas surface. The initial pressure of an acetylene monomer was in the range 1.0–1.6 kPa. Polymerization was carried out at room temperature to maintain the solvent in nematic liquid crystal phase.<sup>19,22</sup> The polymerization time was 3–7 min. A magnetic field of 1.4 T was applied during the polymerization to align the liquid crystal molecules unidirectionally. The film was washed with high-purity toluene repeatedly even after the solution became colorless.

Reflection spectra were measured using the lock-in technique. The chopping frequency was 164 Hz. Resonant Raman scattering (RRS) spectra excited at 514.5 nm (2.41 eV) were obtained using a JASCO NR-1800 laser Raman spectrometer. Infrared (IR) absorption spectra were measured using a JIR-WINSPEC 50 spectrometer. Scanning electron micrographs (SEM) were taken on a JEOL JSM T-220. The polyacetylene films prepared on quartz substrates were used for the measurements except for the IR spectra measurements.

**Results and Discussion.** An ordinary as-grown polyacetylene film has two oscillatory structures in absorption/reflection spectra. One is on the lower energy side (1.4–2.0 eV) coming from *trans*-segments, and the other is on the higher energy side (2.0–2.5 eV) coming from *cis*-segments. Figure 1 shows the reflection spectra of polyacetylene prepared by (a) ordinary ther-



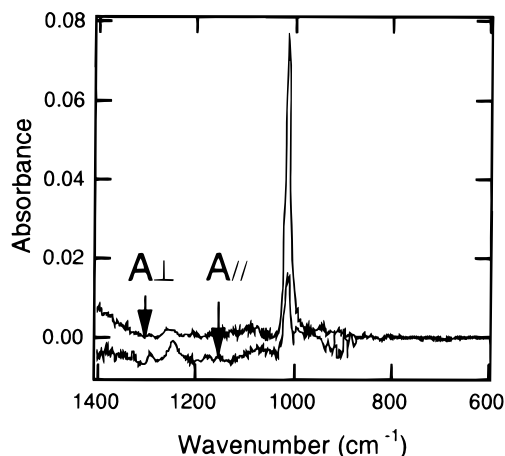
**Figure 1.** Reflection spectra of polyacetylene prepared by (a) an ordinary thermoisoimerized and stretched film and (b) a directly synthesized film.



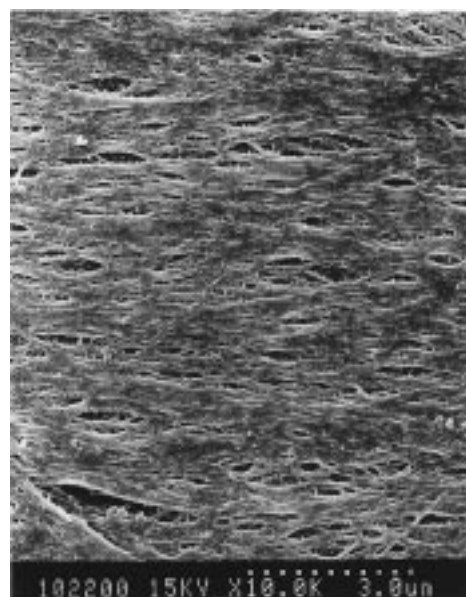
**Figure 2.** Polarized resonance Raman scattering spectra of an oriented *trans*-polyacetylene film excited at 514.5 nm (2.41 eV) using (a) ( $\parallel, \parallel$ ) and (b) ( $\perp, \perp$ ) polarization conditions.

moisoimerized and stretched film and (b) directly synthesized film. The structure of *cis*-segments can hardly be observed in Figure 1b, which indicates that the film contains very small or negligible amounts of *cis*-segments. Moreover, the peak of the *trans*-segments of Figure 1b shifts to the lower energy side and shows a narrower width in comparison with the peak of Figure 1a. Nishioka et al. reported that this peak shift and narrower peak width means that an effective conjugation length distribution of the directly synthesized *trans*-polyacetylene film has a longer averaged length and narrower width than that of the ordinary film.<sup>14</sup>

Figure 2 shows the polarized resonant Raman scattering (RRS) spectra excited at 514.5 nm (2.41 eV). The polarizations for the incident and the scattered light were chosen as (a) ( $\parallel, \parallel$ ) and (b) ( $\perp, \perp$ ), respectively, with respect to the averaged orientation direction. The *cis* C—C stretching mode at 1252  $\text{cm}^{-1}$  can hardly be seen in Figure 2.<sup>23</sup> The main Raman bands show peaks at 1105 and 1486  $\text{cm}^{-1}$  in the ( $\parallel, \parallel$ ) configuration and 1109 and 1488  $\text{cm}^{-1}$  in the ( $\perp, \perp$ ) configuration, which are attributed to the *trans* C—C and C=C stretching modes, respectively. The positions of the *trans* C—C and C=C stretching modes of the directly synthesized film shift to the lower Raman shift than those of the ordinary film,<sup>24</sup> also indicating the directly synthesized film has



**Figure 3.** Polarized infrared absorption spectra of an oriented *trans*-polyacetylene film.  $A_{\perp}$  and  $A_{\parallel}$  are absorbances perpendicular and parallel to the orientation direction of the film, respectively.



**Figure 4.** Scanning electron micrograph of an oriented *trans*-polyacetylene film. The direction of a magnetic field is horizontal.

a longer averaged conjugation length than that of the ordinary film. The polarization anisotropy of the *trans* C=C stretching mode is 4.6.

Figure 3 shows the polarized infrared absorption (IR) spectra of an oriented *trans*-polyacetylene film,  $A_{\perp}$  and  $A_{\parallel}$ . The *cis* C—H out of plane vibration band at 740  $\text{cm}^{-1}$  can hardly be seen in Figure 3.<sup>25</sup> As a measure of optical anisotropy of the film, the IR dichroic ratio,  $A_{\perp}/A_{\parallel}$ , was evaluated to be 3.5 using an absorption peak (1011  $\text{cm}^{-1}$ ) attributable to the *trans* C—H out of plane vibration, indicating a good orientation of *trans*-polyacetylene chains along the fibril alignment of the film.

Figure 4 shows the scanning electron micrograph (SEM) of an oriented *trans*-polyacetylene film. A high degree of fibril alignment is clearly observed along the direction of the magnetic field.

In conclusion, we have shown that highly oriented *trans*-polyacetylene films can be prepared directly without thermal treatment and stretching. These films polymerized in a macroscopically aligned nematic liquid crystal phase of catalyst solution attained by a magnetic

field. These films have a longer averaged conjugation length than those of the ordinary thermally treated films.

**Acknowledgment.** We are grateful to Mr. R. Ohki at the Research Cooperation Division, Tokyo Institute of Technology, for taking the SEM images. We also would like to thank Merck Japan for providing the liquid crystals. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

## References and Notes

- (1) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 11.
- (2) Naarmann, H.; Theophilou, N. *Synth. Met.* **1987**, *22*, 1.
- (3) Tsukamoto, J.; Takahashi, A.; Kawasaki, K. *Jpn. J. Appl. Phys.* **1990**, *29*, 125.
- (4) Lugli, G.; Pedretti, U.; Perego, G. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 129.
- (5) Woerner, T.; MacDiarmid, A. G.; Feldblum, A.; Heeger, A. J. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 119.
- (6) Ozaki, M.; Ikeda, Y.; Arakawa, T. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 989.
- (7) Edwards, J. H.; Feast, W. J. *Polym. Commun.* **1980**, *21*, 595.
- (8) Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W.-P. *Rev. Mod. Phys.* **1988**, *60*, 781.
- (9) Eckhardt, H. *J. Chem. Phys.* **1983**, *79*, 2085.
- (10) Kubo, T.; Watanabe, T.; Nishioka, T.; Takezoe, H.; Fukuda. *Jpn. J. Appl. Phys.* **1992**, *31*, 3372.
- (11) Nishioka, T.; Suruga, K.; Natsume, N.; Ishikawa, K.; Takezoe, H.; Fukuda, A. *Synth. Met.* **1996**, *80*, 315.
- (12) Shibahara, S.; Nishioka, T.; Natsume, N.; Ishikawa, K.; Takezoe, H.; Fukuda, A. *Synth. Met.*, in press.
- (13) Nishioka, T.; Suruga, K.; Natsume, N.; Ishikawa, K.; Takezoe, H.; Fukuda, A. *Synth. Met.* **1995**, *69*, 65.
- (14) Nishioka, T.; Suruga, K.; Ishikawa, K.; Takezoe, H.; Fukuda, A. *Jpn. J. Appl. Phys.* **1994**, *33*, L953.
- (15) Coustel, N.; Foxon, N.; Ribet, J. L.; Bernier, P.; Fischer, J. E. *Macromolecules* **1991**, *24*, 5867.
- (16) Shirakawa, H.; Akagi, K.; Katayama, S.; Araya, K.; Mukoh, A.; Narahara, T. *J. Macromol. Sci., Chem.* **1988**, *A25*, 643.
- (17) Akagi, K.; Katayama, S.; Ito, M.; Shirakawa, H.; Araya, K. *Synth. Met.* **1989**, *28*, D51.
- (18) Aldissi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 167.
- (19) Akagi, K.; Katayama, S.; Shirakawa, H.; Araya, K.; Mukoh, A.; Narahara, T. *Synth. Met.* **1987**, *17*, 241.
- (20) Suruga, K.; Natsume, N.; Nishioka, T.; Ishikawa, K.; Takezoe, H.; Fukuda, A. *Synth. Met.* **1995**, *69*, 19.
- (21) Okuda, T.; Zhang, Y. X.; Akagi, K.; Shirakawa, H. *Polym. Prepr. Jpn.* **1992**, *41*, 2460.
- (22) Araya, K.; Mukoh, A.; Narahara, T.; Shirakawa, H. *Synth. Met.* **1986**, *14*, 199.
- (23) Kuzmany, H. *Phys. Stat. Sol.* **1980**, *97*, 521.
- (24) Schügerl, F. B.; Kuzmany, H. *J. Chem. Phys.* **1981**, *74*, 953.
- (25) Shirakawa, H.; Ikeda, S. *Polym. J.* **1971**, *2*, 231.

MA971677I