Highly Conducting Polyacetylene Films Prepared in a Liquid Crystal Solvent

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ABSTRACT: Polyacetylene films prepared by the liquid crystal polymerization method with gravity flow technique are investigated through measurements of scanning electron micrographs, polarized infrared absorption spectra, and electrical conductivities. It is explored that the films have significant orientation of conjugated polyene chains along fibril alignment, and that upon doping by I_2 or AsF_5 they exhibit the highest electrical conductivity among those reported so far. By taking account of both morphological structure and activation energy for electrical conduction, the high conductivity is rationalized with preferential increase of parallel fraction of fibril achieved in the highly oriented polyacetylene films.
KEY WORDS   Polyacetylene / Liquid Crystal / Scanning Electron Micrograph / Morphology / Orientation / Polarized Infrared Spectra / Electrical Conductivity / Anisotropy / Doping / Activation Energy /

Electrical conductivity is a central matter to be concerned in characterizing polyacetylene as low-dimensional conductive materials.[1,2] Randomly oriented fibrillar morphology formed in usual as-grown polyacetylene film causes a variety of conduction pathways and screens an intrinsic conductivity of conjugated polyene chain. Since stretch-aligned polyacetylene film has been verified to exhibit an enhanced conductivity as well as an electrical anisotropy,[3,4] it becomes a current focus to align fibrils in order to achieve a crucial one-dimensionality for polyacetylene. Very recently, a novel method by virtue of nematic liquid crystal as polymerization solvent was developed for preparation of highly oriented polyacetylene film.[5,6] Usage of the films obtained by this method should promise to yield deeper insights into electrical and optical properties from aspects of anisotropy. In this study, we will show that the present films used have significant orientation of polyene chains along fibril alignment, and that upon the doping I_2 or AsF_5 they exhibit the highest conductivity among those reported so far, primarily due to preferential increase of parallel fraction of fibril realized in highly oriented film.

EXPERIMENTAL

Polyacetylene films were prepared by using a Ziegler–Natta catalyst in a nematic liquid crystal solvent according to the procedure recently

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put forward.[5,6] Typical concentration of the catalyst was 0.05 mol l^{-1} of Ti(OBu)$_4$ and ratio of AlEt$_3$ to Ti(OBu)$_4$ was 3.0. As a liquid crystal solvent was used an equimolar mixture of 4-(*trans*-4-*n*-propylcyclohexyl)-ethoxybenzene and 4-(*trans*-4-*n*-propylcyclohexyl)-butoxybenzene. The catalyst solution was aged for 30 minutes at room temperature. Six-nine grade acetylene monomer supplied from Koatsu Gas Kogyo Co., Ltd., was used without further purification. Polymerization was carried out on a vertical glass wall of a flask over which the catalyst solution flowed down by the gravity. During the polymerization, temperature was kept at 10—13°C in order to maintain nematic phase of the liquid crystal solution. Initial pressure of acetylene was 450—470 Torr, and reaction time 1—120 minutes. After polymerization, polyacetylene film was washed with toluene several times under inert gas and then immersed in an acetic acid solution (90 vol% methanol). Thickness of polyacetylene films thus obtained was 1–30 μm, depending on polymerization time. Scanning electron micrograph (SEM) of the polyacetylene film was measured using a Hitachi S-540 type scanning microscope. Infrared absorption spectra of the films were measured by using a JASCO IR-810 spectrometer.

RESULTS AND DISCUSSION

As shown in Figure 1, the film exhibits a highly oriented fibrillar morphology. The orientation of fibrils was confirmed to correspond to the flow direction of the liquid crystals. Such a macroscopic alignment of fibrils is quite in contrast to the randomly oriented fibrillar morphology of usual as-grown films.[3,6] This promotes us to carry out measurements of optical and electrical properties for the present films.

Convenient formulae for analysis of IR spectra were used to grasp *cis* and *trans* contents of polyacetylene films,[1] *i.e.*, % *cis* =
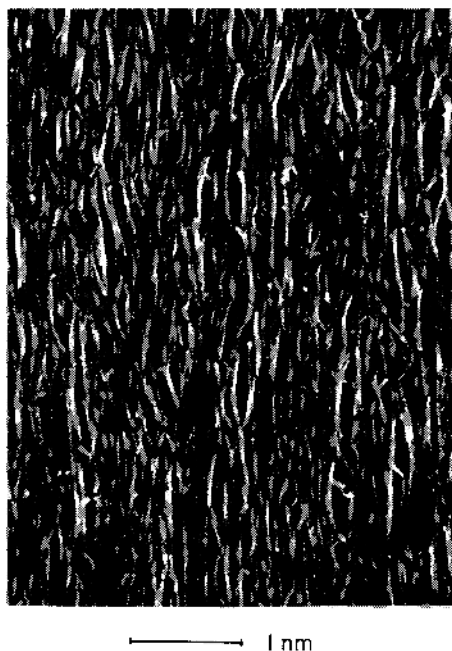

Figure 1. Scanning electron micrograph of polyacetylene film obtained by the gravity flow polymerization method.

$100 \times 1.3A_{cis}/(1.3A_{cis} + A_{trans})$ and % *trans* = $100 \times A_{trans}/(1.3A_{cis} + A_{trans})$, where A_{cis} and A_{trans} are absorbances of *cis* and *trans* peaks located at 740 and 1015 cm^{-1}, respectively. The present films are found to be composed of 53—60% *cis*-form and 40—47% *trans*-form. Subsequently, measurements of polarized infrared absorption spectra were carried out with polarized cells attached to the above mentioned spectrometer. Representative spectra are shown in Figure 2. Therein, $A_{\parallel}$ and $A_{\perp}$ stand for absorbances of polarized lights parallel and perpendicular to the orientation direction of the film, respectively. It is evident that in-plane and out-of-plane vibrations of polyacetylene respectively correspond to parallel and perpendicular directions of polarized lights.[7,8] It is therefore straightforward to estimate roughly an optical anisotropy with respect to each absorption peak. That is, since absorption peaks at 450, 1330 and 3045 cm^{-1} are attributed to in-plane vibrations of *cis*-form, optical anisotropies
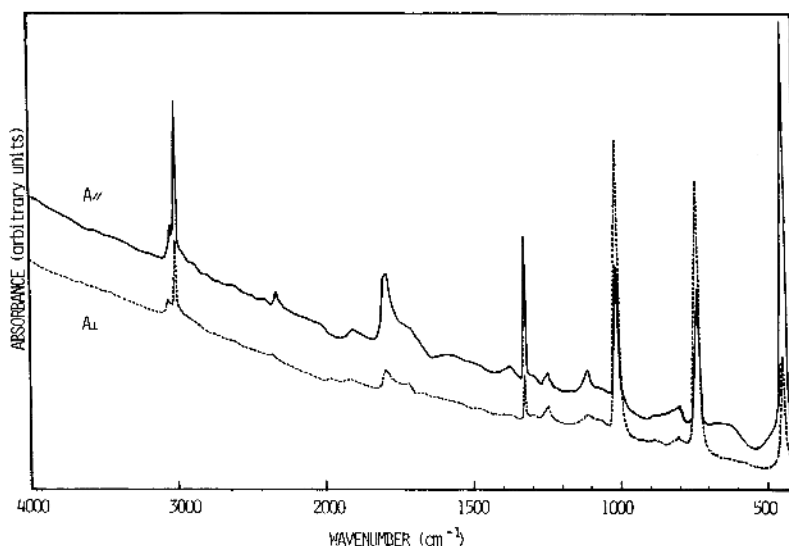
Figure 2. Polarized infrared absorption spectra of the highly oriented polyacetylene film: $A_{\parallel}$, parallel; $A_{\perp}$, perpendicular.

based on these peaks were calculated by $A_{\parallel}/A_{\perp}$. On the other hand, since those at 740 and 1015 cm^{-1} are respectively out-of-plane vibrations of *cis*- and *trans*-forms, anisotropies were calculated by $A_{\perp}/A_{\parallel}$. As a result, optical anisotropies were 2.0—3.8, which confirms significant orientation of polyacetylene chains along fibril alignment.

The polyacetylene films were doped by exposure to vapor of iodine (I_2) or arsenic pentafluoride (AsF_5). In I_2-doping vapor pressure was kept below 0.03—0.04 Torr by cooling the dopant apparatus, while in AsF_5-doping it was controlled from 0.01 to 5—7 Torr by monitoring with digital manometer. In the latter, the doping process was stopped tentatively to evacuate such gaseous product as AsF_3 which might prohibit an uniform doping. Electrical conductivity was measured with four-probe method. Figure 3 shows changes of electrical conductivities of I_2-doped polyacetylene film as a function of doping time. Note that initial values of 10^{-6} S cm^{-1} measured before doping is located between those of 10^{-9} S cm^{-1} for *cis*-form and 10^{-5} S cm^{-1} for *trans*-form.[9] This may be due to

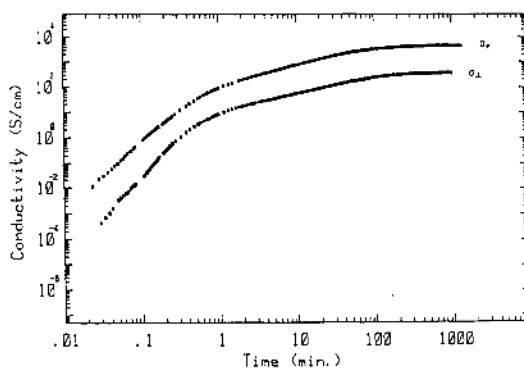**Figure 3.** Electrical conductivity of the highly oriented polyacetylene film during the course of vapor phase I_2-doping: $\sigma_{\parallel}$, parallel; $\sigma_{\perp}$, perpendicular.

the almost same contents of *cis* and *trans* forms in the present film which has been synthesized at 10—13°C to maintain liquid crystal phase. As the doping proceeds, both parallel and perpendicular conductivities increase with monotonous manners. Maximum values of parallel and perpendicular conductions were 4.6×10^3 and 3.9×10^2 S cm^{-1}, respectively. Electrical anisotropy, defined as a ratio of parallel conductivity ($\sigma_{\parallel}$) to perpendicular one ($\sigma_{\perp}$), was calculated to be 12. These re-

sults are summarized in Table I, together with those of AsF$_5$-doping. In case of AsF$_5$-doping, parallel and perpendicular conductivities have maximum values of 1.1×10^4 and 2.4×10^3 S cm^{-1}, respectively, by which electrical anisotropy is calculated to be 5. It must be emphasized that each maximum value of parallel conductivity attained through I$_2$- or AsF$_5$-doping is the highest value among those reported so far, e.g., higher by 3 and 8 times than those of stretched aligned films and randomly oriented films, respectively.[10] Especially, the conductivity with order of 10^4 S cm^{-1} attained by the AsF$_5$-doping corresponds to that of Mercury (1.04×10^4 S cm^{-1} at 0°C) and is also close to an estimated value of intrinsic conductivity in heavily AsF$_5$-doped polyacetylene with metallic state (ca. 4×10^4 S cm^{-1} at room temperature).[10]

It is of interest to note that the electrical anisotropy of 12 obtained for the present I$_2$-doped film is comparable to those (10—13) of I$_2$-doped stretched films with elongation ratio of 2.9.[3,4] However, the conductivity of the forms is 3 times higher than that of the latter, as mentioned above. These results may indicate that the present film has apparently the same degree of fibril alignment as in the case of mechanically stretched films by three times, but that it is free from cleavage of fibrils encountered in mechanical elongation of film and also has less interfibril contacts to cause various conduction pathways and barriers for conduction.

Figure 4 shows temperature dependence of normalized conductivity in the AsF$_5$-doped polyacetylene film in the range of room temperature down to liquid nitrogen temperature. Both parallel and perpendicular conductivities are found to decrease gradually with decreasing temperature. Arrhenius plots gave approximately straight lines in the range of 250—

Table I. Electrical conductivity and anisotropy of highly oriented polyacetylene film doped with I$_2$ and AsF$_5$

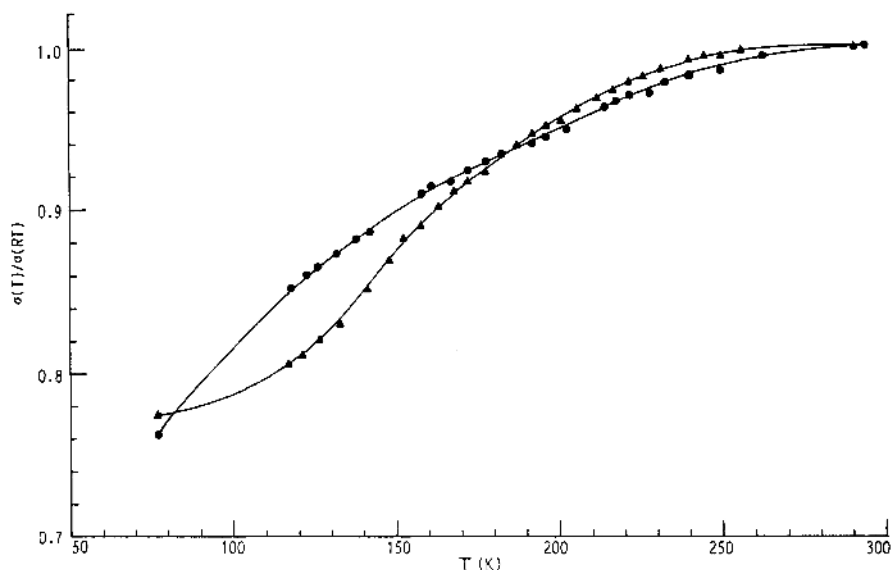| Dopant species	$\sigma_\parallel$ S cm^{-1}	$\sigma_\perp$ S cm^{-1}	$\sigma_\parallel/\sigma_\perp$
I$_2$	4.6×10^3	3.9×10^2	12
AsF$_5$	1.1×10^4	2.4×10^3	5

Figure 4. Temperature dependence of normalized conductivity of AsF$_5$-doped highly oriented polyacetylene film: ●, parallel; ▲, perpendicular.

125 K. Activation energies calculated for parallel and perpendicular conductions were 3.9 and 4.3 meV, respectively. Such small activation energies unambiguously indicate a so-called 'metallic state' in doped polyacetylene films.[10] In spite of significant anisotropy of *ca.* 5 in electrical conductivity, there is only small difference in activation energies between parallel and perpendicular directions. This implies a similar role of interfibril contacts in each direction, in agreement with the case of stretch-aligned films.[10,11] It is therefore argued that the high electrical conductivities achieved in the present film is primarily due to high orientation of fibrils, allowing a preferential increase of fibril fraction in the parallel direction and decrease in the perpendicular one.

In conclusion, we have first attained the electrical conductivity of 10^4 S cm^{-1} by using AsF$_5$-doped highly oriented polyacetylene film prepared through liquid crystal polymerization method. These results demonstrate profound potentialities of highly oriented polyacetylene films as organic conductors, leading us to an advanced stage of one-dimensional conductive polymers.

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