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SYNTHESIS, CHARACTERIZATION, AND PROPERTIES OF ALIGNED POLYACETYLENE FILMS

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ABSTRACT

Highly aligned polyacetylene films are synthesized by three different methods in which nematic liquid crystals are used as an ordered matrix solvent: Method 1, polymerization of acetylene is carried out in a quiescent nematic solution in which a $\text{Ti}(\text{OBu})_4\text{-AlEt}_3$ Ziegler-Natta catalyst is dissolved homogeneously; Method 2, macroscopic alignment is attained by gravity flow of the nematic liquid crystal-catalyst system; and Method 3, the nematic liquid crystal-catalyst solution is aligned under a magnetic field. Characterization of these films is carried out through SEM observation and measurements of polarized visible and infrared absorption spectra. Results indicate that as-prepared films have highly aligned fibrils.

Upon doping by I_2 and AsF_5 , these films exhibit high electrical conductivity of the order of 10^4 S/cm.

INTRODUCTION

Polyacetylene is the simplest conjugated polymer. It consists of CH units in which each carbon atom has one π -electron forming a linear chain of π -electrons. Thus, high electrical conduction along the polymer chains is anticipated, giving rise to a large anisotropy in electrical properties. Electron microscopy studies show that the as-grown films of polyacetylene consist of randomly oriented fibrils. Typical fibril diameter is about 200 Å but can be varied to some extent (60 to 1000 Å) by different polymerization conditions.

In order to study the intrinsic one-dimensional properties of polyacetylene, preparation of oriented films by uniaxial stretching of the as-prepared films or direct polymerization of aligned films is essential. In this paper we present direct synthetic methods of highly oriented polyacetylene films in which simultaneous polymerization of acetylene and alignment of fibrils are attained in an aligned molecular matrix of nematic liquid crystals.

EXPERIMENTAL

Polyacetylene films were prepared by using a $Ti(OBu)_4-AlEt_3$ Ziegler-Natta catalyst in nematic liquid crystal solvents according to a procedure recently reported [1-5]. Typical concentration of the catalyst was 0.05 mol/L of $Ti(OBu)_4$, and the ratio of $AlEt_3$ to $Ti(OBu)_4$ was 3.0. An equimolar mixture of 4-(*trans*-4-*n*-propylcyclohexyl)ethoxybenzene and 4-(*trans*-4-*n*-propylcyclohexyl)butoxybenzene supplied by E. Merck was used to give the liquid crystals which were used without further purification except for degassing prior to use. The catalyst solution was aged for 30 min at room temperature. Six-nine grade acetylene monomer, supplied by Koatsu Gas Kogyo Co. (Osaka, Japan), was used without further purification.

In the gravity flow method, polymerization was carried out on a vertical glass wall of a flask over which the catalyst solution flowed down by gravity, as shown in Fig. 1. An apparatus for polymerization under a magnetic field is given in Fig. 2. During polymerization the temperature was kept at 5-15°C in order to maintain a nematic phase of the liquid crystal catalyst solution. The initial pressure of acetylene was 450-470 torr for the flow method and 600-760 torr for the magnetic field method, and the reaction time was 1-120

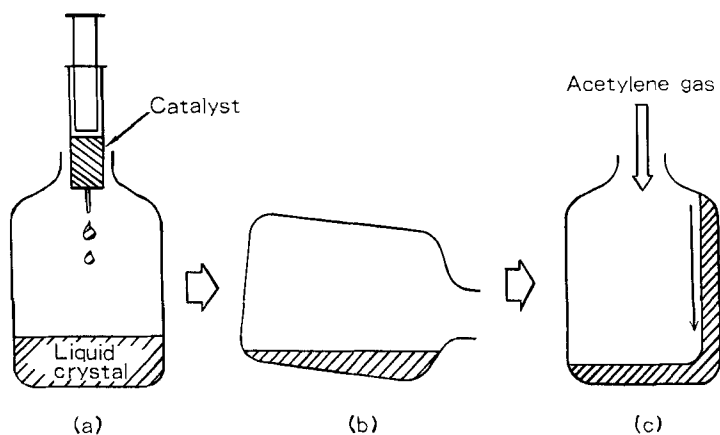


FIG. 1. Apparatus and procedure used in the flow method.

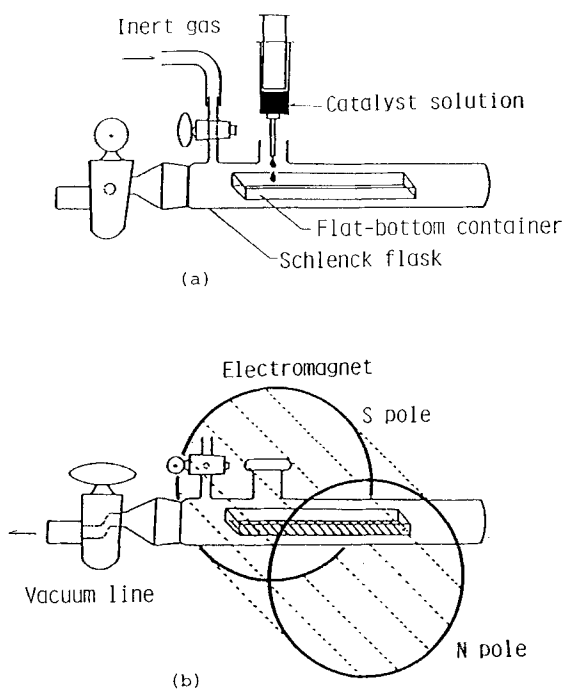


FIG. 2. Apparatus and procedure used in the magnetic field method.

min. The apparatus shown in Fig. 2(a) was used for polymerization in a quiescent nematic phase of the catalyst solution under no magnetic field. Polymerization was carried out at 5–15°C in a flat-bottom reactor on which the catalyst solution of the nematic phase was spread to give a controlled thickness of the catalyst solution.

After polymerization, the polyacetylene films were washed several times with toluene under inert gas. The films were dried under vacuum on a Teflon sheet and stored in a freezer at –20°C. The thickness of the polyacetylene films thus obtained was 5–160 μm for films prepared in a quiescent nematic phase of the catalyst solution: 1–30 μm by the flow method and 2–50 μm by the magnetic field method.

Scanning electron micrographs were taken on Hitachi Models S-450 and S-800 scanning electron microscopes. Infrared absorption spectra were recorded by a JASCO IR-810 infrared spectrophotometer. Electrical conductivities in the parallel and perpendicular directions of the films were measured simultaneously at room temperature by a four-probe method during vapor-phase chemical doping. Two four-probe samples cut parallel and perpendicular to the orientation direction of the original film were used for this measurement.

RESULTS AND DISCUSSION

Method 1: Polymerization in a Quiescent Nematic Phase of the Catalyst Solution

We observed a partial alignment of the fibrils in a limited microscopic region when polymerization of acetylene was carried out in a nematic liquid crystal phase in which homogeneous Ziegler-Natta catalyst, $\text{Ti}(\text{OBu})_4\text{-AlEt}_3$, is dissolved. Figure 3 shows the partial alignment of fibrils, which causes an enhancement of electrical conductivity when the film is doped with iodine and other dopants.

The enhancement depends strongly upon the thickness of the films. As shown in Fig. 4, the electrical conductivities of thin films fully doped by I_2 are unusually high, up to 6000 S/cm, which is one order magnitude higher than those of films prepared by the traditional method. The conductivity decreases with increasing thickness of the films and tends to be constant at 600 S/cm for thicknesses above ~60 μm. This value is identical to that of isotropic films prepared in normal solvents, whose conductivity is independent of the film thickness. This observation suggests that macroscopic in-plane alignment of fibrils occurs when the nematic phase of the catalyst system is sufficiently thin.



FIG. 3. Scanning electron micrograph of a polyacetylene film prepared in a quiescent nematic phase of the catalyst solution.

Encouraged by this observation, we tried two methods to align the nematic catalyst solution on the macroscopic scale: Method 2, flowing the solution down a glass wall of a reaction flask; and Method 3, applying a magnetic force to the solution as an external perturbation.

Method 2: Flow Technique

Polymerization was carried out on a vertical glass wall of a flask over which the catalyst solution flowed down by the gravity. 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 morphol-

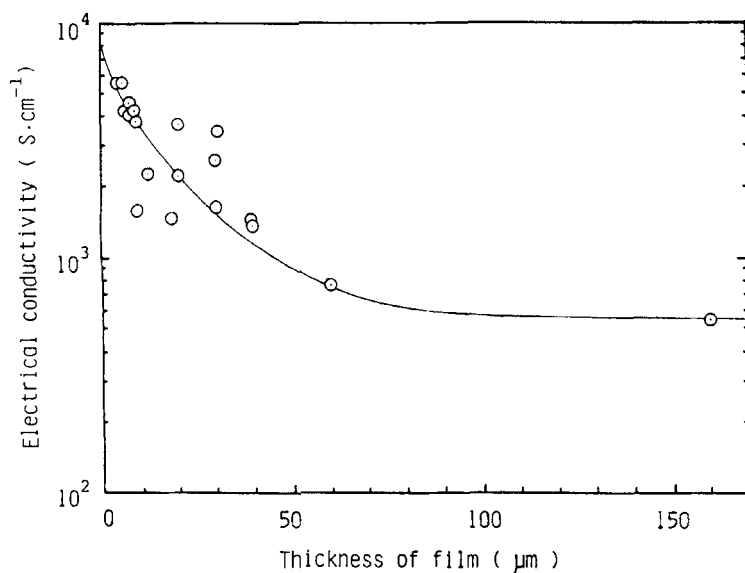


FIG. 4. Relationship between electrical conductivity and thickness of films prepared in a quiescent nematic phase of catalyst solution.

ogy of the usual as-grown films. Optical anisotropies measured by polarized IR absorption spectra were 2.0-3.8, which confirms significant orientation of polyacetylene chains along the flow direction of the nematic catalyst solution.

The relationship between the polymerization conditions and the thickness of the films prepared by the flow method is summarized in Table 1. In this table, samples A, B, and C were used for measurements of visible absorption spectra, infrared absorption spectra, and electrical conductivity, respectively.

The polyacetylene films were doped by exposure to vapor of iodine (I_2), of arsenic pentafluoride (AsF_5), or of sulfuric acid (H_2SO_4). The electrical conductivity was measured by the conventional four-probe method. These results are summarized in Table 2.

Method 3: Magnetic Field Method

The applied magnetic force was 2-14 kG, and the temperature was kept at 5-15°C during the polymerization in order to maintain the nematic phase of the catalyst solution. The morphology of the films was the same as that of

TABLE 1. Relationship between Polymerization Conditions and Film Thickness

Sample	Temperature, °C	Time, min	Pressure, torr	Thickness, μm
A	19	0.2	456	1
B	13	10	464	1-10
C	10	120	467	10-30

films prepared by the flow technique. The orientation of the fibrils was confirmed to be consistent with the direction of magnetic field. IR dichroic ratios of 3.3-3.5 demonstrate significant orientation of the polyacetylene chains along the applied magnetic field.

Films prepared by either the flow method or the magnetic field method exhibit a highly oriented fibrillar morphology, as shown in Figs. 5 and 6, respectively. The orientation of the fibrils is confirmed to correspond to either the flow direction of the liquid crystals or the direction of the magnetic field. There is no doubt that this orientation is due to macroscopic alignment of the nematic liquid crystal caused by a shearing stress between the glass wall of the reactor and the liquid crystal layer in the former method and by the magnetic field in the latter method. The size of the oriented films can be controlled by changing the size of the reaction flask in the case of the flow method. However, the magnet gap size restricts the size of oriented polyacetylene films for the magnetic field method. Because of this restriction, the maximum size of ori-

TABLE 2. Anisotropic Electrical Conductivity of Fully Doped Oriented Polyacetylene Films

Preparative method	Dopant	σ_{\parallel} , kS/cm	σ_{\perp} , kS/cm	Anisotropy ^a
Flow method	I ₂	4.6	3.9	1.2
	AsF ₅	11	2.4	4.6
Magnetic method	I ₂	12	4.8	2.4
	H ₂ SO ₄	4.5	1.6	2.8

^aRatio of parallel to perpendicular conductivities.

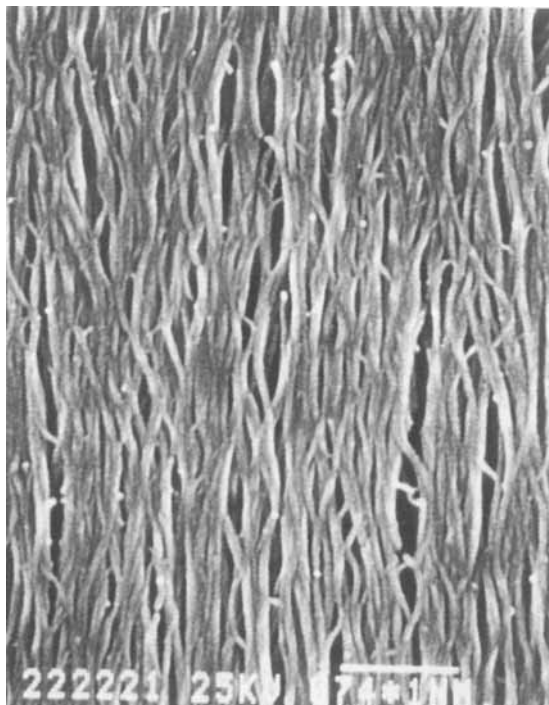


FIG. 5. Scanning electron micrograph of a polyacetylene film prepared by the flow method at 18°C . The flow direction is vertical.

ented films prepared by this method is 3×18 cm, in which alignment is along the short side. The thickness can be controlled by adjusting the polymerization temperature, the time, and the acetylene pressure.

Polarized absorption spectra in the ultraviolet and visible regions were measured on thin films (*A*). The optical anisotropy (R) of the absorption peak at ~ 2 eV was about 5. According to the order parameter defined by $(R - 1)/(R + 2)$ [6], this value corresponds to an order parameter of 0.57 with respect to the linear conjugated chains, and is approximately equal to the value for nematic liquid crystals [7].

Figure 7 shows the polarized IR absorption spectra. The dichroic ratio of the peak at 1015 cm^{-1} , assigned to *trans* C–H out-of-plane vibration, is calculated to be 3.5–5.6 for several polymerization batches under different condi-

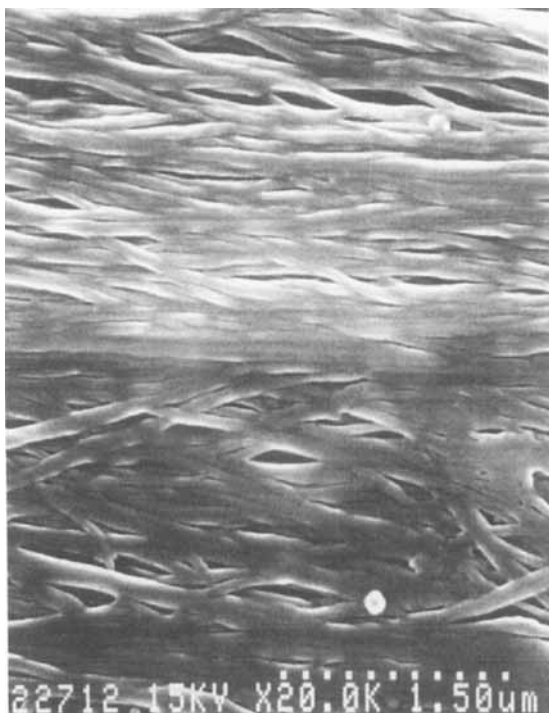


FIG. 6. Scanning electron micrograph of a polyacetylene film prepared by the magnetic field method under 10 kG at 10-15°C. The direction of the magnetic field is horizontal.

tions. These values correspond to order parameters of 0.45-0.61, in agreement with the value obtained from the dichroic ratio of visible absorption spectra. It is worth mentioning that the optically determined order parameters of polyacetylene chains coincide very closely with that of the nematic liquid crystals.

Electrical conductivities in the parallel and perpendicular directions of the films were measured simultaneously with the conventional four-probe method by exposing the films to vapor of dopants such as I_2 , AsF_5 , and H_2SO_4 . Two samples cut parallel and perpendicular to the orientation direction of the original films were used for this measurement. Figure 8 shows the conductivity of an I_2 -doped film as a function of doping time. At the initial stage of doping,

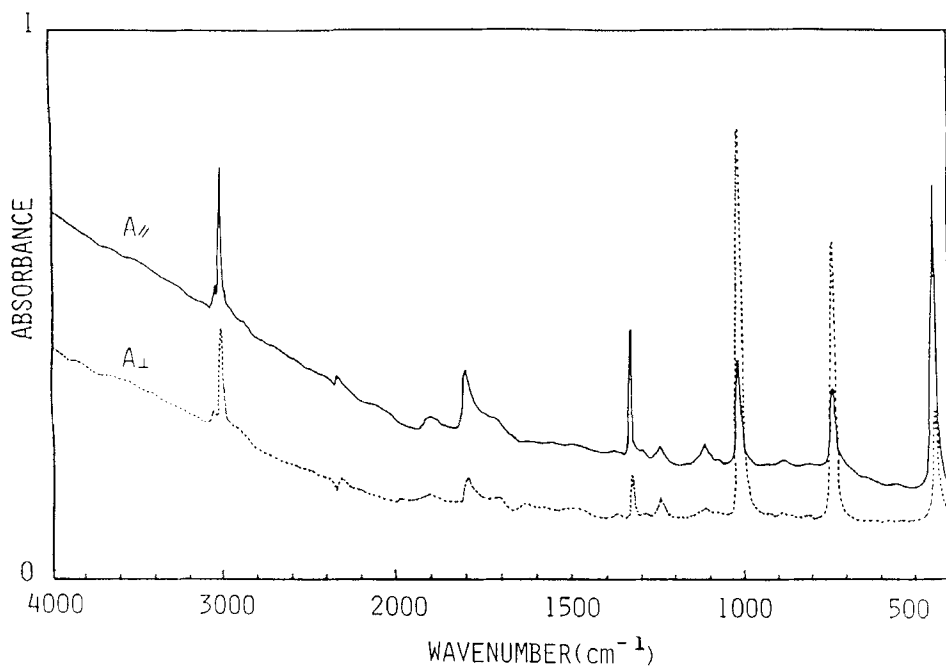


FIG. 7. Polarized infrared absorption spectra of highly oriented polyacetylene films prepared by the magnetic field method. A_{\parallel} and A_{\perp} are absorbances parallel and perpendicular to the orientation direction of chains, respectively.

both parallel and perpendicular conductivities increased more rapidly than in the usual as-grown or mechanically stretched films, and then they attained a first plateau of 10 S/cm order of magnitude. With increasing iodine vapor pressure, they increased in the same manner to the second plateau, corresponding to a saturated state in the iodine doping. As a consequence, the maximum values of parallel and perpendicular conductivities were 12 and 4.8 kS/cm, respectively. Electrical anisotropy, defined as the ratio of parallel to perpendicular conductivity, was calculated to be 2.4. It is interesting to note that the parallel value corresponds to that of mercury (10.4 kS/cm at 0°C) and that it is also close to an estimate value of intrachain conductivity (~40 kS/cm at room temperature) predicted by thermopower measurements of heavily AsF_5 -doped polyacetylene film [8]. Results of conductivity measurements are summarized in Table 2.

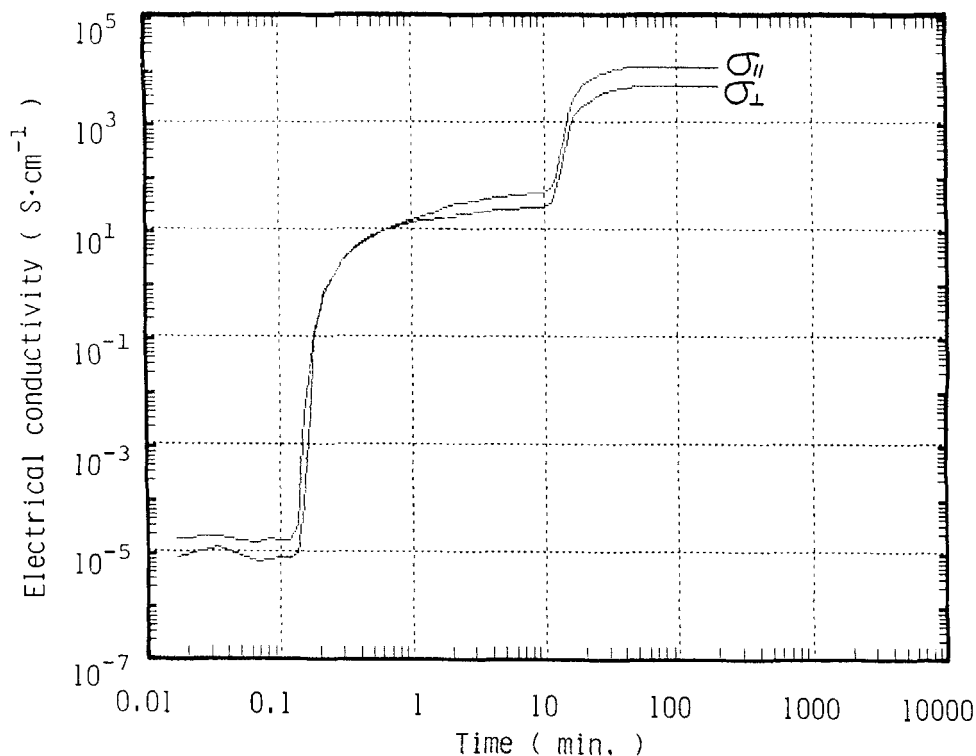


FIG. 8. Anisotropic electrical conductivity of polyacetylene film upon iodine doping. The films were prepared by the magnetic field method. Vapor pressure of iodine was kept below 0.03 torr up to 10 min, then it was increased to the saturated vapor pressure at room temperature, ~ 0.11 torr.

Lastly, it must be mentioned that the unexpectedly small value of the electrical anisotropy might be rationalized by the high alignment of fibrils as shown in Figs. 2 and 3. Thus, contracted interfibril distances would enhance interfibril jumps of the carriers by lowering their potential barriers, producing π -electron overlaps between interfibrils. Otherwise, it can be explained with an alternative morphology in which each fibril is not isolated from the others but in which a bundle of polyacetylene chains in one fibril penetrates into another fibril to form a network structure, resulting in the small ratio between parallel and perpendicular conductivities.

CONCLUSION

We have shown that highly oriented polyacetylene films can be prepared in a macroscopically aligned nematic phase of catalyst solution attained by two different methods, orientation by gravity flow of the solution (flow method) and alignment in a magnetic field (magnetic field method). It was shown that the films prepared by these two methods have significant orientation of conjugated polyene chains along the fibril alignment by scanning electron microscope observation and by polarized infrared and visible absorption measurements, and that they exhibit very high electrical conductivities upon doping by I_2 , AsF_5 , and H_2SO_4 .

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