

Side-Chain Liquid Crystalline Polyacetylene Derivative – Synthesis, Chemical Doping, and Magnetically Forced Alignment

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The mono-substituted acetylene monomer with the liquid crystalline group was polymerized using a rhodium complex catalyst. The polymer exhibited smectic A phase. The liquid crystalline behavior was examined by XRD, DSC and polarizing optical microscope measurements. The polymer main chain was confirmed to be *cis* form. The charge transfer interaction between the polymer and a dopant such as iodine or AsF₅ was observed using UV-Vis absorption spectroscopy. Electrical conductivity along the main chain of the magnetically oriented polymer film was $\sim 10^{-4}$ S/cm. Electrical anisotropy between the parallel and perpendicular directions in the oriented sample was an order of 10^2 .

Key words: polyacetylene derivative, liquid crystal, AsF₅ doping, magnetic forced alignment, electrical conductivity.

1. INTRODUCTION

Conjugated polymers have been attracting much attention because of their electrical transportation phenomena, nonlinear optics, and organic magnetism. Especially, iodine-doped polyacetylene has been regarded as a representative organic conductor whose electrical conductivity is comparative to those of metals. Such a high conductivity has been achieved in macroscopically aligned polyacetylene films. Akagi *et al.* synthesized a directly aligned polyacetylene film using liquid crystal as a solvent under magnetic force field¹. It has been confirmed through scanning electron micrography that high conductivity is attributed to highly aligned fibrillar morphology. Recently, we synthesized a series of polyacetylene derivatives with liquid crystalline group in the side chain, to develop advanced polymers with solubility, fusibility, and liquid

crystallinity². Here, we focus on a liquid crystalline polyacetylene derivative synthesized with rhodium-based catalyst. Doping effects of arsenic pentafluoride (AsF₅) and iodine (I₂), as well as the effect of magnetically forced alignment, in the electrical conductivity were examined.

2. EXPERIMENTAL

2.1 Polymerization

A typical procedure is described as follows. In a Schlenk tube, 2.1 mg (0.045 mmol) of [Rh(NBD)Cl]₂ was added to 1 ml of NEt₃. After aging for 30 min, 1.41g (4.5 mmol) of the monomer (1) in 1.8 ml of tetrahydrofuran (THF) was dropwise added to the solution. After stirring for 19h, the reaction was terminated by pouring it into a large amount of methanol. The solution was thoroughly washed with methanol, filtered off, and dried in *vacuo*. The polymer yield decreased with increasing of the monomer/catalyst ratio. However, *M_n* (number average molecular weight) showed a maximum for the monomer/catalyst ratio of 1000. This result indicates that the monomer/catalyst ratio between 100 and 1000 is suitable for the polymerization.

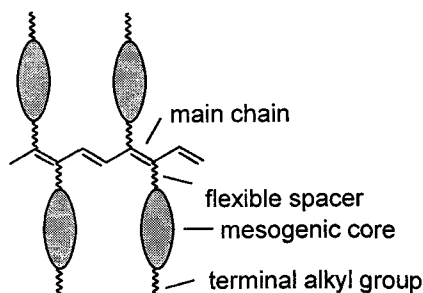
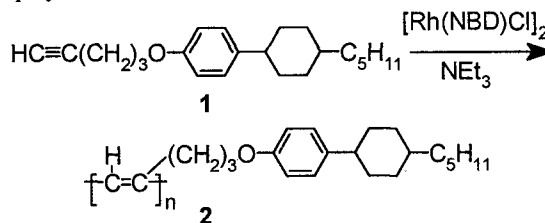


Figure 1. Molecular structure of liquid crystalline polyacetylene derivatives.



Scheme 1.

2.2 Characterization

The polymer structure was confirmed by ^1H - ^1H COSY (2D shift correlated spectroscopy) NMR and ^1H - ^{13}C COSY NMR, as shown in Fig. 2 and Fig. 3, respectively. The peak at 5.98 ppm, characteristic of the proton attached to the *cis* sequence of the double bond, was observed in the ^1H -NMR spectrum. The polymer thus prepared with the $[\text{Rh}(\text{NBD})\text{Cl}]_2\text{-Et}_3\text{N}$ catalyst had predominantly the *cis* form. Figure 4 shows the UV-Vis absorption spectra of the monomer and the polymer. Absorption at 270 nm is due to the $\pi \rightarrow \pi^*$ transition of the benzene ring in the mesogen, while absorption at 320 nm is due to the $\pi \rightarrow \pi^*$ transition of the conjugated double bonds on the polymer main chain.

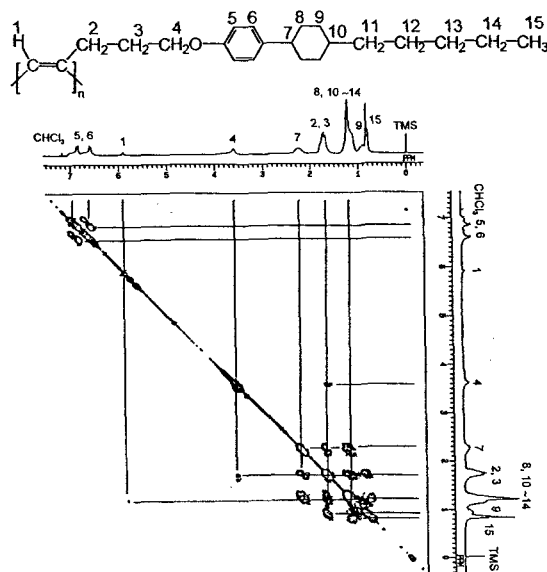


Figure 2. ^1H - ^1H COSY NMR.

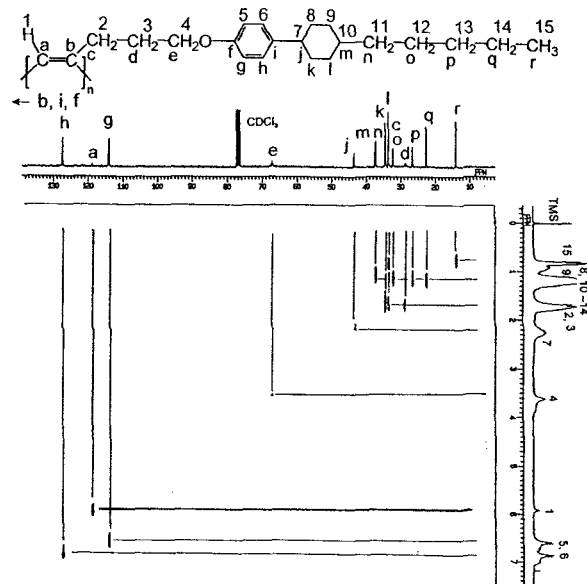


Figure 3. ^1H - ^{13}C COSY NMR.

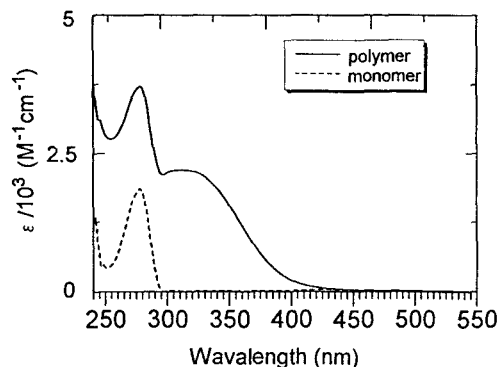


Figure 4. UV-Vis absorption spectra of the monomer and the polymer in THF.

2.3 Liquid crystalline behavior

Although the monomer exhibited a schliien texture characteristic of nematic phase, the polymer showed a simple fan-shaped texture characteristic of smectic phase. Figure 5 shows the DSC curves of the polymer in the heating and cooling processes. The exothermic peak in the first heating process is due to the *cis* to *trans* isomerization. No peak due to the mesophase was observed in the first heating. The polymer before heating is predominantly the *cis* (*cis-cisoidal* or *cis-transoidal*) form; the thermal isomerization of the polymer leads to the conformational change from *cis* to *trans* (*trans-transoidal*) form (Fig. 6). After the first heating, the polymer exhibited a liquid crystalline phase in both the heating and cooling processes. This indicates that the polymer with *trans* form exhibits an enantiotropic liquid crystallinity. Figure 7 shows a conoscopic photograph of the homeotropic region of the polymer on a glass substrate. A Maltese cross was observed; an insertion of $1/4 \lambda$ wavelength plate resulted in a color figure, the second and fourth quadrants were black; in case of the insertion of gypsum first order red plate, the first and third quadrants were blue while the second and fourth were yellow, which is characteristic of optically positive uniaxial material. Therefore, the liquid crystalline phase of the polymer is a smectic A one (Fig. 8). The atomic force microscope (AFM) image of the polymer is shown in Fig. 9. It is found that the polymer forms a higher order structure due to the spontaneous orientation within domain region. Such a higher order structure well coincides with the smectic A structure. Meanwhile, X-ray diffraction (XRD) measurements gave two diffraction peaks of 40.2 and 4.6 Å, which correspond to the interlayer and inter-sidechain distances, respectively (see, Fig. 8). The assignments are supported by the molecular mechanics (MM) calculations using the stereoregular head-head-tail-tail configuration, as shown in Fig. 10. That is, the interlayer and inter-sidechain distances were calculated to be 41.0 and 5.0 Å, respectively.

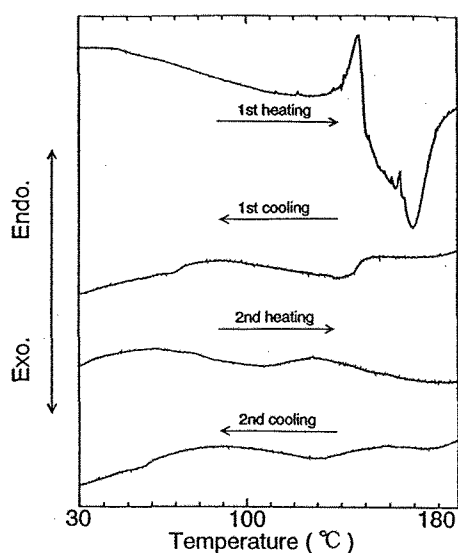


Figure 5. DSC curves of the polymer.

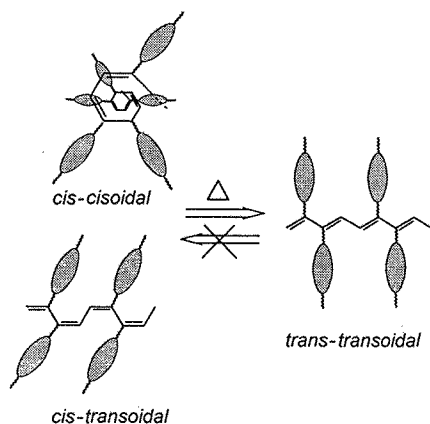


Figure 6. Thermally induced isomerization of the polymer.

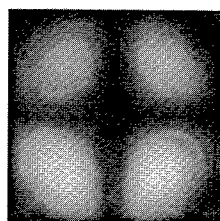


Figure 7. Conoscope pattern of the polymer.

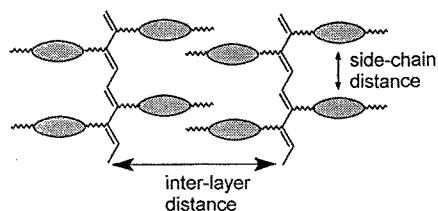


Figure 8. Molecular structure of the polymer in the liquid crystalline state.

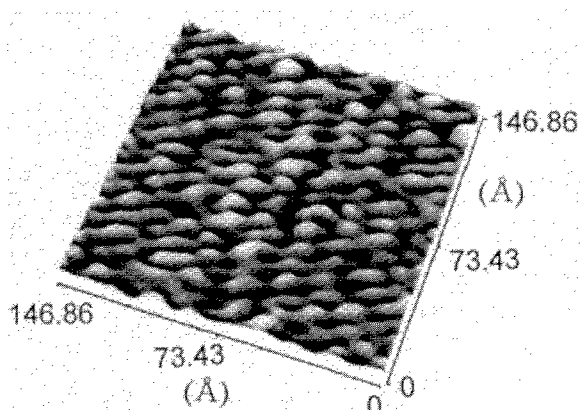


Figure 9. AFM image of the polymer in liquid crystalline state.

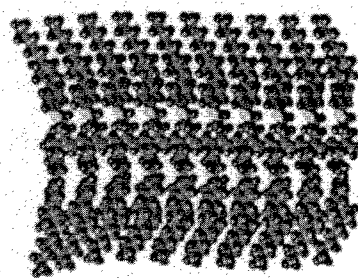


Figure 10. Polymer structure optimized with MM calculation.

2.4 Gas phase doping

The UV-Vis absorption spectra of the polymer during *in-situ* gas phase doping with iodine are shown in Fig. 11. As the doping proceeded, the absorption band at 320 nm, assignable to $\pi \rightarrow \pi^*$ transition of polyene chain, gradually decreased in intensity, while an absorption band around 400 nm appeared and increased in intensity. At the same time, a new band around 700 nm gradually decreased in intensity. In the course of the doping, two isosbestic points were observed at 355 and 655 nm. These spectroscopic features suggest an existence of molecular interacting reaction under equilibrium, probably due to charge transfer interaction between the polyacetylene derivative and iodine dopant. Next, the similar *in-situ* doping of the polymer was performed using AsF_5 . Owing to the strong dopability of AsF_5 , the polymer was smoothly doped to give a more drastic change of absorption spectra; in the beginning of the doping, there appeared a new and extremely broad absorption band whose band edge extended into the near-infrared region. Then, a new absorption band at 370 nm remarkably grew up, while a shoulder band at 450 nm and a broad one around 520 nm increased slightly in intensity. Although the crucial assignments of these new bands still remain unsettled, it is evident that not only iodine but also AsF_5 are feasible for chemical doping to the liquid crystalline polyacetylene derivative with larger ionization potential compared with that of unsubstituted polyacetylene.

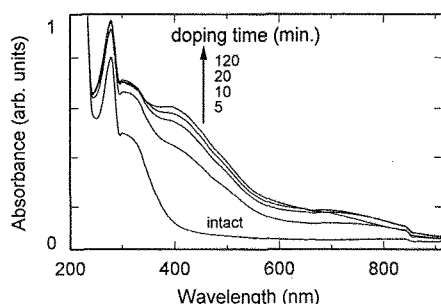


Figure 11. *In-situ* UV-Vis absorption spectra of the polymer doped with iodine in gas phase.

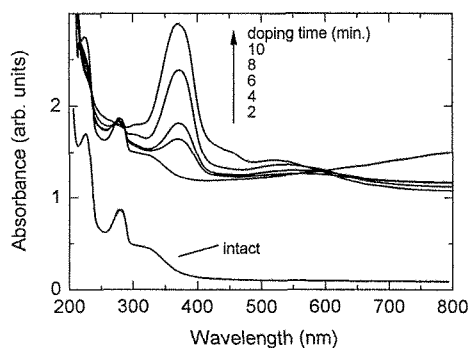


Figure 12. *In-situ* UV-Vis absorption spectra of the polymer doped with AsF₅ in gas phase.

2.5 Temperature dependence of the conductivity

Figure 13 shows a change of the conductivity of the iodine-doped polymer as a function of temperature. It is clear that the conductivity increases with an increase of temperature. Such a tendency is commonly seen in the semi-conducting materials. However, it is of keen interest that the conductivity is further enhanced in the liquid crystalline temperature region from 100 to 150 °C. This may be due to the formation of smectic mesophase, in which the coplanarity of main chain increases in accompany with spontaneous alignment of LC side chains.

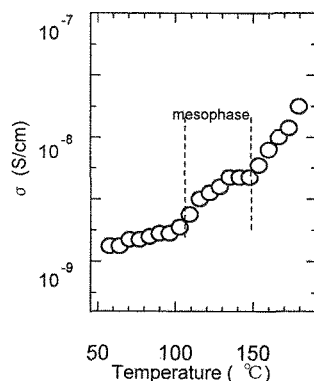


Figure 13. Temperature dependence of the conductivity of the iodine-doped polymer.

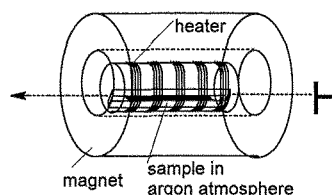


Figure 14. Apparatus to prepare oriented sample by external magnetic force (8 Tesla).

2.6 Orientation of the polymer by magnetic force field and the electrical conductivity

The polymer was first melted and gradually cooled to liquid crystalline phase under magnetic field of 8 Tesla which was generated by a superconducting magnet, as illustrated in Fig. 14. The liquid crystalline domain was aligned parallel to the magnetic field to become a mono-domain structure. The electrical conductivity of the oriented sample was measured by the four-probe method. The results are summarized in Table I. The conductivity of the AsF₅-doped polymer was about 10² times higher than that of the iodine-doped one. The electrical anisotropy ($\sigma_{\parallel} / \sigma_{\perp}$) was from 10 to 100. It is evident that the noticeable electrical anisotropy owes to magnetically forced alignment of polyene chains, as seen in Fig. 15.

Table I. Conductivity^a of the polymer doped with iodine or AsF₅ at room temperature.

dopant	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\sigma_{\text{multi-domain}}$
iodine	1.8×10^{-6}	5.2×10^{-8}	8.1×10^{-8}
AsF ₅	9.1×10^{-4}	2.5×10^{-5}	4.0×10^{-5}

^aconductivity without doping: $\sigma = 10^{-11} \sim 10^{-10}$ S/cm.

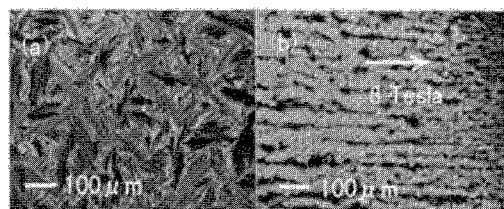


Figure 15. Polarizing optical micrographs of the polymers, (a): without magnetic force, (b) with magnetic force of 8 Tesla.

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