Macromolecules **2002,** *35,* 1307−1313

Structure and Electroconductivity of a Sheared Liquid-Crystalline Polyacetylene Derivative: Poly(5-*p*-(*trans*-4-pentacyclohexyl)phenoxy-1-pentyne)

Hidekatsu Kuroda,[†] Hiromasa Goto,[‡] Kazuo Akagi,[‡] and Akiyoshi Kawaguchi*,[†]

Department of Applied Chemistry, Faculty of Science and Engineering, Ritsumeikan University, Nojihigashi, Kusatsu, Shiga 525-8577 Japan; and Institute of Materials Science, University of Tsukuba, Ibaraki 305-8573 Japan

Received April 20, 2001; Revised Manuscript Received August 6, 2001

ABSTRACT: The crystal structure of the compound 5-*p*-(*trans*-4-pentacyclohexyl) phenoxy-1-pentyne (PCH503A) was determined by X-ray diffraction. The structure and orientational behavior of the polymer (PPCH503A), prepared from the monomer compound, was examined. As a result, it was found that the polymers form an alternating comblike conformation of side chains and are stacked into a smectic hexagonal structure. When shear stress was applied to the polymers, polymeric chains were oriented with their axes of mesogenic groups parallel to the shearing direction; that is, the polymer backbones were aligned perpendicular to the shearing direction. The oriented polymer exhibited a high anisotropy of electroconductivity, i.e., $\sigma_{\parallel}$ (the electroconductivity parallel to the backbone) became 1.7×10^{-5} S/cm upon doping iodine, and the ratio of $\sigma_{\parallel}$ to $\sigma_{\perp}$ (the electroconductivity perpendicular to the backbone) was about 10.

Introduction

Polyacetylene is an archetypical conducting polymer, but it further warrants research for practical use because it is difficult to process the polymer and because the polymer is easily oxidized. Chemically modifying polyacetylene by introducing an alkyl or aromatic substituent into its backbone, many researchers have tried to make the polymers soluble and fusible. In particular, if the substituent is a liquid crystalline mesogen, the polyacetylene derivatives thus modified are soluble and fusible, and they form a liquid crystalline texture by self-assembling of the mesogen groups.[1−4] Because of their liquid crystalline nature, the derivatives are advantageous because they can be oriented easily by applying external force, such as shear stress[1−3] or an electric or magnetic field.[1,2] Previous papers have reported and compared the structure and electroconductivity of liquid crystalline polyacetylene homologues to the one in the present paper: poly(5-*p*-(*trans*-4-pentacyclohexyl)phenoxy-1-pentyne) (PPCH503A). When external force is applied to the liquid crystalline state, the liquid crystalline groups are aligned with their molecular axis in the direction parallel to the external force, and they are organized into a layered structure of smectic form. In the ordered texture, the electroconductivity is higher in the direction perpendicular to the applied force, i.e., in the direction parallel to the polymer backbone comprising conjugated double bonds. Thus, it was found that the electrical properties are largely improved by aligning polymer chains. However, the layered structure is not always explained in the molecular dimension, although a textural model is demonstrated from results of X-ray diffraction and modeling from a molecular mechanics simulation.[5] In the present work, focusing on the present homologue with a spacer $-(CH_2)_3O-$ and an *n*-pentyl group as a terminal moiety, we bagan analysis of the crystal structure of the monomer, and on the basis of the result, we investigated the liquid crystalline texture of the polymer by X-ray and electron diffraction. Furthermore, since it was not examined very much in ref 2, dependence of the molecular orientation on shear stress and on temperature was studied, together with the electroconductivity of the sheared sample.

Experimental Section

A monomer compound, 5-*p*-(*trans*-4-pentacyclohexyl)phenoxy-1-pentyne (PCH503A), was synthesized and polymerized according to the scheme in ref. 1. Seven grams of *p*-(*trans*-4-pentylcyclohexyl)phenol and 2.9 g of 5-chloro-1-pentyne were dissolved in sodium ethoxide. After adding 0.46 g of potassium iodide to the reaction mixture, as a catalyst, the mixture was refluxed for 1 week. A 1.5 g amount of the thus-prepared monomer was dissolved in 9.6 mL of THF, with 0.022 g of $[Rh(NBD)Cl]_2$ catalyst, and this was polymerized by stirring the reaction for 24 h at room temperature. The polymerization reaction was terminated by pouring the reaction mixture into a large amount of methyl alcohol. The polymer product was filtered off, washed with methyl alcohol, and then dried under a vacuum. The molecular weight and polydispersity (M_w/M_n) of the polymer were 1.9×10^4 and 1.44, respectively.

A single crystal of PCH503A was prepared, by slow evaporation of solvent for 3 weeks, from a solution in ethyl alcohol. X-ray diffraction data of the single crystal were accumulated by a four-circle auto-measurement instrument, a Rigaku AFC-5R diffractometer. The X-ray beam was Cu Kα monochromatized with a graphite monochromator. All of thus-accumulated data on PCH503A were processed using the teXsan graphic crystal software package.

We examined the relation between the molecular orientation and the strain rate and/or shearing temperature, when the polymer was solidified from the melt or liquid crystalline state after shearing. Using a system as shown in Figure 1, the structural change was monitored when shear stress was applied to the polymer melt. The hot-stage consists of two glass plates: one is settled in a temperature-controllable hotplate, and the other is able to slide on it. The rate of shear strain was regulated by changing the drawing rate of the upper glass plate, by use of a motor. The polymer was dissolved at a

---

* To whom correspondence should be addressed. Fax: +81-(0)-77-561-2659. E-mail: akiyoshi@se.ritsumei.ac.jp.

[†] Ritsumeikan University.

[‡] University of Tsukuba.

10.1021/ma010684a CCC: $22.00

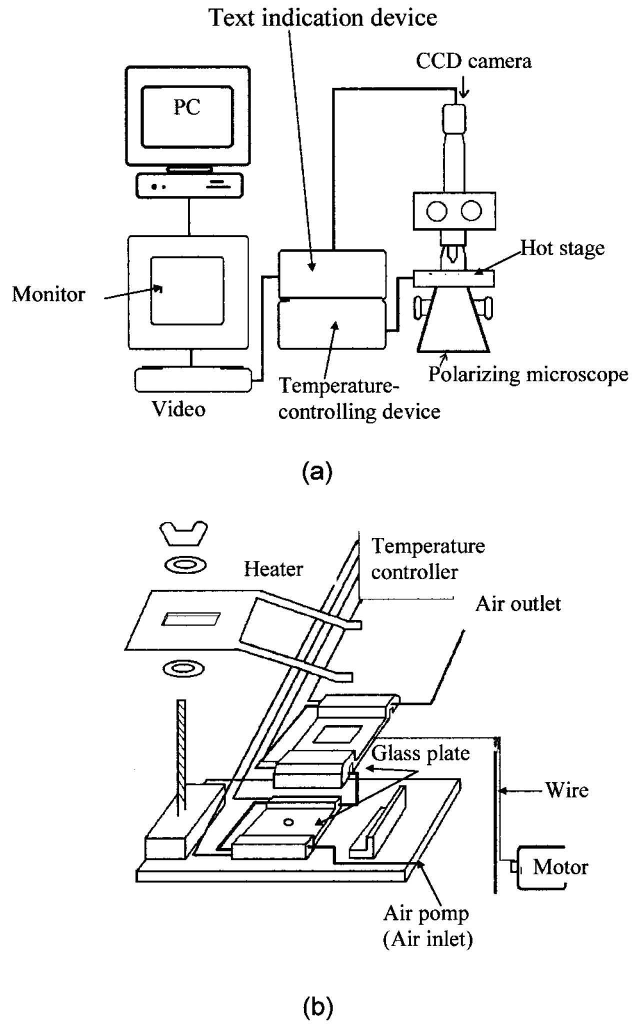


Figure 1. Apparatus for measuring the birefringence of polymers by changing temperature and rate of shear: (a) overview, and (b) sketch of the hot stage.

concentration of 0.9 wt % in decahydronaphthalene (decalin). Some drops of the solution were put between two slide glasses kept at a given temperature. After the solvent was evaporated, the upper glass plate was slid at that temperature and cooled. The degree of molecular orientation of the resultant sample was graded at high, medium, or low, by visual evaluation of birefringence, by monitoring with a polarizing microscope equipped with a CCD camera.

Very thin samples for electron microscopy were prepared using another small-scale, temperature-controllable copper device, the setup and usage of which was the same as for the hot-stage of Figure 1. By confirmation of high birefringence with a polarizing microscope, highly oriented samples were selected out of the sheared samples. The upper glass plate was easily detached from the shearing device. Subsequently, it was dipped in a dilute hydrofluoric acid solution to float off a thin film from it. The thin film was picked up on a Cu grid for electron microscopy.

Samples for measurement of electroconductivity were also prepared at 145 °C, in the manner described above. Electroconductivity of the samples was measured by a two-probe method. The sample was doped with iodine vapor at room temperature.

Results and Discussion

Crystallographic data of PCH503A that were obtained by X-ray diffraction analyses are summarized in Table 1. Parts a and b of Figure 2 show the molecular conformation of PCH503A and packing models in the unit cell, respectively. Two molecules with identical conformation are packed in the cell in an antiparallel way. The end pentyl group of the compound has a trans conformation. The cyclohexyl group is in a stable chair conformation. The plane consisting of C_{13}, C_{14}, C_{16}, and C_{17} of the cyclohexyl group, is almost perpendicular to the plane of the phenyl group. The chain conformation from C_3 to C_6 is gauche, and as a whole, the molecule is extended in an almost straight fashion. The linear distance from C_2 to C_{22} is 1.895 nm, corresponding to the length of the side chain of the polymer.

Table 1. Crystallographic Data of PCH503A

chem formula	$C_{22}H_{32}O$
fw	312.49
cryst dimens, mm	0.30 × 0.20 × 0.40
cryst color, habit	colorless, plate
no. of reflcns	2818
cryst syst	triclinic
space group	*P*1 (No. 2)
lattice params	
a, nm,	1.1251(2)
b, nm	1.7182(2)
c, nm	0.5447(2)
α, deg	93.319(2)
β, deg	103.731(2)
γ, deg	72.580
Z value	2
d_{calcd}, g/cm^3	1.060
μ(Cu Kα), cm^{-1}	4.72
R (R_w) factor, %	7.1 (12.3)

Figure 3 shows an electron diffraction pattern of a sheared thin film. Sharp spots up to the third order are observed in the direction parallel to the shearing direction. The diffraction feature explains that the samples are composed of regularly stacked layers, the normal of which is parallel to the shearing direction. The long spacing is evaluated at 3.726 nm from the spots and is comparable to the distance between the centers of gravity of adjacent neighboring layers. From X-ray analyses of the monomer crystal, it is found that the length of the sequence of C_2 to $C_{22,}$ depicted in Figure 2a, is 1.895 nm. The long spacing is nearly equal to twice the C_2 to C_{22} length. This equality explains that the side chains are fully extended in a conformation similar to that of monomer, and that their axes are oriented almost perpendicular to the backbone. Strictly speaking, however, the long spacing is a little shorter than twice the C_2 to C_{22} length, when the thickness of the backbone chain and the van der Waals radii of atoms at the end groups are taken into account. The side chains may be a little tilted from normal to the layer plane. Akagi et al. proposed that the polymerization proceeds through a head-to-head or a tail-to-tail reaction.[2] On the basis of their idea of the polymerization mechanism, they put forward such a polymer configuration and stacking plan as shown in Figure 4: The fully extended, linear side groups are arrayed such that they protrude in the direction perpendicular to the linear backbone, alternatively on both sides along it, and the alternating comblike molecules are stacked into a layer structure. This model explains the long period obtained from the X-ray diffraction profile. The present ED is basically interpreted by this model. It is found, from DSC and IR measurements, that when the polymer is heated in the temperature range 167−175 °C, the cis form is easily isomerized into the trans form.[6,7] A specimen annealed above the temperature exhibits an ED pattern similar to that in Figure 3, giving an identical long period of 3.726 nm. As the long periods of both forms

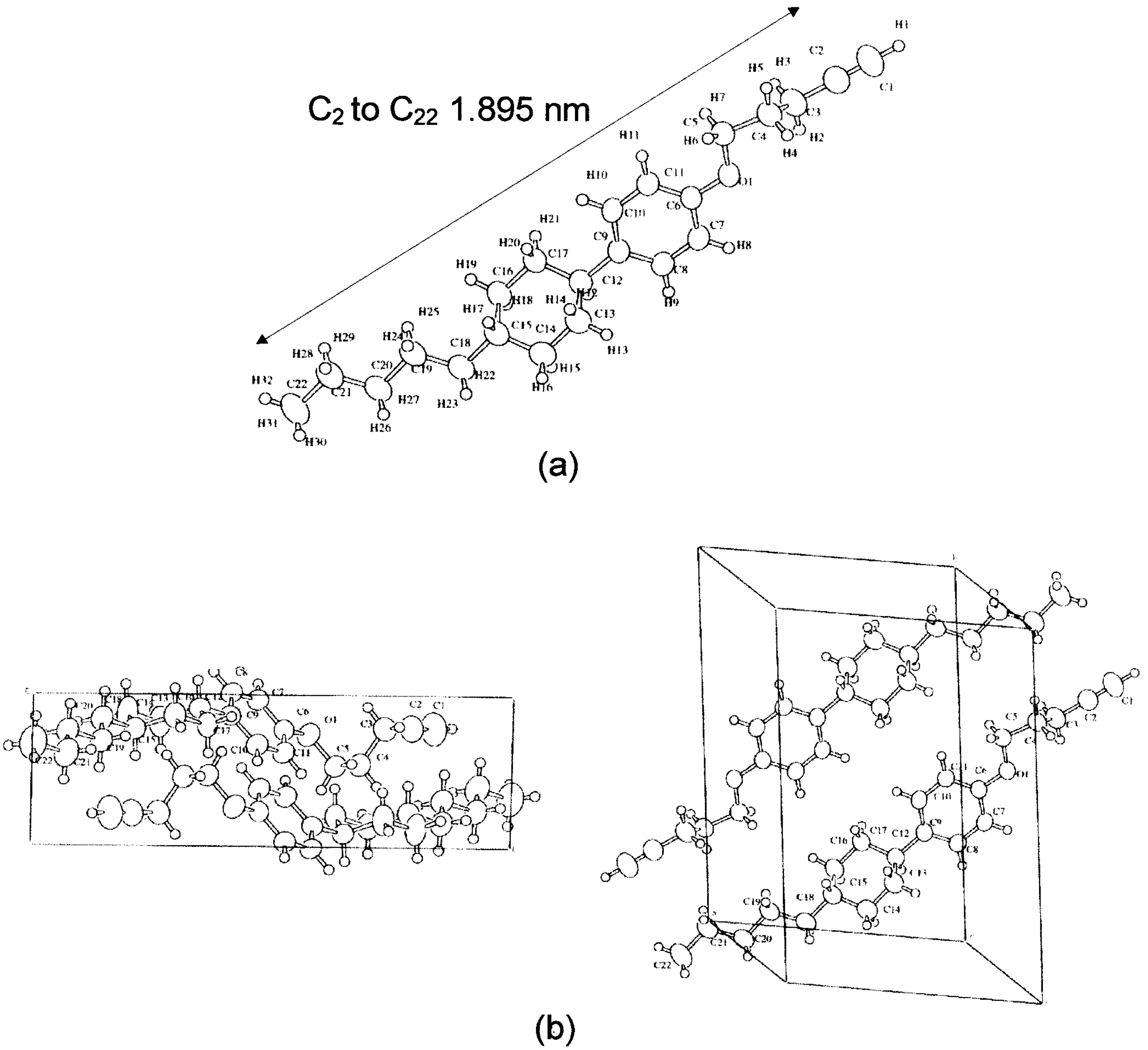


Figure 2. (a) Molecular conformation of PCH503A in a crystal, and (b) the packing model of molecules in the unit cell: the projection on the $a-c$ basal plane (left) and the three-dimensional view (right).

are identical, the stacking models for cis and trans forms of PPCH503A are considered to be as shown in Figure 4. We shall inquire into the conformations of the backbone and side chain for both cis and trans stacking patterns, taking account of the following requirements experimentally obtained here: (1) the side chains have an almost fully extended conformation, (2) their axes are oriented nearly perpendicular to the backbone, and (3) the long periods for both cis and trans backbone conformations are identical. These requirements are fulfilled when the cis and trans forms of molecules take the conformations shown in the magnified models in Figure 4, parts a and b, respectively. The distance from the central backbone to the end atom of the side chain may differ between cis and trans forms, depending on the rotation angle around the C_2-C_3 or $C'_2-C'_3$ bond. Of course, this results in a change of the long period. The difference in the side chain length would be offset by loose stacking between neighboring layers, and consequently, the long spacing would remain unchanged. This is acceptable in consideration of the rather disordered stacking of layers as discussed later on.

We should notice here the following about the ED pattern: Meridian reflections only up to the 003 spot are observed even if the ED patterns are deliberately taken, and no discrete reflections are observed in the equatorial direction. In the X-ray diffraction profile, a reflection of the third order in the small angle region is also barely observable.[1] First, we shall consider the diffraction feature that only reflections up to the third order are observed in electron or X-ray diffraction. Diffraction theory tells us that how high an order of diffraction may be observable will depend on the order of stacking, in the present case, of the alternating comblike polymers.[8,9] According to Hosemann's paracrystalline theory,[8] we evaluated the g value, which is a measure of the stacking disorder. It means the fluctuation of the distance between the centers of gravity of layers, and is defined as $\Delta l/l$, where l is the average

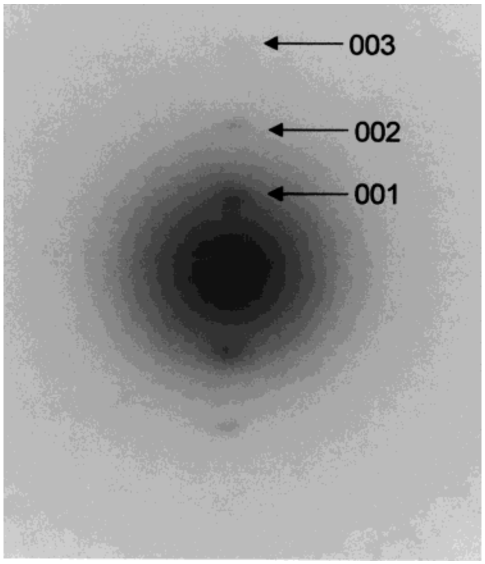


Figure 3. (a) Electron diffraction pattern of a sheared thin film of PPCH503A. The sheared direction is vertical. The sample was prepared at 145 °C and at a rate of shear over 40 s^{-1}.

distance between the centers, i.e., the long spacing. According to the criterion that loss of reflection may be characterized by the range in which the intensity maxima do not exceed the background by more than 10∼20%, the g value is estimated at about 0.08 in the present case, where reflections up to the third order are observable. This value corresponds to $\Delta l \sim 0.3$ nm. The difference in side chain length between cis and trans forms would be trivial in comparison with the long period fluctuation.

Figure 5 shows the wide-angle X-ray diffraction profile of PPCH503A polymer. Sharp, small-angle X-ray diffractions up to the third order and a rather sharp, wide-angle single peak are observed.[1] A similar diffraction feature is commonly observed in other liquid crystalline polyacetylenes with different long chain moieties from the present polymer.[3,4] Since the wide angle reflection ($2\theta = 18.68°$) is quite different in appearance from the so-called amorphous halo, it is reasonable to consider that the reflection should be attributed to a diffraction of a crystalline nature. From the peak angle, the lattice spacing is evaluated at 0.47 nm. In consideration of the layered texture, it is natural to assume that this reflection should be caused by the lateral packing of mesogen chains. The diffraction feature, with a single peak, implies that the packing mode is *nearly hexagonal,* although less-ordered. It is expected that when the chain packing is hexagonal, higher order reflections at $\sqrt{3}$ and, possibly, twice the fundamental wave vector should be observed. However, no such reflections are actually observed. Paying attention to the broad profile again, it is explained as follows: The fluctuation of side-by-side packing among side chains is so large, that is, roughly, g value ≈ 0.2, that only the first order of diffraction could be observable. It explains that they are very loosely packed laterally. On the assumption of hexagonal packing, the average distance between the neighboring mesogen stems is calculated at 0.54 nm, with a fluctuation of ∼0.1 nm. Furthermore, assuming the side chains as rods (cf. Figure 2a), their diameter is calculated at about 0.6 nm, including van der Waals radii of hydrogen atoms. On the other hand, the separation of every four backbone carbons, to which the mesogens extending on the same side are anchored, is estimated at 0.5 nm at a maximum in the trans conformation. The four-carbon "topological" repeat is too short for the side chains to accommodate in the coplanar way. To avoid their steric hindrance, possibly it might be accompanied by a slight twisting of the backbone. It could result in the tilting of moiety chains to the layer surface, leading to a shorter long period and to loose side-by-side packing of the side chains. Although the explanation is speculative, the packing model of the smectic hexagonal mode shown in Figure 6 is probably set up to explain the diffraction feature. Since the present solidus state is not "crystalline" in the strict sense, the change from liquid to solidus state is described not as "crystallization".

The polymer sample was sheared by changing the rate of shear at various temperatures, followed by cooling. Through visual evaluation, we estimated the birefringence of samples thus obtained. Figure 7 shows an example of polarizing optical micrographs of the sheared sample. The photographs indicate large birefringence, i.e., a high degree of molecular orientation. When such high birefringence as shown in Figure 7 was observed, we defined this as a state of "high molecular orientation". In the same way as shown for a main-chain thermotropic liquid crystalline polymer,[10] the results are mapped as a diagram of molecular orientation in the temperature−shear rate space in Figure 8. Two things are to be noted from the present experimental viewpoint. First, limit lines are not always as definite as shown in Figure 8 but have some range, because the birefringence was not so definitely determined, since it is measured by visual observation. Second, the birefringence evaluation was done using samples in which solidification occurred by cooling, not in situ during shearing. The relaxation behavior of strained polymers after cessation of shear is not taken into account.[11] The upper line (1) shows a limiting line showing whether birefringence is observed; i.e., solidification is accelerated by shear stress, accompanying molecular orientation in the sample. In the region above the upper limit line, the sample remains molten, even under shear, and exhibits no birefringence during shearing. The lower line (3) shows the limit that the following situation is experimentally accessible: The sample still remains liquid crystalline when cooled at a given temperature—the molten phase is not retained but is transformed into the liquid crystalline phase at the temperature—and solidification does not occur until shear stress is applied. In other words, even if no shear stress is applied to the sample, solidification takes place as soon as the sample is brought to temperatures below line 3, and consequently, no molecular orientation takes place. Line 2 denotes the borderline indicating the phase before being sheared; above the line, the material is in the molten phase, and below it, it is in the liquid crystalline phase. The polymer exists in the liquid crystalline state over the temperature range indicated by a vertical, arrowed bar. Line 2 just corresponds to the upper limit of the temperature range. In the limited region between lines 1 and 2, the molten polymer chains are aligned when the shear stress is applied. Below line 2, the liquid crystalline state is realized. The molecularly oriented texture in the area between lines 2 and 3 is produced from the liquid crystalline phase. From the phase diagram, we see that the liquid crystalline phase is not always transformed into a uniaxially oriented state of

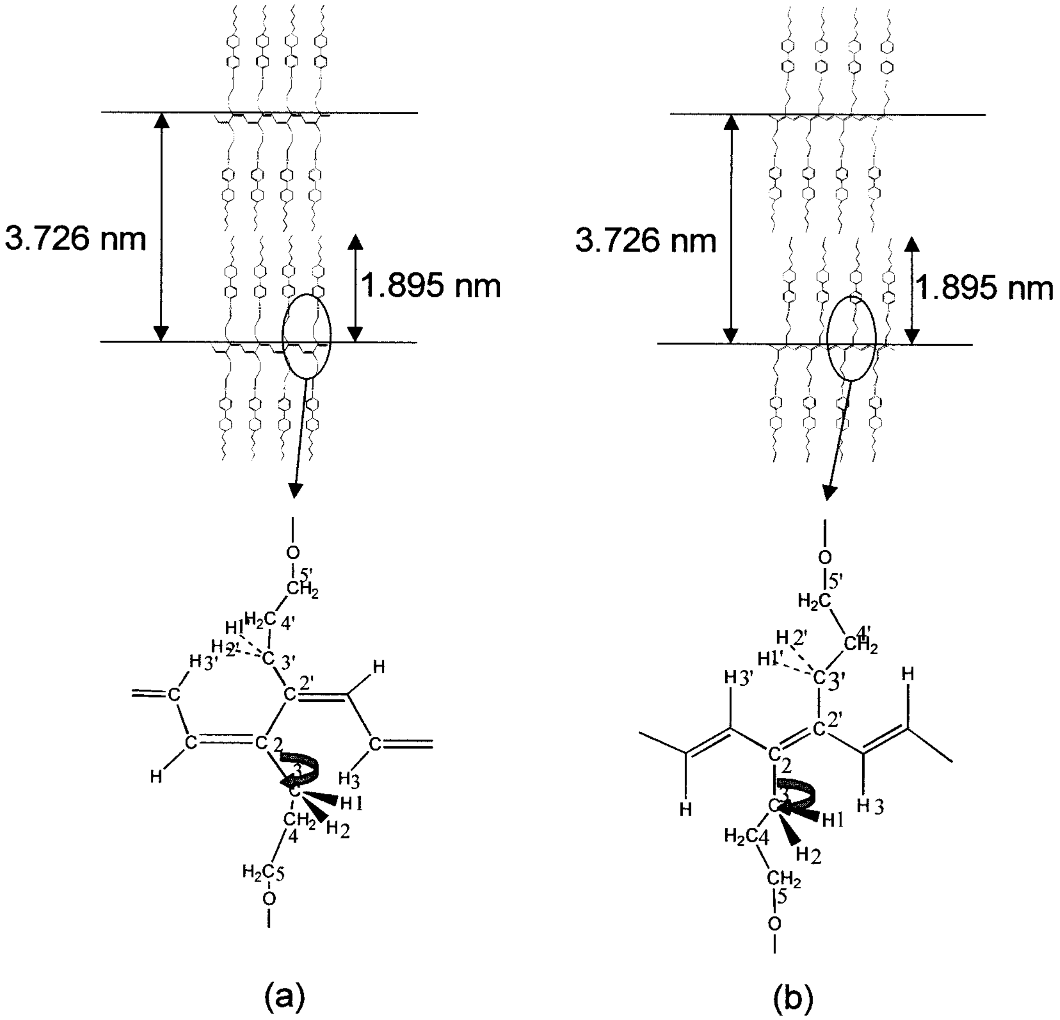


Figure 4. Stacking models of (a) cis and (b) trans forms of comblike polymers and magnified sketches of their core parts. The side chain molecules are twisted about the C_2-C_3 bond, so that the H_1 and H_2 hydrogen atoms are directed upward from the figure plane (the plane containing the backbone), so as to release repulsion with the neighboring H_3 hydrogen. About the $C'_2-C'_3$ bond, the side chains would be rotated reversewise to the above rotation, so that the two mesogens would be disposed in the antipode position with respect to the intervening double bond.

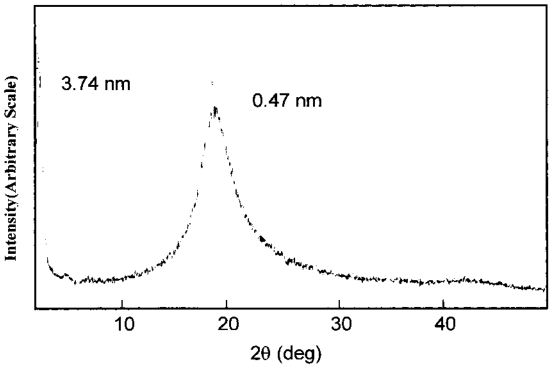


Figure 5. Wide-angle X-ray diffraction profile of PPCH503A.

texture. Whether or not the oriented texture is obtained is largely dependent on the relaxation behavior of strained chains.[11]

The lowest rate of shear to induce a molecular orientation is 3 s^{-1} at about 115 °C, and with an increase in the rate of shear, the solidification temperature becomes higher. Acceleration of crystallization by shear or elongational strain, which leads to an increase of crystallization temperature, is common in the crystallization of polymers, and hence it is important to control the strain rate and/or temperature in the processing of polymers and plastics. In liquid crystalline substances, it is expected, as well, that the larger the rate of shear, the higher the solidification temperature. In reality, the orientation temperature of molecules increases with an increased rate of shear, while the rate of increase becomes dull at a rate of shear above 20 s^{-1}. Here, however, the following experimental uncertainty is to be noticed: When shear stress over 50 s^{-1} was applied, polymer molecules solidified so quickly that they adhered to the slide glass, and hence some parts of the sample were broken due to sliding of the glass during observation.

Figure 9 shows a typical example of the changes in electroconductivity (σ) of the oriented and unoriented cis samples (which were prepared at 145 °C) with doping of iodine. $\sigma_{\parallel}$ and $\sigma_{\perp}$ denote the electroconductivities in the direction parallel to and perpendicular to the extended backbone, respectively, that is, those in the directions perpendicular to and parallel to the shearing direction, respectively. For the first hour in Figure 9, the sample was not exposed to iodine vapor, and after that, iodine vapor was introduced. The change in electroconductivity of unoriented sample with doping iodine is shown as curve 3 in Figure 9. Before doping,

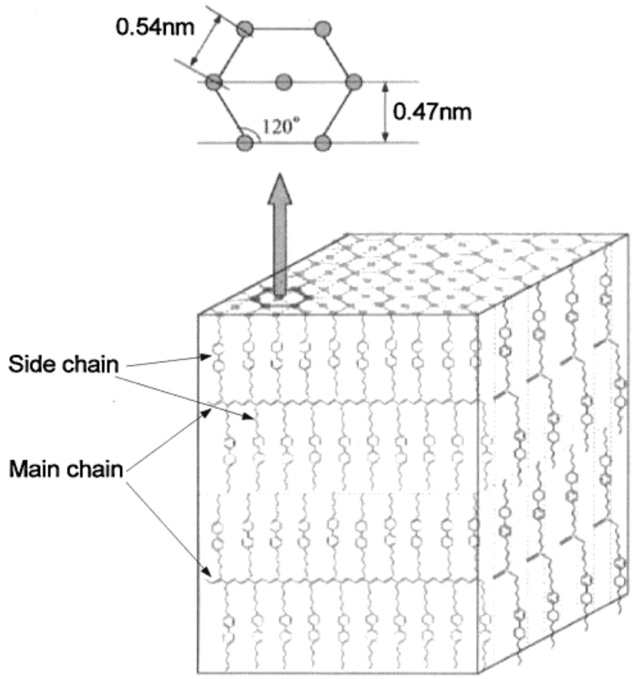
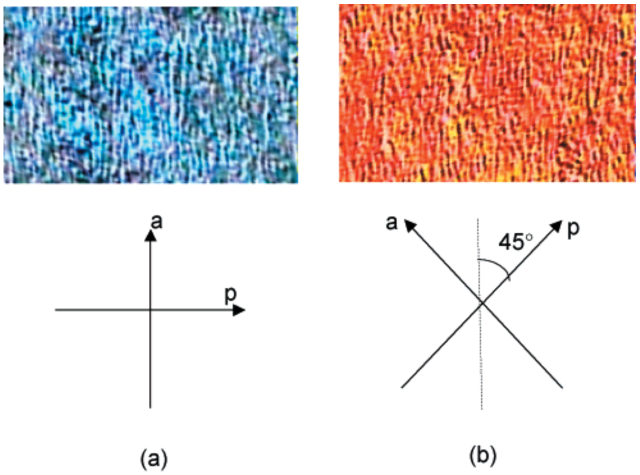


Figure 6. Three-dimensional model of the smectic texture of PPCH503A. Neighboring comblike chains in a layer are shifted one another in the direction parallel to the backbone, by half the distance between neighboring side chains along the chain, and thus are packed in a nearly hexagonal mode.



(a) (b)

Figure 7. (a) Polarizing optical microscopic images of a sample prepared as follows: sheared at 145 °C, at 25 s^{-1}, and cooled. The arrows of *a* and *p* denote the directions of the analyzer and polarizer, respectively. (b) Polarizer and analyzer rotated by 45° counterclockwise from the position in Figure 8a. Between the analyzer and polarizer, a sensitive color plate with $R = 530\ \mu$m is inserted. The shearing direction is vertical.

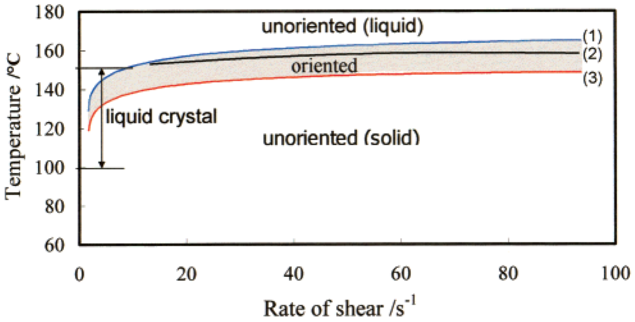


Figure 8. Map of molecular orientation in the temperature–shear rate space. In the shaded region, molecular orientation takes place. The vertical arrow bar indicates the temperature range over which the liquid crystalline state occurs under quiescent conditions.

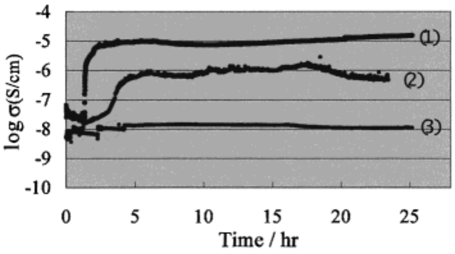


Figure 9. Change in electroconductivity of PPCH503A against doping time: $\sigma_{\parallel}$(1) and $\sigma_{\perp}$(2) of an oriented sample and σ_{unorient} (electroconductivity of unoriented sample) (3).

Table 2. Electroconductivity of PPCH503A before and after Doping

	$\sigma_{\perp}$ (S/cm)	$\sigma_{\parallel}$ (S/cm)	σ_{unorient} (S/cm)
intact	8.5×10^{-9}	4.7×10^{-8}	2.5×10^{-8}
doped	1.5×10^{-6}	1.7×10^{-5}	1.2×10^{-8}

$\sigma_{\perp}$ and σ_{unorient} (the electroconductivity of the unoriented sample) are almost the same, and both are slightly lower than $\sigma_{\parallel}$. Immediately after the sample is doped, $\sigma_{\parallel}$ rapidly increases by 3 orders of magnitude while $\sigma_{\perp}$ gradually increases by 2 orders of magnitude over almost 3 h. σ_{unorient} decreases slightly with doping. Electroconductivities before doping and after prolonged doping are summarized in Table 2. For the oriented sample that was prepared by applying the magnetic field of 0.7~1.0 T, $\sigma_{\parallel}$ and $\sigma_{\perp}$ have been measured.[1] $\sigma_{\parallel}$ in the present sample is significantly larger, roughly by 1 order of magnitude, than that of the magnetically oriented sample, while $\sigma_{\perp}$s of both samples are comparable. This may be caused by the difference in the degree of molecular orientation, and it suggests that electroconductivity is very sensitive to molecular orientation.

In summary, it was found that a side-chain-type polymer, poly(5-*p*-(*trans*-4-pentacyclohexyl)phenoxy-1-pentyne), forms an alternating comblike conformation and that when shear strain was applied to the polymer, it forms a smectic texture, where the normal to the smectic layers is parallel to the shearing direction, that is, the long axes of the side-chains are aligned along the direction. Using X-ray structural data of the monomer, it was found, experimentally, that the side chains are extended in an almost straight fashion in the texture. The textural structure of the sheared polymers was greatly affected by the rate of shear. Here, the region of the temperature and rate of shear where the molecular orientation was performed was depicted as a temperature–shear rate space diagram. The molecular orientation does not always orient over the entire range of liquid crystalline state when shear stress is applied; it depends on the temperature and the rate of shear. The highly oriented sample exhibited high electroconductivity. The diagram is expected to be useful to determine the processing condition needed to obtain a molecularly ordered structure exhibiting high performance of such physical properties as electroconductivity.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas, “Mechanism of Polymer Crystallization” (No. 12127207), from the Ministry of Education, Culture, Sports, Science, and Engineering, and partly by the Ritsumeikan Fund for Research and Faculty, 2000. The authors are grateful to Professor M. Cakmak of the University of Akron, Akron, OH, for his constructive criticism of the manuscript.

References and Notes

(1) Akagi, K.; Shirakawa, H. *Curr. Trends Polym. Sci.* **1977**, *2*, 107−124.

(2) Iino, K.; Goto, H.; Akagi, K.; Shirakawa, H.; Kawaguchi, A. *Synth. Me.* **1997**, *84*, 967−968.

(3) Tang, B. Z.; Kong, X.; Wan, X.; Peng, H.; Lam, W. Y.; Fen, X.-D.; Kwok, H. S. *Macromolecules* **1998**, *31*, 2419−2432.

(4) Lam, J. W. J.; Kong, X.; Tang, B. T. *Macromolecules* **2000**, *33*, 5027−5040.

(5) Goto, H.; Akagi, K.; Itoh, K. *Trans. Mater. Res. Soc. Jpn.* **1999**, *24*, 473−476.

(6) Goto, H.; Akagi, K.; Shirakawa, H.; OH, S.-Y.; Araya, K. *Synth. Met.* **1995**, *71*, 1899−1900.

(7) Akagi, K.; Goto, H.; Shirakawa, H. *Jpn. J. Polym. Sci. Technol.* **1999**, *56* (4), 217−233.

(8) Hosemann, R.; Bagchi, S. W. *Direct analysis of diffraction by matters*; Elsevier: Amsterdam, 1962.

(9) Vainshtein, B. K. *Diffraction of X-rays by chain molecules*; Elsevier Publishing Co.: Amsterdam, 1966.

(10) Jun, J.-W.; Kornfield, J. A.; Ugaz, V. M.; Burghart, W. R.; Link, D. R.; Clark, N. A. *Macromolecules* **1999**, *32*, 5581−5593.

(11) Kielhorn, L.; Colby, R. H.; Han, C. C. *Macromolecules* **2000**, *33*, 2486-2496.

MA010684A