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Orientation analysis of polyacetylene with liquid crystalline side chains

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Abstract

Polyacetylene substituted by liquid crystalline side chains and its monomer were characterized by ¹³C NMR spectroscopy in order to investigate their orientation and dynamics in the liquid crystalline state. Anisotropic chemical shifts of phenylene carbons, acetylene carbons and ethylene carbons were analysed. In both the monomer and the polymer, phenylene carbons showed downfield chemical shifts indicating their orientation to the magnetic field. On the other hand, by comparing observed chemical shifts and theoretical ones, acetylene carbons in the monomer were found to move freely in the liquid crystalline state. For the polymer, the dynamics of ethylene carbons (polyacetylene backbones) was interpreted in terms of a swing model, while that of side-chain phenylene carbons was explained as a swing model synchronized with the main chain accompanied by rotation around the director. These results directly reveal the scheme of the alignment of the main chain induced by the side chain orientation, and also suggest that the polymer structure is constructed by head-to-head or tail-to-tail type connection of monomers. © 1998 Elsevier Science B.V.

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1. Introduction

There is a growing interest in side-chain liquid crystalline polymers due to their applications to electrical conductive materials, electro-optics or non-linear optics [1-3]. Among these applications, polyacetylenes substituted by side chains containing mesogen groups have been synthesized and studied in order to enhance electrical conductivity of the polyacetylene backbones by their alignment induced by the side-chain orientation [4–8]. Akagi et al. proposed syntheses of polyacetylenes from mono-substituted acetylene monomers which contain alkyl ether spacers and mesogen groups, such as phenylcyclohexyl or biphenyl moieties, finding a large enhancement of the electrical conductivity by the magnetic or electrical alignment [4-6].

NMR techniques, solid-state NMR, ¹H NMR, ²H NMR or ¹³C NMR, have been widely used to characterize liquid crystalline molecules [9–19]. Pines et al. [9] and Oulyadi et al. [10] reported orientation analyses of liquid crystalline small molecules containing phenylene carbons by measuring anisotropic ¹³C chemical shifts of the oriented molecules in the magnetic field. Such a treatment is advantageous because of the theoretical and experimental simplicity compared with other NMR methods such as a

0022-2860/98/\$19.00 © 1998 Elsevier Science B.V. All rights reserved *PII* \$0022-2860(97)00297-4 line shape analysis or a dipole-dipole interaction analysis.

In our laboratory, high-temperature ¹³C-NMR measurements have been developed for melted samples without solvents and applied to analyses of mesophase pitches, coal-derived liquids and polymers [20–22]. The orientation of a thermotropic copolyester, which is one of the main chain liquid crystalline polymers, was also analysed by aniso-tropic ¹³C chemical shifts in the liquid crystalline state [21].

In this paper, similar analytical methods were applied to the substituted polyacetylene, one of the side-chain liquid crystalline polymers in order to discuss the orientation and dynamics of the polymer in the liquid crystalline state.

2. Experimental

2.1. Sample

5-*p*-(*trans*-4'-octylcyclohexyl)phenoxy-1-pentyne (MONOMER) was synthesized through the reaction of *p*-(*trans*-4-octylcyclohexyl) phenol and 5-chloro-1pentyne. The polymer (POLYMER) was obtained by the polymerization reaction of the monomer using a Ziegler–Natta catalyst, $Fe(acac)_3$ –AlEt₃. Molecular structures of the MONOMER and the POLYMER are shown in Fig. 1. By means of DSC and polarized light microscope, liquid crystalline phases of the MONOMER and the POLYMER were observed in the temperature ranges of 30–40°C and 83–136°C, respectively. Synthetic methods and the liquid crystalline characteristics were reported in detail elsewhere [4-6].

2.2. NMR measurement

 13 C NMR measurements were carried out for bulk samples with a Bruker AMX-400 equipped with a high temperature probe for a 5 mm diameter tube under a static magnetic field of 9.7 T (100 MHz for 13 C). This high-temperature probehead, whose r.f. coils are made of Pt, allows high power (up to 50 W) proton decoupling. NMR spectra of the MONOMER and the POLYMER in the isotropic state were measured at 340 K and 464 K, respectively, while those in the liquid crystalline state were measured at 305 K and 370 K, respectively. Decoupling power of 25 W was applied in order to eliminate the large dipole–dipole interaction.

Principal values (σ_{11} , σ_{22} and σ_{33}) of ¹³C chemical shifts for calculation were taken from values of similar compounds reported in the literature [8,23,24]. The orientation analysis using anisotropic chemical shifts will be described later.

2.3. Molecular modeling and conformational analysis

In order to obtain atomic coordinates of molecules to be used for orientation analyses, molecular modeling and a conformational analysis were carried out using a force field calculation method with DreidingII potential functions and parameters [25]. The software used was 'Cerius²' of Teijin– Molecular Simulation Inc.



Fig. 1. Molecular structures of MONOMER and POLYMER.



Fig. 2. ¹³C NMR spectra of MONOMER in the isotropic and liquid crystalline states. Spectra of the sample at (1) 340 K and (2) 305 K. Carbon numbers corresponds to those shown in Fig. 1.

3. Results and discussion

3.1. ¹³C NMR chemical shift

Fig. 2 shows ¹³C NMR spectra of the MONOMER in the isotropic and liquid crystalline states. The corresponding spectra for the POLYMER are shown in Fig. 3. The chemical shifts obtained from these figures are summarized in Table 1 for acetylene, ethylene and phenylene carbons. The numbers in the first column correspond to those of carbons shown in Figs. 1 and 2. σ_{iso} means the isotropic chemical shift of the samples in the isotropic states, and $\Delta \sigma_{obs}$ means the shift of those in the liquid crystalline states compared with σ_{iso} ($\Delta \sigma_{obs} > 0$ in case of downfield shift).

In both samples, chemical shifts of phenylene carbons, C_6-C_9 , shift toward downfield. The chemical shifts of the acetylene carbon, C_1 , in the MONO-MER shifts toward upfield, while that of an ethylene carbon, C'_1 in the POLYMER shifts to downfield.

3.2. Orientation analysis

3.2.1. MONOMER

Orientation behavior of the phenylene ring in the MONOMER was investigated by the method



Fig. 3. ¹³C NMR spectra of POLYMER in the isotropic and liquid crystalline state. Spectra of the sample at (1) 464 K and (2) 397 K. Carbon numbers correspond to those shown in Fig. 1.

proposed by Pines et al. [9]. They showed that chemical shifts of phenylene carbons in the mesogen group of the liquid crystalline molecules can be calculated using the structural parameters shown in Fig. 4. The equations used for the analysis are as follows, where

$$\Delta \sigma = \sigma_{\rm LC} - \sigma_{\rm iso} = (2/3)S(\sigma_{//} - \sigma_{\perp}) \tag{1}$$

$$\sigma_{//} = \sigma_{11} \cos^2 \phi_{\rm p} + \sigma_{22} \sin^2 \phi_{\rm p} \tag{1a}$$

$$\sigma_{\perp} = (1/2)(\sigma_{11} \sin^2 \phi_p + \sigma_{22} \cos^2 \phi_p + \sigma_{33})$$
(1b)



Fig. 4. Definition of φ_p and *D*. (*D* is the molecular director of MONOMER and φ_p is the angle between *D* and the bond axis of the phenylene ring.)

Carbon ^a		Chemical shift (ppm)			Principal values of chemical shift tensors ^b (ppm)			
		σ_{iso}^{c}	$\Delta \sigma^{\rm d}_{\rm obs}$	$\Delta \sigma^{e}_{ m calc}$	σ_{11}	σ22	σ33	Ref. ^f
MONOMER	C1	68.4	-16.9	-11.3	84	84	-168	[23]
	C ₆	156.7	36.6	39.0	80	9	-89	[10]
	C 7	114.1	15.5	17.5	80	21	-101	[10]
	C ₈	126.9	17.0	15.9	79	17	-96	[10]
	C ₉	139.2	39.5	36.6	75	7	-82	[10]
POLYMER	C ₁ '	126.6	47.7		97	8	-105	[23,24]
	C ₆	158.3	48.3		80	9	-89	[10]
	C ₇	115.8	19.2		80	21	-101	[10]
	C ₈	127.7	20.7		79	17	-96	[10]
	C ₉	140.2	50.3		75	7	-82	[10]

Table 1 ¹³C Chemical shift values in the isotropic and liquid crystalline states

^a Numbers correspond to those in Fig. 1 and Fig. 2.

^b Values are normalized such as $(\sigma_{11} + \sigma_{22} + \sigma_{33}) = 0$.

^cObserved ¹³C chemical shift value in the isotropic state.

^d Observed difference of the chemical shift in the liquid crystalline state from that in the isotropic state.

^e Calculate chemical shifts for carbons of the MONOMER. Values for C₆, C₇, C₈ and C₉ carbons were calculated by introducing S = 0.488 and φ_P to Eq. (1) and value for C₁ was calculated by Eq. (4) after taking into account 27 conformations of the acetylene-containing side chain. ^f Reference number where these principal values are reported.

for C₆ and C₉
$$\sigma_{//} = (1/4)(1 + 2\sin^2\phi_p)\sigma_{11} + (1/4)(1 + 2\cos^2\phi_p)\sigma_{22}$$
(1c)

$$\sigma_{\perp} = (1/2)\{(1/4)(1 + 2\cos^2\phi_p)\sigma_{11} + (1/4)(1 + 2\sin^2\phi_p)\sigma_{22} + \sigma_{33}\}$$
(1d)

for C₇ and C₈. σ_{iso} are the chemical shifts (ppm) in the isotropic state, σ_{LC} are the chemical shifts in the liquid crystalline states, σ_{\parallel} are the chemical shift components parallel to the magnetic field, σ_{\perp} are the chemical shift components perpendicular to the magnetic field, *S* is the order parameter of the molecular director *D* of the MONOMER, σ_p is the angle between *D* and the bond axis of the phenylene ring, σ_{11} , σ_{22} are the principal values of the chemical shift tensor parallel to the phenylene plane, σ_{11} , σ_{22} are the principal values of the chemical shift tensor parallel to the phenlyene plane and σ_{33} are the principal values of the chemical shift tensor perpendicular to the phenylene plane.

By following procedures as reported in previous literature [9,10], $\Delta \sigma_{obs}$ values were introduced to the equations using with principal values of similar compounds [10,23,24], S = 0.488 and $\phi_p \approx 0(\sin^2 \phi_p = -0.009)$ were determined by regression analysis. The deviation of estimated values of $\Delta\sigma$ from experimental values was within 4 ppm. The result, $\phi_p \approx 0$, indicates that the bond axis of the phenylene ring is aligned to the molecular director. It also suggests that conformations of the octylcyclohexyl- and acetylene-containing side chains connecting to the phenylene ring may be symmetrical around the molecular director.

The side chain conformations are investigated by analysing chemical shift change of the acetylene carbon. For acetylene carbons, the equations should be modified. Fig. 5 shows principal vectors of the chemical shift tensors of acetylene carbons $(\vec{\sigma}_{11}, \vec{\sigma}_{22}, \vec{\sigma}_{33})$. If ϕ_a is defined as an angle between *D* and the direction of the triple bond of the acetylene unit, as shown in Fig. 5, equations for acetylene carbons can be modified from Eq. (1) to Eq. (2) by arranging the numbering of principal values as $(\sigma_{11}, \sigma_{22}, \sigma_{33}) \rightarrow (\sigma_{33}, \sigma_{22}, \sigma_{11})$.

$$\Delta \sigma = (2/3)S(\sigma_{\parallel} - \sigma_{\perp}) \tag{2}$$

$$\sigma_{\parallel} = \sigma_{33} \cos^2 \phi_{\rm a} + (1/2)(\sigma_{11} + \sigma_{22}) \sin^2 \phi_{\rm a}$$
(2a)

$$\sigma_{\perp} = (1/2) \{ \sigma_{33} \sin^2 \phi_a + (1/2)(\sigma_{11} + \sigma_{22})(1 + \cos^2 \phi_a) \}$$
(2b)



Fig. 5. Molecular geometry around acetylene carbons of the MONOMER and definition of φ_a . (*D* is the molecular director of the MONOMER, ϕ_a is the angle between *D* and the triple bond of acetylene carbons, and $\vec{\sigma}_{11}$, $\vec{\sigma}_{22}$, $\vec{\sigma}_{33}$ are principal vectors of the chemical shift tensor.

 $\sigma_{a,opt}$, which is ϕ_a of the energy-optimized conformation of the MONOMER (the all *trans* conformation for the side chain) shown as Conf-1 in Fig. 5, is determined to be 23° by the force field calculations. Applying this value to the above equations, $\Delta \sigma$ is estimated to be -63 ppm, which greatly differs from the experimental value, -16.9 ppm. This large difference in $\Delta \sigma$ values is thought to be due to the contribution of conformers having relatively low upfield shifts or downfield shifts, like a model shown as Conf-2 in Fig. 5, as well as the energy-optimized conformer.

Therefore, a conformational analysis was carried out for the side chain containing acetylene carbons. This side chain is composed of three bonds with rotational freedom as shown in Fig. 5, so that the steric energies are calculated for 27 (3³) conformers. For each conformer *i*, $\phi_{a,i}$ was measured from coordinate values to calculate its chemical shift difference from the isotropic one, $\Delta \sigma_i$ by Eq. (2), while the probability of each conformer, g_i , is evaluated by assuming the Boltzmann distribution from its steric energy E_i calculated by the force field method. Then, a weighed average chemical shift change of these conformers, $\Delta \sigma_{ave}$, was calculated by accounting probabilities, as shown in the following equations.

$$g_i = \exp\left(-\frac{(E_i - E_0)}{kT}\right) \tag{3}$$

$$\Delta \sigma_{\text{ave}}(N) = \frac{\left\{ \sum_{i=1}^{N} (g_i \cdot \Delta \sigma_i) \right\}}{\sum_{i=1}^{N} g_i}$$
(4)

where k is the Boltzmann constant, N is the number of conformers, and E_0 is the steric energy of the energy-optimized conformer (the all *trans* conformation).

Fig. 6 shows the $\Delta \sigma_{ave}(N)$ as a function of Σg_i , varying the *N* value. Here, *N* is increased in the order of increasing steric energy for conformers. The observed chemical shift change, $\Delta \sigma_{obs}$ of the acetylene carbon is in accord with the $\Delta \sigma_{ave}(N)$ value when almost all 27 conformers are taken into account to the average. The difference between observed, $\Delta \sigma_{obs}$ and calculated chemical shifts from all 27 conformers, $\Delta \sigma_{calc}(27)$, is about 6 ppm, but it may be insignificant because the chemical shift tensors used here are taken from those of similar compounds. It is, therefore, concluded that the acetylene-carbon-containing side chains are freely



Fig. 6. Effect of amount of conformers considered for the calculation of anisotropic chemical shift of the MONOMER acetylene carbon. g_i is the probability of each conformer evaluated by assuming the Boltzmann distribution as shown in Eq. (3) and Eq. (4) in the text, $\sum_{i=1}^{N} g_i$ is the summation of the probability of conformers varying the *N* value, where *N* is increased in the order of increasing steric energy of conformers.

changed in conformation on the oriented phenylene ring in the liquid crystalline state. On the analogy of this result, the other side chain (C8 alkyl chain) may also move freely on the oriented phenylene ring in the liquid crystalline phase.

3.3. Polymer

In order to introduce the model for the orientation analysis of the POLYMER, its molecular structure was investigated by the molecular modeling. The model structure of the POLYMER can be constructed in two ways as shown in Fig. 7. Model A is constructed by connecting the head of the MONOMER to the tail of another one (head-to-tail), and Model B by connecting the head of the MONOMER to the head of another one (head-to-head). In Model A, the distance between side chains are too close to cause bending of the polyacetylene backbones because of large steric hindrance. On the contrary, in Model B, each side chain stands at a distance. Although reaction models causing the head-to-head structures have not been clarified, X-ray diffraction analysis suggesting this type has been reported [26]. Therefore, Model B is used for the orientation analysis of the POLYMER.

In Model B, side chains are in the plane formed by the polyacetylene main chain and the long axis of the side chains are almost perpendicular to that of the



Fig. 7. Model structures of the POLYMER. Model structures were constructed by connecting the MONOMER with head-to-tail connection (Model A) and head-to-head connection (Model B).

polyacetylene backbone. Therefore, the motion of the POLYMER might be represented as that of a plate as shown in Fig. 8. If side chains containing phenylene unit tend to be oriented to the magnetic field, as shown in the analysis of the MONOMER orientation, $\vec{\sigma}_{11}$ of the main chain is also oriented to the magnetic field. In the liquid crystalline phase, the POLYMER molecules arrange in the same direction and the translational motion of the molecule is allowed only in the direction parallel to the polyacetylene backbone. In such situations, the fluctuation along the POLYMER backbone must be small. Therefore, the limited swing motion around the long axis of the polyacetylene backbone, a swing model, of the 'plate' was assumed in this analysis, as shown in Fig. 8(b) and (c). By assuming the swing model and using the chemical shift tensor of the ethylene carbon of the polyacetylene, as shown in Fig. 8(d), chemical shift change in the liquid crystalline phase can be described using the angle between the $\vec{\sigma}_{11}$ and the magnetic field, φ , as follows.

For a carbon atom in a magnetic field, its chemical shift, $\sigma(\theta_{11}, \theta_{22}, \theta_{33})$ is a function of direction cosines



Fig. 8. Dynamics model of the POLYMER. (a) A *plate*-like model for the structure of the POLYMER, where side chains are in the plane formed by polyacetylene main chain. (b) A swinging *plate* for a model of the motion of the POLYMER. (c) The side view of the motion; φ indicates the angle between the magnetic field, H_0 , and the *plate*. The *plate* swings between $-\varphi_{max}$ and $+\varphi_{max}$. (d) The geometry of the chemical shift tensor; σ_{11} and σ_{22} of the ethylene carbon are parallel to the plane of this *plate*, σ_{33} is perpendicular to the plane.

of principal vectors of chemical shift tensor to the magnetic field, H_0 , [23], as shown in Eq. (5):

$$\sigma(\theta_{11}, \theta_{22}, \theta_{33}) = \sigma_{11} \cos^2 \theta_{11} + \sigma_{22} \cos^2 \theta_{22} + \sigma_{33} \cos^2 \theta_{33}$$
(5)

Applying Eq. (5) to the ethylene carbon at a given position, as indicated by φ in Fig. 8, its chemical shift can be expressed as a function of φ by replacing as $\theta_{11} = \varphi$, $\theta_{22} = 90^\circ - \varphi$ and $\theta_{33} = 90^\circ$,

$$\sigma(\varphi) = \sigma_{11} \cos^2 \varphi + \sigma_{33} \sin^2 \varphi \tag{6}$$

When the chain swings from $-\varphi_{\text{max}}$ to φ_{max} , an observed change in the chemical shift of the ethylene carbon can be calculated as an average value, $< \Delta \sigma_{\text{calc}} >$.

$$\Delta \sigma_{\text{calc}} = \langle \sigma(\varphi) \rangle - \sigma_{\text{iso}} = \frac{\int_{0}^{\varphi_{\text{max}}} \sigma(\varphi) \cdot \sin \varphi \, \mathrm{d}\varphi}{\int_{0}^{\varphi_{\text{max}}} \sin \varphi \, \mathrm{d}\varphi} - \sigma_{\text{iso}}$$
(7)



Fig. 9. Relation between chemical shift change and φ_{max} for C_1 ' of the POLYMER. $\Delta\sigma_{calc}$ is the simulated chemical shift change of C_1 ' on the assumption of the dynamics model as shown in Fig. 8, $\Delta\sigma_{obs}$ is observed chemical shift change of C_1 ' listed in Table 1. $\Delta\sigma_{calc}$ and $\Delta\sigma_{obs}$ agree where φ_{max} is 43°.

Fig. 9 shows calculation results of $\Delta \sigma_{calc}$ by Eq. (7) for various φ_{max} values. The observed chemical shift, $\Delta \sigma_{obs}$, is in accord with the calculated one, $\Delta \sigma_{calc}$, using $\varphi_{max} = 43^{\circ}$.

As shown in Fig. 2, each NMR signal of C_7 and C_8 carbons shows one peak, indicating that such carbon at ortho or meta positions of the C_6 is averaged during NMR analysis. Therefore, as shown in Fig. 10, rotational motion of the phenylene ring is considered to the analysis besides the swing motion accounted above analyses. Assuming such dynamics, chemical shift of C_6 carbon can be expressed as a function of φ .

$$\sigma(\varphi) = \sigma_{11} \cos^2 \varphi + (1/2)(\sigma_{22} + \sigma_{33})\sin^2 \varphi \tag{8}$$



Fig. 10. Dynamics model of side chains of the POLYMER. The phenylene plane in the side chain rotates around the axis perpendicular to the polyacetylene backbone because there is no split of C_7 and C_8 carbons, which are in the ortho and meta position of C_6 carbon.



Fig. 11. Relation between chemical shift change and ϕ_{max} for C₆ of the side chain of the POLYMER. $\Delta \sigma_{calc}$ is the simulated chemical shift change of C₆ on the assumption of the dynamics model as shown in Fig. 8 and Fig. 10, and $\Delta \sigma_{obs}$ is the observed chemical shift change of C₆ listed in Table 1.

In the same manner, $\Delta \sigma_{obs}$ of C₆ was calculated by integrating Eq. (8) for various φ_{max} values. As shown in Fig. 11, the observed chemical shift of C₆ is in accord with the value calculated using $\varphi_{max} = 45^{\circ}$ which is almost the same as the ethylene carbon. The agreement of φ_{max} suggests that the chemical shift of the main chain carbon and the side chain carbons are explained by the same swing motion.

The effect of spacer length of the side-chain liquid crystalline polymers has appeared in several reports and it has been recognized that spacer units are necessary to allow the motion of the mesogen units to make polymers behave as liquid crystals [12–14]. In this study, mesogen phenylene rings were found to be oriented to the magnetic field with free rotation. The spacer length of this POLYMER may be long enough to cause free rotation but it may not be too long to cause random configuration which lowers the orientation of the polymer.

Free motion of acetylene carbons found in the MONOMER was restricted by polymerization, resulting in the orientation of the main chain induced by the side chain orientations. Our study clarified these schemes directly by characterizing the orientation and the motion of the main chain and side chains by means of the analysis of anisotropic chemical shifts of phenylene carbons and main chain carbons.

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