

## Crowned polyacetylene. 4.

### Solid state NMR studies on molecular motions and *cis-trans* isomerization of poly(4'-ethynylbenzo-15-crown-5)

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#### Summary

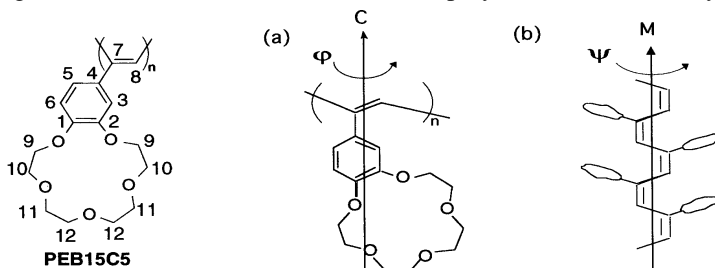
Chain conformations and molecular motions of poly(4'-ethynylbenzo-15-crown-5) (**PEB15C5**) and its annealed sample (**AN-PEB15C5**) in the solid state were investigated by <sup>1</sup>H NMR and CP-MAS <sup>13</sup>C NMR measurements. The chain conformation was determined to be *cis-transoidal* for **PEB15C5** and 70°-deflected *trans-transoidal* for **AN-PEB15C5**. The exothermic peak at 180 °C observed in the DSC thermogram was due to the *cis-trans* isomerization. Motional modes of each chain were observed in the three temperature regions of  $\gamma$ ,  $\beta$  and  $\alpha$  with an increase of temperature, which are attributed to the sterically hindered oscillation of the side chains and the vibrational and free rotations of the main chain with the oscillating side chain. The free rotation of the *trans* chain in the  $\alpha$ -region occurred in a lower temperature region by 15 °C, comparing with that of *cis* chain.

#### Introduction

In contrast to poly(acetylene), a good solubility of substituted polyacetylenes in a solvent bring about high processability, so that they have been designed and synthesized as special materials with electric conductive, non-linear optical and other properties. A drastic increase in electric conductivity over 10-15 orders of magnitude for substituted polyacetylene with doping by acceptors and an increase in temperature are comparable to that obtained with a semiconductor, which may be attributed to bond alternation in the *trans* chain (1).

In previous papers (1,2), we reported the synthesis and characterization of poly(4'-ethynylbenzo-15-crown-5) (**PEB15C5**), e.g., the NMR spectrum of **PEB15C5** showed a *cis* form of the chain in solution and in the solid state as well as poly(phenylacetylene), the cation-binding ability of **PEB15C5** was in the order of  $K^+ > Rb^+ \gg Cs^+ \gg Na^+, Li^+$ , and the electrical conductivity increased from  $1.3 \times 10^{-10}$  to  $1.3 \times 10^{-6}$  S/cm on  $I_2$ -doping.

*Cis-trans* isomerization of substituted polyacetylenes is found to generally occur at temperatures higher than 120 °C, and for the annealed polymer, there are many noncoplanar



**Scheme 1.** Axial coordinate systems of (a) side and (b) main chains of **PEB15C5**

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conformations in which the double bond twists out of coplanarity due to the steric hindrance of the side group (1). However, such structural change due to the cis-trans isomerization does not always elucidate. Thus, in advance of the study of **PEB15C5** as an electric conductive material, it is necessary to clarify the cis-trans isomerization by determining cis and trans structures of **PEB15C5** and chain mobilities.

In this study, we report that the chain structures and motions of **PEB15C5** and its annealed polymer (**AN-PEB15C5**) in the solid state are investigated with solid state  $^{13}\text{C}$  and  $^1\text{H}$  NMR measurements. Furthermore, the effects of cis-trans isomerization on the chain configuration and chain motions are discussed based on  $^1\text{H}$  NMR second moment analyses.

## Experimental

### Polymers

Poly(4'-ethynylbenzo-15-crown-5) (**PEB15C5**) with an averaged number molecular weight of 5,700 was prepared by the same method described in previous papers (1,2). After **PEB15C5** was heated in a glass tube under Ar gas at 190 °C for 1 h, an annealed polymer (**AN-PEB15C5**) was obtained.

### Measurements

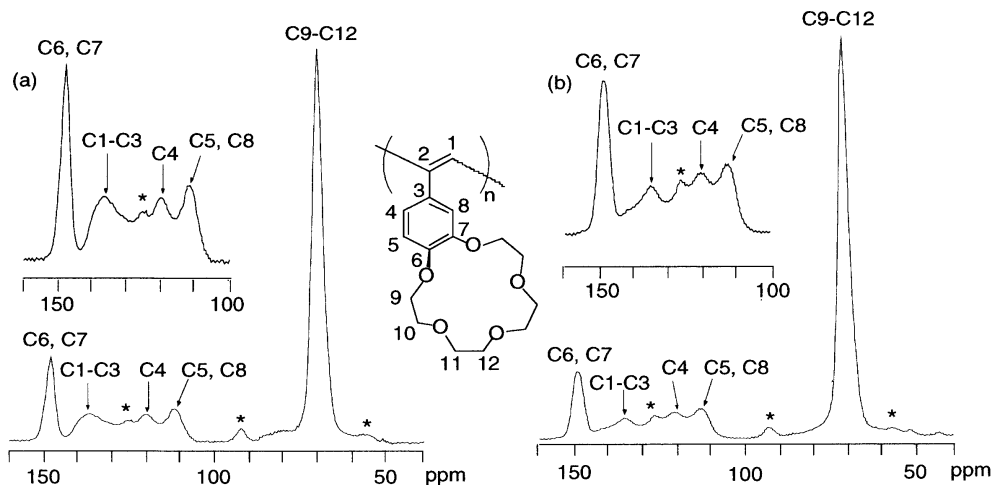
High resolution solid state  $^{13}\text{C}$  NMR measurements were made using a Bruker ASX 300 (MSL400) spectrometer operating at a frequency of 75(100) MHz for  $^{13}\text{C}$  nuclear. The solid state  $^{13}\text{C}$  NMR spectra of **PEB15C5** and **AN-PEB15C5** at room temperature were obtained by the combined use of high-power proton dipole decoupling (DD) and magic-angle sample spinning (MAS) at 5 kHz. The contact time of cross-polarization was 3 ms. 176.03 ppm for carbonyl resonance relative to TMS in glycine was used as the chemical shift reference.

Differential  $^1\text{H}$  NMR absorption curves of  $f'$  ( $\Delta\text{H}$ ) for **PEB15C5** and **AN-PEB15C5** were measured in the temperature region between -175 and 195 °C using a Nippon Denshi JNM-WL40 NMR CW-Spectroscopy operating at 40 MHz. The respective spectra of the narrow and broad components,  $f'_n(\Delta\text{H})$  and  $f'_b(\Delta\text{H})$  in  $f'(\Delta\text{H})$ , were separated by connecting the origin by a straight line with the peak of the broad component of  $f'(\Delta\text{H})$  in accordance with the Wilson-Pake method (3).

## Results and discussion

Figures 1a and b show the solid CP-MAS  $^{13}\text{C}$  NMR spectra of **PEB15C5** and **AN-PEB15C5** at 25 °C, respectively. The asterisked peaks represent the spinning side band peak. All peaks were assigned on the basis of the result for the solution  $^{13}\text{C}$  NMR measurement (1). For **PEB15C5**, there are five peaks at chemical shifts  $\delta = 149.5$ , 141.3 (a broader peak overlapping a peak at  $\delta = 138.6$  ppm), 138.6, 121.3, 113.1 and 70.9 ppm. **AN-PEB15C5** shows five peaks at  $\delta = 149.0$ , 139.0 (a broad shoulder peak overlapping a peak at  $\delta = 135.8$  ppm), 135.8, 120.6, 113.1 and 71.0 ppm. All broad peaks in the region between 140 and 110 ppm in each spectrum overlap each other within peak errors of  $\pm 0.3$  ppm.

The  $^{13}\text{C}$  resonance peaks of  $\text{C}_7$  and  $\text{C}_8$  in the  $^{13}\text{C}$  NMR spectrum of **PEB15C5** due to the double bonds of the main chain were observed at 141.3 and 130.7 ppm in the  $^{13}\text{C}$  spectrum in solution, respectively. However, they were not seen for **AN-PEB15C5** solution due to the anomalous broadening of the  $^{13}\text{C}$  NMR spectrum (1). In Figure 1, the  $^{13}\text{C}$  resonance peaks of  $\text{C}_8$  due to the main chains for **PEB15C5** and **AN-PEB15C5** also may not be significantly confirmed in the region near 130.7 ppm, in contrast to that of the **PEB15C5** solution (2). The  $\text{C}_7$  peak for **AN-PEB15C5** shifts to a higher field by about 2.3 ppm from 141.3 ppm for **PEB15C5**. This is opposite to the experimental finding of polyacetylene that the  $^{13}\text{C}$  resonance peak of the trans-transoidal chain shifts to a relatively lower field by 10 ppm from

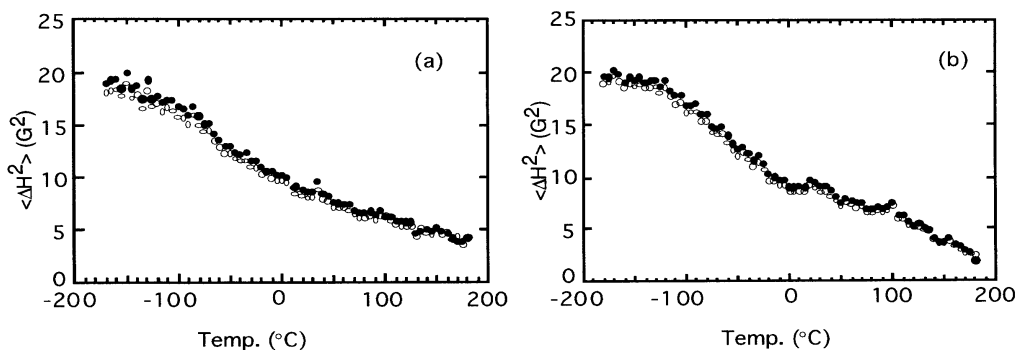


**Figure 1.** CP/MAS  $^{13}\text{C}$  NMR spectra of **PEB15C5** (a) and **AN-PEB15C5** (b)

that of the cis-transoidal chain. The better quality CP-MAS spectra for both samples were never obtained under the reasonable measurement conditions, for example, phase, contact time, pulse width, repeat times of FID and magic angle adjustments, etc. The broadening and higher field shift of the  $^{13}\text{C}$  resonance peaks of  $\text{C}_7$  and  $\text{C}_8$  for this annealed polymer seem to come essentially from the physical property of the double bond in the main chain, we believe, due to localized conduction electrons and the conjugated chain strain. Therefore, it is difficult to determine the chain configuration of **AN-PEB15C5** as well as **PEB15C5** from such broadening  $^{13}\text{C}$  peak data of  $\text{C}_7$  and  $\text{C}_8$  in the main chain using solid state high resolution NMR techniques.

Figures 2a and b show the temperature dependence of the NMR second moment  $\langle\Delta\text{H}^2\rangle$  for **PEB15C5** and **AN-PEB15C5**, respectively. The open and solid circles represent the second moments of the observed line shape  $f^2(\Delta\text{H})$  and the broad line component one  $f^2(\Delta\text{H})$ , hereafter, referred to as  $\langle\Delta\text{H}^2\rangle_{\text{ob}}$  and  $\langle\Delta\text{H}^2\rangle_{\text{b}}$ , respectively. In Figure 2a,  $\langle\Delta\text{H}^2\rangle_{\text{ob}}$  for **PEB15C5** between  $-175$  and  $-130$  °C are the average value of  $18.4 \pm 0.4$   $\text{G}^2$ . When temperature increases from  $-130$  °C,  $\langle\Delta\text{H}^2\rangle_{\text{ob}}$  and  $\langle\Delta\text{H}^2\rangle_{\text{b}}$  decrease greatly in the temperature region between  $-130$  and  $70$  °C and gradually in the temperature region between  $70$  and  $180$  °C. In Figure 2b,  $\langle\Delta\text{H}^2\rangle_{\text{ob}}$  for **AN-PEB15C5** is observed more clearly as three narrowed stages in the whole temperature region, in contrast to those of **PEB15C5**. The  $\langle\Delta\text{H}^2\rangle_{\text{ob}}$  has an almost constant value of  $19.2 \pm 0.2$   $\text{G}^2$  between  $-175$  and  $-160$  °C. When the temperature increases from  $-160$  °C,  $\langle\Delta\text{H}^2\rangle_{\text{ob}}$  decreases largely by the values of  $10.6$ ,  $2.2$  and  $4.0 \pm 0.2$   $\text{G}^2$  between  $-160$  and  $10$  °C, between  $10$  and  $80$  °C and between  $80$  and  $180$  °C, respectively.  $\langle\Delta\text{H}^2\rangle_{\text{b}}$  has an average value of  $19.9 \pm 0.2$   $\text{G}^2$  between  $-175$  and  $-160$  °C, and then decreases by  $10.9$ ,  $2.4$  and  $4.1 \pm 0.2$   $\text{G}^2$  in the respective temperature regions. Hereafter, these narrowing processes of  $\langle\Delta\text{H}^2\rangle_x$  ( $x = \text{ob}$  and  $\text{b}$ ) for **AN-PEB15C5** are referred to as  $\alpha$ ,  $\beta$  and  $\gamma$  for **AN-PEB15C5** and as  $\alpha$  and  $\beta + \gamma$  for **PEB15C5** in the order of descending temperature of their appearance, respectively.

The characteristic temperature of each narrowing process, which corresponds to the motional critical point of  $\tan^{-1}\{\tau_c\Delta\text{H}\} \approx 1$ , is defined as a narrowing temperature  $T_n$ , at which the curve of  $\langle\Delta\text{H}^2\rangle_x$  ( $x = \text{ob}$  and  $\text{b}$ ) against temperature is the steepest inflection point. Table 1 shows the classification of the  $\alpha$ -,  $\beta$ - and  $\gamma$ -narrowing processes, the narrowing tempera-



**Figure 2.** Temperature dependence of NMR second moments ( $\circ$ ,  $\langle \Delta H^2 \rangle_{ob}$  and  $\bullet$ ,  $\langle \Delta H^2 \rangle_b$ ) for **PEB15C5** (a) and **AN-PEB15C5** (b)

ture regions, the narrowing temperatures of  $T_n$  and the decrements in  $\langle \Delta H^2 \rangle_{ob}$  and  $\langle \Delta H^2 \rangle_b$  for **PEB15C5** and **AN-PEB15C5**, respectively. The parentheses in Table 1 denote the arbitrary value of **PEB15C5** since the narrowed stages do not appear clearly between the respective processes.

Previously, we reported that the cis-transoidal form of the chain in **PEB15C5** in the solid states is determined theoretically from the NMR analysis of the second moment in the rigid state (2). In particular, the strong proton dipole-dipole interaction between the side groups in the chain played an important role as a clue to elucidate the trans- and cis-configuration structures. The classical Van Vleck  $^1\text{H}$  NMR second moment analysis (4) is also a method worth using to investigate theoretically the chain structure of such a conjugated polymer having an effect on localized conduction electrons as well as those for poly(acetylene).

#### Determinations of Chain Conformation and Cis-Trans Isomerization

The total NMR second moment  $\langle \Delta H^2 \rangle_{tc}$  for **PEB15C5** can be written as

$$\langle \Delta H^2 \rangle_{tc} = 1/2 \cdot \langle \Delta H^2 \rangle_{mc} + 19/20 \cdot \langle \Delta H^2 \rangle_{sc} \quad (1)$$

where the respective coefficients of the first and second terms are the fractions of protons in the main and side chains.  $\langle \Delta H^2 \rangle_{mc}$  and  $\langle \Delta H^2 \rangle_{sc}$  denote the second moments of the main and side chains, respectively. Hereafter, the index "x" of  $\langle \Delta H^2 \rangle_x$  refers to tc, mc and sc for the total, main and side chains, respectively. They depend on the intra- and intermolecular second moments ( $\langle \Delta H^2 \rangle_x^{\text{intra}}$  and  $\langle \Delta H^2 \rangle_x^{\text{inter}}$ ):

$$\langle \Delta H^2 \rangle_x = \langle \Delta H^2 \rangle_x^{\text{intra}} + \langle \Delta H^2 \rangle_x^{\text{inter}}, \quad x = tc, mc \text{ or } sc. \quad (2)$$

The NMR second moment of  $\langle \Delta H^2 \rangle_{\text{rigid},x}$  in the rigid state for a powder sample is simply given by (4)

$$\langle \Delta H^2 \rangle_{\text{rigid},x} = 3/5 \cdot (\gamma h)^2 I(I+1) \sum_{i>j} r_{ij}^{-6}. \quad (3)$$

The chain conformation calculated using the modified MM2 program for **AN-PEB15C5** can not assume the planar trans-transoidal form due to the steric hindrance between the side groups, benzo-15-(crown-5) (**B15C5**) in **AN-PEB15C5**, in contrast to the planar zigzag conformation of trans-poly(acetylene). Therefore, we assume that the chain conformation of **AN-PEB15C5** in the rigid state is the alternately-deflected trans-transoidal zigzag form, which is deflected alternately by the angle  $\pm\tau$  about a single bond (11), as shown in Scheme

**Table 1.** The classification of the  $\alpha$ ,  $\beta$ , and  $\gamma$ -narrowing processes, the narrowing temperature regions, the narrowing temperatures of  $T_n$  and the decrements in  $\langle\Delta H^2\rangle_{ob}$  and  $\langle\Delta H^2\rangle_b$  for **PEB15C5** and **AN-PEB15C5**

Narrowing Process Temp. Region /	$\gamma$ -160 ~ 10 (-160 ~ -10) <sup>a</sup>	$\beta$ -10 ~ 80 (-10 ~ 100) <sup>a</sup>	$\alpha$ 80 ~ 180 (100 ~ 180) <sup>a</sup>
$T_n / ^\circ\text{C}$	-75 (-80) <sup>a</sup>	45 (-) <sup>a</sup>	130 (145) <sup>a</sup>
$\delta \langle\Delta H^2\rangle_{ob} / \text{G}^2$	10.6 (7.5) <sup>a</sup>	2.2 (4.6) <sup>a</sup>	4.0 (1.8) <sup>a</sup>
$\delta \langle\Delta H^2\rangle_b / \text{G}^2$	10.9 (8.0) <sup>a</sup>	2.4 (5.2) <sup>a</sup>	4.1 (2.0) <sup>a</sup>

<sup>a</sup> The values in parentheses are each parameter for **PEB15C5**.

1, and the plane of the side group is orthogonal to the alternately conjugated bond plane of the main chain, reducing steric hindrance between neighboring side chains. The theoretical values of  $\langle\Delta H^2\rangle_{tc}$  were calculated as a function of the dihedral angle  $\varphi = 180 - \tau$  of the deflected trans bond and that at  $\varphi = 0^\circ$  for the cis-transoidal form of the chain. Their  $\langle\Delta H^2\rangle_{tc}^{intra}$ 's values were calculated using equation (3) from the atom coordinates of protons based on the modified MM2 program. The value of the angle  $\beta$  between the M- and C-axes is  $60^\circ$  for the cis-transoidal and trans-transoidal forms. The intermolecular second moment  $\langle\Delta H^2\rangle^{inter}$  for each form was assumed to be  $4.4 \text{ G}^2$ , which was estimated from comparison between the experimental and the theoretical  $\langle\Delta H^2\rangle$ 's of **B15C5** (2). The second moment against the deflected angle  $\tau$  shows an interesting curve which has two minima at  $\tau = 180$  and  $90^\circ$  and two maxima at  $\tau = 0$  and  $40^\circ$ . Such behavior of the second moment comes from the changes in the proton-proton vector distance between neighboring side chains and that between the main and side chains. The trans chain at  $\varphi = 0^\circ$  corresponds to the trans-cisoidal form, of which  $\langle\Delta H^2\rangle_x$  has almost the same value as  $14.7 \text{ G}^2$  for the cis-transoidal form.

We previously reported that the experimental values of  $\langle\Delta H^2\rangle_x$  ( $x = ob, b$  and  $n$ ) at  $-175^\circ\text{C}$  for **PEB15C5** are in good agreement with the theoretical values of  $x = total, sc$ , and  $mc$  for the cis form, in contrast to the theoretical values for the trans form:  $\langle\Delta H^2\rangle_{ob} \cong \langle\Delta H^2\rangle_{total}$  (cis),  $\langle\Delta H^2\rangle_b \cong \langle\Delta H^2\rangle_{sc}$  (cis) and  $\langle\Delta H^2\rangle_n \cong \langle\Delta H^2\rangle_{mc}$  (cis) (2). This finding indicates that the plane of the side chain, i.e., the benzo-15-crown-5 group, is orthogonal to the alternately conjugated cis-bond-plane in the main chain in the solid state.

The experimental values of  $\langle\Delta H^2\rangle_{ob}$ ,  $\langle\Delta H^2\rangle_b$  and  $\langle\Delta H^2\rangle_n$  for **AN-PEB15C5** at  $-175^\circ\text{C}$  are 19.2, 19.9 and  $5.2 \text{ G}^2$ , respectively. They consist of the theoretical values of  $\langle\Delta H^2\rangle_{tc} = 20.1 \text{ G}^2$ ,  $\langle\Delta H^2\rangle_{sc} = 20.9 \text{ G}^2$  and  $\langle\Delta H^2\rangle_{mc} = 5.8 \text{ G}^2$  for the  $70^\circ$ -deflected trans forms of the chains, which are calculated using the values of lattice sum;  $R_0 = 19.98 \text{ G}^2$ ,  $R_2 = 7.03 \text{ G}^2$  and  $R_4 = 4.75 \text{ G}^2$ . The narrow component fraction is 5 %, which almost equals the proton percent of the main chain relative to all of the protons in the chain in equation (1). The exothermic peak at  $180^\circ\text{C}$  was observed in DSC measurement. These findings mean that the exothermic peak is attributed to cis-trans isomerization from the cis-transoidal to the deflected trans-transoidal conformations of the chain. The enthalpy of the exothermic peak at  $180^\circ\text{C}$  for **PEB15C5** is about  $6.2 \text{ kcal/mol}$ , which is much smaller than  $17.0 \text{ kcal/mol}$  for poly(acetylene) (6). This indicates that the deflected trans structure of the main chain may be thermodynamically more stable than the cis-transoidal form, although the trans form is deflected alternately by  $\pm 70^\circ$ .

In the X-ray reflection measurement using  $K\alpha\text{Cu}$  radiation at  $25^\circ\text{C}$ , the X-ray reflections of **PEB15C5** were observed at  $2\theta = 4.3, 8.5, 14.2, 17.6, 21.0$  and  $41.1^\circ$ , which corre-

spond to 20.5, 10.4, 6.2, 5.0, 4.2 and 2.2 Å, respectively. The reflections of **AN-PEB15C5** were observed at  $2\theta = 2.9, 4.7, 13.3, 16.9, 21.4$  and  $42.2^\circ$ , which correspond to 31.0, 18.8, 6.7, 5.3 and 4.2 Å, respectively. The respective three X-ray reflection curves at  $2\theta = 13.3, 21.4$  and  $42.2^\circ$  for **AN-PEB15C5** were very broad as well as those at  $2\theta = 14.2, 21.0$  and  $41.1^\circ$  for **PEB15C5**. By annealing **PEB15C5**, the two X-ray reflections from 8.5 and 4.3° shifted remarkably into the lower reflection angles of 4.7 and 2.9°, respectively.

The six X-ray reflections for **PEB15C5** and **AN-PEB15C5** originate from the crystal, as well as those for cis and trans poly(acetylenes) (7). However, the structure analyses of both samples are made very difficult by the relatively few X-ray reflection lines and the overlapping of intensities due to different reflections for the powder samples, because highly oriented samples are not yet available. The broadening of a few X-ray reflection peaks may be attributed to a disordered crystal having the large side chain of **B15C5** and the main chain. Although the rotational radius  $R_{trans}$  of the trans-transoidal chain about the M-axis is half of  $R_{cis}$  of the cis-transoidal chain:  $R_{trans} \cong 5.5$  Å and  $R_{cis} \cong 11$  Å, the space lengths of 20.5 and 10.4 Å ( $2\theta = 4.3$  and  $8.5^\circ$ ) for **PEB15C5** are smaller than those of 31.0 and 18.8 Å ( $2\theta = 2.9$  to  $4.7^\circ$ ) for **AN-PEB15C5**, respectively. This suggests that the large **B15C5** group of the cis-transoidal form for **PEB15C5** packs more closely between the interchains in the crystalline unit, but that of the  $70^\circ$ -deflected trans-transoidal form packs closely on the intrachain.

### $\gamma$ , $\beta$ - and $\alpha$ -Motional Narrowing Processes

In Figure 2a,  $\langle\Delta H^2\rangle_{ob}$  and  $\langle\Delta H^2\rangle_b$  for **PEB15C5** decrease largely in the  $\gamma$ -region and gradually in the  $\beta$ - and  $\alpha$ -regions. However, we cannot clearly determine the stages of  $\langle\Delta H^2\rangle_{ob}$  and  $\langle\Delta H^2\rangle_b$  against temperature between the respective narrowing processes. On the other hand, in Figure 2b,  $\langle\Delta H^2\rangle_b$  and  $\langle\Delta H^2\rangle_{ob}$  for **AN-PEB15C5** take place more clearly in the same temperature regions as the  $\gamma$ - and  $\beta$ -narrowing regions of **PEB15C5**, respectively, but the  $\alpha$ -narrowing occurs in the lower temperature region by  $15^\circ\text{C}$ . The respective decrements in  $\langle\Delta H^2\rangle_{ob}$  and  $\langle\Delta H^2\rangle_b$  are 10.6 and 10.9  $\text{G}^2$  in the  $\gamma$ -region, 2.2 and 2.4  $\text{G}^2$  in the  $\beta$ -region and 4.0 and 4.1  $\text{G}^2$  in the  $\alpha$ -region.  $\Delta H_n$  for each sample did not change significantly in the  $\gamma$ -region and decreased gradually in the  $\beta$ - and  $\alpha$ -regions.

Therefore, let us consider qualitatively the relationship between the observed decreases in  $\langle\Delta H^2\rangle_x$  ( $x = ob$  and  $b$ ) and the motions of the main- and side chains in **PEB15C5**, after the quantitative discussions of the  $\gamma$ -,  $\beta$ - and  $\alpha$ -motional narrowings for **AN-PEB15C5**.

$\gamma$ -Motional Narrowing of **AN-PEB15C5**: It is assumed that the side group of **B15C5** oscillates in amplitude  $\delta$  about the  $C_4$ - $C_7$  axis of the side chain in the  $\gamma$ -narrowing region, due to large steric hindrances between neighboring side chains and between the benzo- and vinylic groups in the cis-transoidal intrachain. The decrement in the NMR second moment  $\langle\Delta H^2\rangle_x(\phi)$  against  $\langle\Delta H^2\rangle_{nidid,x}$  in the rigid state for  $x = \text{total, main and side chains}$  in **PEB15C5** and **AN-PEB15C5** is theoretically given by using the values of  $R_{0x}$ ,  $R_{2x}$  and  $R_{4x}$  (1) and  $\langle\text{cosm}\phi\rangle$ , ( $m = 1, 2$ ) which is expressed by the zero-order Bessel function of the first kind,  $J_0(m\delta)$ , when the displacement of  $f$  oscillates harmonically as  $\phi = \delta\cos\omega t$ ,  $-\delta < \phi < \delta$  and the probability function,  $P(\phi) = 1 / \{\pi(\delta^2 - \phi^2)^{-1/2}\}$  (8).

These observed decrement values of  $\delta\langle\Delta H^2\rangle_{ob}$  and  $\delta\langle\Delta H^2\rangle_b$  in the  $\gamma$ -narrowing region for **AN-PEB15C5** are 10.6 and 10.9  $\text{G}^2$ , respectively. These values nearly equal the values of  $\delta\langle\Delta H^2\rangle_{ic} = 10.72$   $\text{G}^2$  and  $\delta\langle\Delta H^2\rangle_{sc} = 11.01$   $\text{G}^2$  for the  $70^\circ$ -deflected trans chain which are calculated theoretically when the oscillational amplitude of **B15C5** around the C-axis is  $\delta = 60^\circ$ . In the MM2 calculation, the value of  $\delta = 60^\circ$  equals the maximum oscillation amplitude of **B15C5** due to the steric hindrance between the neighboring side chains. This agreement between experiment and theory means that the molecular motion of the main chain does not take place significantly in the  $\gamma$ -region and that the side group of **B15C5** oscillates about the

C<sub>4</sub>-C<sub>7</sub>-axis in the maximum amplitude of the steric hindrance.

The steric hindrance of **B15C5** suggests evidently that the respective decreases in the second moments in the  $\beta$ - and  $\alpha$ -temperature regions for **AN-PEB15C5** may be attributed to two kind rotations about the main chain with the reorientation of oscillating side group.

$\beta$ -Motional Narrowing of AN-PEB15C5: When the side group of **B15C5** oscillates about the side chain axis in an amplitude  $\delta$  and furthermore the main chain rotates about the axis in an amplitude of  $\chi$ , the decrement in the NMR second moment  $\delta\langle\Delta H^2\rangle_x(\psi, \phi)$  from  $\langle\Delta H^2\rangle_{\text{rigid},x}$  is given by the functions of  $\langle\cos n\phi\rangle$ ,  $\langle\cos^m n\gamma_M \cos^m n\beta_c\rangle$ ,  $\langle\sin^m n\gamma_M \cos^m n\beta_c\rangle$ , ( $n, m = 2, 4$ ) and  $R_{0x} = 5/4 \langle\Delta H^2\rangle_{\text{rigid},x}$ , and the zero-order Bessel function of the first kind,  $J_0(m\chi)$ , when  $\psi = c\cos\omega\tau$ ,  $-\chi < \psi < \chi$  (2). The  $\gamma_M$  and  $\beta_c$  are the angles between magnetic field  $H_0$  and M-axis and between C- and M-axes.

The theoretical values of  $\langle\Delta H^2\rangle_{sc}(\psi, \phi)$  and  $\langle\Delta H^2\rangle_{mc}(\psi, \phi)$  for the deflected transoidal form are calculated to be 7.19 and 2.99 G<sup>2</sup>, respectively, when the side group of **B15C5** oscillates about the C-axis in the amplitude of  $\delta = 60^\circ$  and the main chain rotates about the M-axis in an amplitude of  $\chi = 43^\circ$ . These values of  $\langle\Delta H^2\rangle_{sc}$  and  $\langle\Delta H^2\rangle_{mc}$  nearly equal the experimental values of 6.6 and 2.9 G<sup>2</sup> for  $\langle\Delta H^2\rangle_b$  and  $\langle\Delta H^2\rangle_n$  in the  $\beta$ -narrowed stage, respectively. The theoretical value of  $\delta\langle\Delta H^2\rangle_{sc}(\psi, \phi)$  for the reorientation of the side chain is calculated to be 2.51 G<sup>2</sup>, which nearly equals the experimental value of 2.4 G<sup>2</sup> for  $\delta\langle\Delta H^2\rangle_b$  in the  $\beta$ -region. These agreements between experiment and theory mean that the  $\beta$ -motional narrowing is attributed to the rotational oscillation of the main chain about the M-axis in amplitude  $\chi = 43^\circ$  and then the reorientation of the side group oscillating in  $\delta = 60^\circ$  about the c-axis.

$\alpha$ -Motional Narrowing of AN-PEB15C5: The  $\alpha$ -narrowing of **AN-PEB15C5** occurs by  $-15^\circ\text{C}$  in a lower temperature region than that of **PEB15C5**. When the side group of **B15C5** oscillates about the C-axis in an amplitude of  $\delta = 60^\circ$  and the main chain rotates about the M-axis in an amplitude of  $\chi = 180^\circ$ ,  $\delta\langle\Delta H^2\rangle_{tc}$ ,  $\delta\langle\Delta H^2\rangle_{sc}$  and  $\delta\langle\Delta H^2\rangle_{mc}$  are calculated to be 4.72, 4.90, and 2.2 G<sup>2</sup>. These values for the total, side and main chains agree well with the experimental values of 4.0, 4.1 and 2.4 G<sup>2</sup> for  $\delta\langle\Delta H^2\rangle_{ob}$ ,  $\delta\langle\Delta H^2\rangle_b$  and  $\delta\langle\Delta H^2\rangle_n$  in the  $\alpha$ -region, respectively. These agreements between theory and experiment mean that since the space length of the chain in the crystal increases, the  $\alpha$ -narrowing process is due to the larger rotation motion of the chain about its axis, accompanied by the restricted oscillation of the side chain.

$\gamma$ -,  $\beta$ -, and  $\alpha$ -Motional Narrowings for **PEB15C5**: The maximum oscillation amplitude of **B15C5** about the C-axis in the cis-transoidal form for **PEB15C5** is theoretically calculated to be a value of  $\delta = 58^\circ$  due to the steric hindrance of the phenyl group in the side chain to a proton in the main chain. The theoretical values of  $\delta\langle\Delta H^2\rangle_{tc}$  and  $\delta\langle\Delta H^2\rangle_{sc}$  are calculated to be 7.6 and 8.01 G<sup>2</sup>, respectively, when the amplitude of  $\delta$  is  $58^\circ$  (8). These values of  $\delta\langle\Delta H^2\rangle_{tc}$  and  $\delta\langle\Delta H^2\rangle_{sc}$  nearly equal the experimental values of 7.5 and 8.0 G<sup>2</sup> for  $\delta\langle\Delta H^2\rangle_{ob}$  and  $\delta\langle\Delta H^2\rangle_b$  between  $-175$  and  $-10^\circ\text{C}$  in the  $\gamma$ -region, respectively, although these narrowed stages of the  $\gamma$ -process are not observed obviously.

Such steric hindrance of **B15C5** between the interchains suggests that the decrements in  $\delta\langle\Delta H^2\rangle_{ob}$  and  $\delta\langle\Delta H^2\rangle_n$  in the  $\alpha$ - and  $\beta$ -temperature regions above  $-10^\circ\text{C}$  are attributed to the rotational oscillations of the main chain and that the reorientation of the side chain oscillating by  $\delta = 58^\circ$ . NMR analysis gives rise to the motion modes of the main chain that rotates largely about M-axis with an amplitude increase of  $\chi = 73^\circ$  to  $180^\circ$ :  $\delta\langle\Delta H^2\rangle_{tc}(\psi, \phi)$  ( $= 4.32$  G<sup>2</sup>)  $= \delta\langle\Delta H^2\rangle_{ob}$  ( $= 4.6$  G<sup>2</sup>) and  $\delta\langle\Delta H^2\rangle_{mc}$  ( $= 2.26$  G<sup>2</sup>)  $= \delta\langle\Delta H^2\rangle_n$  ( $= 2.6$  G<sup>2</sup>) between  $-10$  and  $100^\circ\text{C}$ ;  $\delta\langle\Delta H^2\rangle_{sc}$  ( $= 2.99$  G<sup>2</sup>)  $= \delta\langle\Delta H^2\rangle_b$  ( $= 2.0$  G<sup>2</sup>) and  $\delta\langle\Delta H^2\rangle_{mc}$  ( $= 4.12$  G<sup>2</sup>)  $= \delta\langle\Delta H^2\rangle_n$  ( $= 4.0$  G<sup>2</sup>) between  $100$  and  $175^\circ\text{C}$ .

The diffusibility of the narrowed stages between  $\alpha$ -,  $\beta$ - and  $\gamma$ -processes for **PEB15C5**

suggests that the axial motion of the main chain is effected by the closed-packing of **B15C5** between the interchains. On the other hand, the appearance of the narrowed stage in each process for **AN-PEB15C5** indicates that the respective motional modes of the main and side chains take place independently in  $\alpha$ -,  $\beta$ - and  $\gamma$ -narrowing regions, due to the closed-packing of **B15C5** between the intrachains and the increase of packing space length. Therefore, these findings of NMR and X-ray suggest that the axial motions of the main and side chains in the  $\alpha$ -region for **PEB15C5** play an important role in the thermal stability of the chain on cis-trans isomerization.

## CONCLUSIONS

Multiplets in the  $^{13}\text{C}$  NMR spectra for **PEB15C5** and its annealed sample, **AN-PEB15C5**, at room temperature were assigned as resonances due to the 13-carbons of the vinylic and **B15C5** groups in the chain. The chain structures and molecular motions of **PEB15C5** and **AN-PEB15C5** were investigated from the  $^1\text{H}$  NMR second moment analyses in the temperature region between  $-175$  and  $180$  °C. The chain configurations of **PEB15C5** and **AN-PEB15C5** were determined to be cis-transoidal and the  $70^\circ$ -deflected trans-transoidal forms, respectively. The configurational change confirmed that the exothermic peak at  $180$  °C in the DSC thermogram is due to the cis-trans isomerization.

Three kinds of  $\gamma$ -,  $\beta$ - and  $\alpha$ -narrowings for **AN-PEB15C5** were obviously observed as the respective narrowed stages in the three temperature regions with an increase in temperature, but for **PEB15C5** were not done clearly. This suggested that the motional mode of the main chain in **PEB15C5** depended on the packing of the side chain between interchains, in contrast to the packing of the side chain between intrachains in **AN-PEB15C5**. According to the harmonic oscillation approximation, the  $\gamma$ -narrowings for **PEB15C5** and **AN-PEB15C5** were attributed to the sterically hindered oscillations of the side chain about its axis in amplitudes of  $58$  and  $60^\circ$ , respectively. The respective  $\beta$ - and  $\alpha$ -narrowings were attributed to the oscillational rotation modes of the main chain about its axis and the reorientation of the sterically hindered oscillation of the side chain, respectively. The axial rotation of the trans-transoidal chains in  $\alpha$ -narrowing for **AN-PEB15C5** occurred in a lower temperature region by  $15$  °C, due to the increase in the packing space lengths of chains in the unit crystal structure after cis-trans isomerization.

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