

## Articles

## Conformational Study of Liquid Crystalline Polymer: Theoretical Studies

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The relaxed torsional potential of a liquid crystalline polymer containing an ester functional group in a mesogenic unit (hereafter **12-4** oligomer) has been calculated with the *ab initio* self-consistent-field using 6-31G\* basis set. GIAO  $^{13}\text{C}$  NMR chemical shifts also have been calculated at the B3LYP/6-31G\* level of theory for each conformational structure obtained from torsional potential calculation. The results show that the phenyl ring-ester linkages are coplanar with the dihedral angle of about  $0^\circ$  and the ring-ring linkages in the biphenyl groups are tilted with the dihedral angle of around  $43\text{--}44^\circ$  in the lowest energy conformer. The biphenyl ring has a comparatively lower energy barrier of internal rotation potential in the ring-ring than that of phenyl ring-ester. The  $^{13}\text{C}$  chemical shifts of carbonyl carbons were found to move to upfield due to  $\pi$ -conjugation with phenyl ring and slightly affected about 0.5 ppm by dihedral angle of the ring-ring linkage.

**Key Words** : Liquid crystalline, Conformation,  $^{13}\text{C}$  chemical shift, Calculation

## Introduction

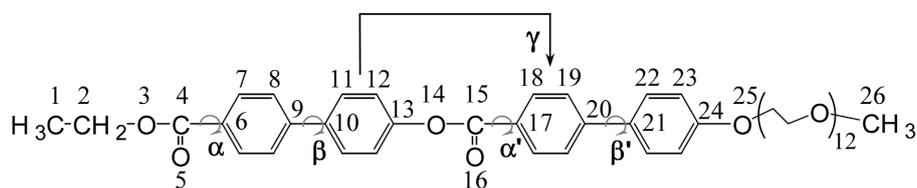
Liquid crystalline polymers (LCPs) containing an ester functional group in a mesogenic unit produce different liquid crystalline states depending on the chemical structures of the constituent units and on the chemical bonds connecting the units.<sup>1-3</sup> LCPs containing an ester functional group in a mesogenic unit have long been the subject of studies of intermolecular interactions. Many theoretical and experimental works have investigated the planarity between the phenyl ring and adjacent carbonyl group, or the location of bond rotation above the phase transition (solid-to-liquid crystal).<sup>4,5</sup>

High resolution solid state NMR spectroscopy<sup>6</sup> is one of the most powerful methods for characterizing structures and molecular motion of polymers in the solid state. In particular, the NMR chemical shift can be used for the structural elucidation of polymers because the chemical shift is a sensitive parameter for the local structure such as conformation, for the packing structure, and for electronic structure of polymers.<sup>7</sup>

In experimental  $^{13}\text{C}$  NMR measurements, the most remarkable concern is directed to the C=O peaks. Especially,  $^{13}\text{C}$  chemical shifts of carbonyl carbons in **12-4** oligomer (Figure 1) are important, accounting for the possibility of

hydrogen bonding between the carbonyl oxygen at the ethyl terminal and one of the hydrogen atoms of the poly(ethylene oxide) (PEO) chain.<sup>2,8</sup> In addition, the behavior of the other C=O group, which is in the mesogen moiety, reflects the phase transition temperature. It is necessary to assign the two free C=O groups unambiguously, in order to correctly identify which C=O group is participated in the hydrogen bonding. However, it is not easy to distinguish the chemical shifts of  $\text{C}_4$  and  $\text{C}_{15}$  in high-resolution solid-state NMR spectra. To assign the chemical shifts correctly, we synthesized **12-4** oligomer  $^{13}\text{C}$ -labeled in position  $\text{C}_4$  to clarify the assignment. We have already reported that the  $^{13}\text{C}$  chemical shift for  $\text{C}_4$  is bigger than that of  $\text{C}_{15}$  in the  $^{13}\text{C}$  MAS (magic angle spinning) spectra using the synthesized **12-4** oligomer  $^{13}\text{C}$ -labeled.<sup>8</sup>

*Ab initio* and DFT (Density Functional Theory) NMR calculations are now the feasible tools which relate the chemical shift and molecular structure. In particular, the calculated  $^{13}\text{C}$  chemical shifts appear to be accurate enough to aid in experimental peak assignment.<sup>9</sup> Moreover, the investigation of the effect of dihedral angle on NMR chemical shift is very helpful to interpret molecular conformation. To aim this, the potential energy surface (PES) scans as a function of dihedral angles ( $\alpha$ ,  $\alpha'$ ,  $\beta$ , and  $\beta'$  in Figure 1) have been



**Figure 1.** Schematic diagram with numbering of carbon atoms for **12-4** oligomer.  $\alpha$  ( $\alpha'$ ) and  $\beta$  ( $\beta'$ ) are dihedral angles about the ring-ester and ring-ring linkages, respectively and  $\gamma$  is dihedral angle for the pairs of the benzene planes separated in space.

calculated at HF/6-31G\* level, which is also useful to examine the planarity of ring-ring and ring-ester linkages of **12-4** oligomer. Then,  $^{13}\text{C}$  NMR chemical shifts of the geometric structures described as a function of  $\alpha$ ,  $\alpha'$ ,  $\beta$ , and  $\beta'$  have been calculated to investigate conformational effect on  $^{13}\text{C}$  chemical shift by using the GIAO approach.

### Computational Method

All calculations were performed by the Gaussian 98 package.<sup>10</sup> The geometry was fully optimized at the Hartree-Fock and the Becke's three-parameter hybrid DFT method with the Lee-Yang-Parr correlation functional (B3LYP)<sup>11</sup> by using the 6-31G\* basis set. In order to investigate the direct effect of the dihedral angles on the chemical shifts, single molecule model was used. To simplify the calculation, in this work only one out of 12 PEO units, which are expected not to affect the conformational energy of the mesogen part, is adopted. The reliability of this approximation has been confirmed by some test calculations showing that the torsional energies are almost independent from the length of the aliphatic chains.<sup>12</sup> The potential energy surface (PES) scan for dihedral angles,  $\alpha$  ( $\text{C}_4\text{-O}_5\text{-C}_6\text{-C}_7$ ),  $\alpha'$  ( $\text{C}_{15}\text{-O}_{16}\text{-C}_{17}\text{-C}_{18}$ ),  $\beta$  ( $\text{C}_8\text{-C}_9\text{-C}_{10}\text{-C}_{11}$ ), and  $\beta'$  ( $\text{C}_{19}\text{-C}_{20}\text{-C}_{21}\text{-C}_{22}$ ), was carried out at every  $15^\circ$  interval with the range of  $0\text{-}180^\circ$  at the HF/6-31G\* level. Nuclear shielding tensors for **12-4** oligomer were obtained from the gauge-including atomic orbital (GIAO) calculations<sup>13</sup> at the HF/6-31G\*\*//HF-6-31G\*, B3LYP/6-31G\*\*//HF-6-31G\*, and B3LYP/6-31G\*\*//B3LYP-6-31G\* levels of theory. For  $\text{C}_4$ ,  $\text{C}_9$ ,  $\text{C}_{15}$ , and  $\text{C}_{20}$  the  $^{13}\text{C}$  chemical shift were performed with B3LYP-GIAO/6-31G\*\*//HF-6-31G\* level of theory. The isotropic shielding constants,  $\sigma_i$ , were transformed to chemical shifts by

$$\delta_i = \sigma_{\text{ref}} - \sigma_i.$$

where  $\sigma_{\text{ref}}$  is the isotropic shielding of the reference compound, in our case, tetramethylsilane (TMS) for  $^{13}\text{C}$ .

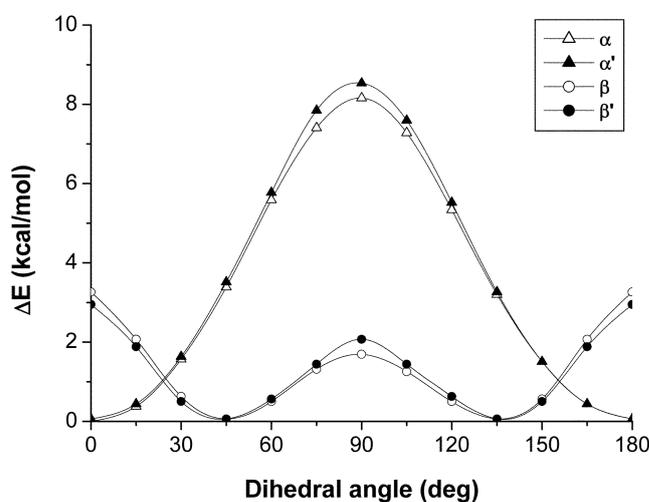
### Results and Discussion

**Geometry and PES scan.** Some of the dihedral angles about the ring-ring and ring-ester linkages for **12-4** are shown in Table 1. According to recent calculation of phenyl benzoate, each bond in the  $\text{Ph-C(=O)-O-}$  fragment is fairly rigid, which means the phenyl ring and carbonyl group ( $\text{Ph-C=O}$ ) lie on the same plane.<sup>14</sup> In our work, the ring-ester linkages are also coplanar with the dihedral angle of about  $0^\circ$  in the lowest energy conformer at the HF/6-31G\* and B3LYP/6-31G\* levels. But, only  $\alpha'$  is very little tilted by about  $1.22^\circ$  at the B3LYP/6-31G\* calculation. The ethyl ester group at the end of the chain has a gauche-type conformation with the dihedral angle ( $\text{C-O-CH}_2\text{-CH}_3$ ) of ca.  $83.73^\circ$  at HF/6-31G\* and  $85.42^\circ$  at B3LYP/6-31G\*, respectively. The biphenyl groups may have the various values of the internal rotation angle depending on the variation of the environmental conditions or the intermolecular interactions. The primary structural difference is the twist angle between

**Table 1.** Selected Dihedral Angles and Isotropic  $^{13}\text{C}$  Chemical Shifts of **12-4** oligomer

Method	dihedral angle (deg)					
	$\alpha$	$\alpha'$	$\beta$	$\beta'$	$\gamma$	$\text{C}_1\text{-C}_2\text{-C}_3\text{-C}_4$
HF/6-31G*	0.4	0.5	-44.8	43.1	75.5	-83.7
B3LYP/6-31G*	-0.1	1.2	-37.0	36.0	51.2	-85.4
	$\delta_{\text{iso}}$ (ppm)					
			$\text{C}_1$	$\text{C}_4$	$\text{C}_{15}$	
HF/6-31G**//HF-6-31G*			15.9	160.2	158.9	
B3LYP/6-31G**//HF-6-31G*			14.8	153.2	152.6	
B3LYP/6-31G**//B3LYP/6-31G*			15.5	158.8	157.2	
Expt. <sup>a</sup>			14.2	166.3	164.2	

<sup>a</sup>Taken from ref. 8.



**Figure 2.** Potential energy surfaces of **12-4** as obtained with SCF method using the 6-31G\* basis. Relative energies without zero point energy (ZPE) corrections are plotted against the dihedral angles ( $\alpha$ ,  $\alpha'$ ,  $\beta$ , and  $\beta'$ ).

the phenyl rings. The inter ring-ring angle is  $44.4^\circ$  in gas phase,<sup>15</sup> but in solution it ranges from  $19^\circ$  to  $32^\circ$  for the parent molecule in various media.<sup>16</sup> Tashiro *et al.*<sup>17</sup> reported that the liquid crystalline arylate polymer has a two kinds of molecular conformation,  $\alpha$  and  $\beta$  forms. The main difference in the molecular conformation between these two crystalline forms is a torsional angle between the two benzene rings of the biphenyl group:  $48^\circ$  for the  $\alpha$  form and  $0^\circ$  for the  $\beta$  form. They indicated that the biphenyl groups in both conformations are still tilted in the liquid crystalline state. In **12-4** oligomer, the dihedral angles of the benzene-benzene linkage in the biphenyl groups are  $44.8^\circ$  for  $\beta$  and  $43.1^\circ$  for  $\beta'$  at the HF/6-31G\* level as shown in Table 1. These values are about  $7^\circ$  bigger than those of B3LYP/6-31G\* calculation, respectively.

The ring-ring internal rotation potential of the biphenyl group has a comparatively low-energy barrier.<sup>18,19</sup> The potential energy surfaces of **12-4**, obtained from HF/6-31G\* calculations, are presented in Figure 2 and consistent with previously reported results. As shown in Figure 2, the energy

calculation is helpful to clarify to what extent the intermolecular interactions affect the twisted structure of the biphenyl parts in the molecular packing during the phase transition. In these types of molecules, the  $\pi$ -conjugation between adjacent phenyl rings should stabilize the coplanar conformer, whereas the steric repulsion should favor nonplanar conformations. In the case of phenyl-phenyl linkage ( $\beta$  and  $\beta'$ ), Figure 2 shows that the most stable structure of **12-4** oligomer is a nonplanar conformation with equilibrium twist angles ( $\alpha = 0.4^\circ$ ,  $\alpha' = 0.5^\circ$ ,  $\beta = -44.8^\circ$ , and  $\beta' = 43.1^\circ$  at the HF/6-31G\*, see Table 1). The internal rotational barrier from coplanar ( $0^\circ$  and  $180^\circ$ ) and orthogonal ( $90^\circ$ ) conformations are 3.3 and 1.7 kcal mol<sup>-1</sup> for  $\beta$  at the HF/6-31G\* level, respectively. Although the experimental electron diffraction investigations on the torsional barrier of biphenyl<sup>15</sup> have been interpreted in terms of a more symmetrical potential curve, *i.e.*, about equal barrier heights for planar and orthogonal saddles, all the previous *ab initio* calculations performed with and without electron correlation contributions result in distinctly different barrier heights for the planar and the orthogonal conformations, the former being about twice as large.<sup>20</sup> Our result has a similar trend to the previous report.<sup>20</sup> It is revealed that the functional groups on para position of phenyl rings do not much affect the ring-ring torsional barrier. In addition, the energy barriers of  $\beta$  and  $\beta'$  are much lower than those of  $\alpha$  and  $\alpha'$  depicted as Figure 2. During phase transition, the dihedral angles of ring-ring linkages,  $\beta$  and  $\beta'$ , would be changed easily compared to those of ring ester linkages,  $\alpha$  and  $\alpha'$ .

**Calculation of GIAO.** The selected GIAO theoretical isotropic <sup>13</sup>C chemical shifts relative to TMS obtained at the Hartree-Fock and DFT levels of theory for **12-4** oligomer are listed in Table 1. The calculated isotropic <sup>13</sup>C chemical shifts of C<sub>4</sub> are bigger than those of C<sub>15</sub> in both the HF-GIAO and B3LYP-GIAO results. These trends are in good agreement with experimental results.<sup>8</sup> From the results, the calculated <sup>13</sup>C chemical shifts at this level of theories show sufficient accuracy to aid in experimental peak assignment. Furthermore, because the chemical shift is very sensitive for conformations, the comparison chemical shifts obtained from experimental spectra and those theoretically calculated at the B3LYP/6-31G\* level of theory can be very useful for understanding the relationship between the <sup>13</sup>C chemical shift and molecular structure.

The effect of dihedral angle on <sup>13</sup>C chemical shifts calculated using the GIAO-B3LYP/6-31G\*\*//HF/6-31G\* level of theory are presented in Figures 3-6. Figure 3 shows the effect of dihedral angle on <sup>13</sup>C chemical shift for C<sub>4</sub> (carbonyl carbon near the ethyl terminal). As expected, the <sup>13</sup>C chemical shifts for C<sub>4</sub> depend sensitively on the dihedral angle of  $\alpha$ . When the dihedral angle  $\alpha$  is  $0^\circ$  or  $180^\circ$  (the most stable conformer from Figure 1), the carbonyl carbon (C<sub>4</sub>) was shielded the most due to  $\pi$ -conjugation with phenyl ring. On the contrary, the carbonyl carbon (C<sub>4</sub>) at the orthogonal conformation ( $\alpha = 90^\circ$ ) is deshielded the most because of completely breaking of ring-carboxyl conjugation. This result reveals that most of electrons for  $\pi$ -conjugation

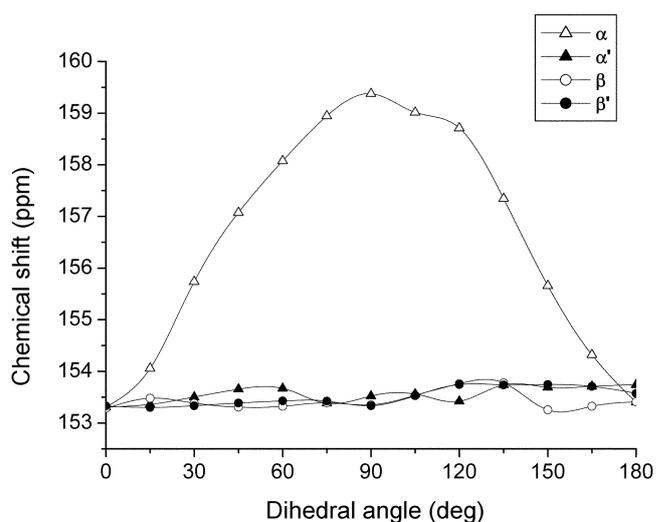


Figure 3. The effect of dihedral angle on <sup>13</sup>C chemical shift for C<sub>4</sub>.

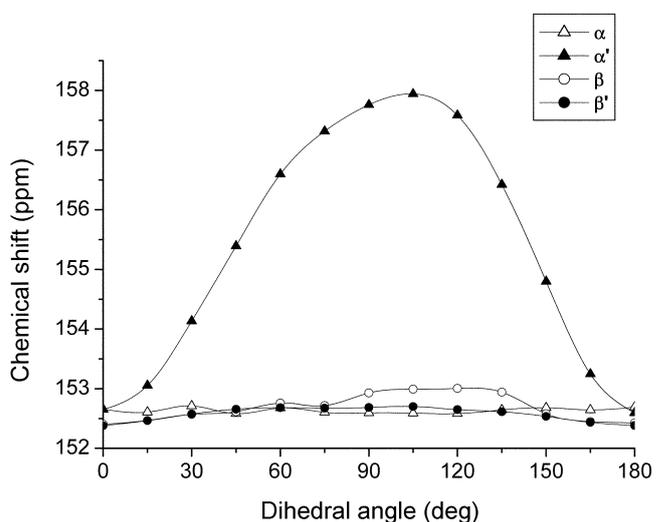
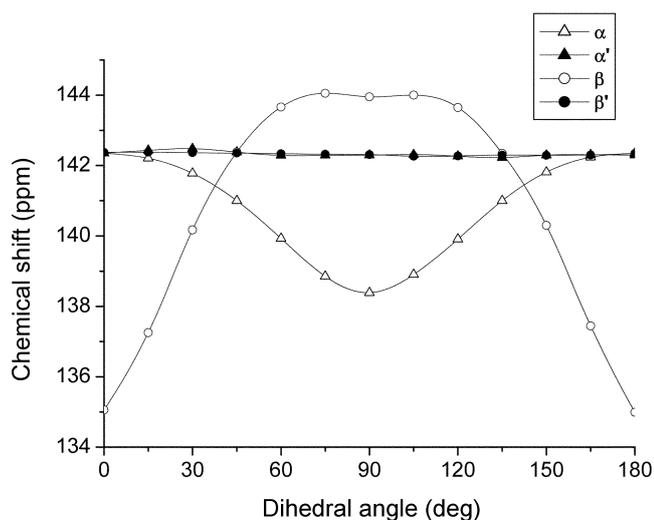


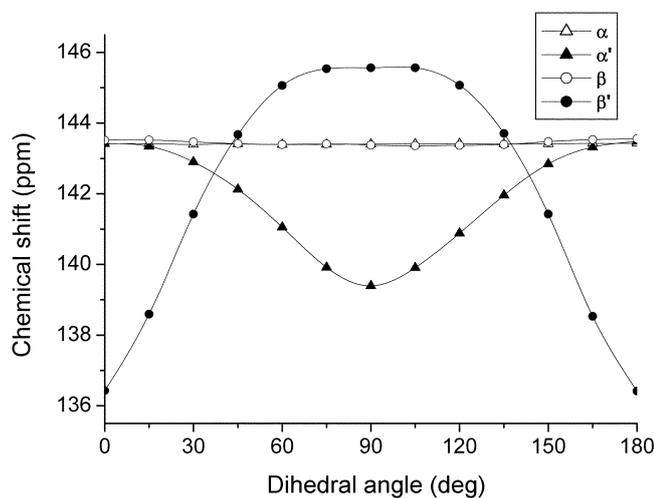
Figure 4. The effect of dihedral angle on <sup>13</sup>C chemical shift for C<sub>15</sub>.

between phenyl ring and ester groups are supplied from the phenyl ring. However, <sup>13</sup>C chemical shifts of carbonyl carbon (C<sub>4</sub>) are not much affected by the other dihedral angles ( $\alpha'$ ,  $\beta$  and  $\beta'$ ) on the whole range.

The effect of dihedral angle on <sup>13</sup>C chemical shift for C<sub>15</sub> (carbonyl carbon in mesogen part) is shown in Figure 4. As like C<sub>4</sub>, the dihedral angle  $\alpha'$  has large effect on the <sup>13</sup>C chemical shift for C<sub>15</sub>. The other dihedral angles ( $\alpha$ ,  $\beta$  and  $\beta'$ ) effect less than 0.5 ppm on the <sup>13</sup>C chemical shift for C<sub>15</sub>. The typical difference between Figure 4 and Figure 3 is that the carbonyl carbon (C<sub>15</sub>) is deshielded the most at  $\alpha = 105^\circ$  because of effect of near phenyl group separated in space ( $\gamma = 75.5^\circ$  in Figure 1). In figures 3 and 4, <sup>13</sup>C chemical shift difference of carbonyl carbons, C<sub>4</sub> and C<sub>15</sub>, were slightly affected around 0.5 ppm by  $\beta$  and  $\beta'$ . This indicates that the chemical shift changes in the phase transitions caused by the conformation change between phenyl groups are expected about 0.5 ppm. This result will give very useful information in interpretation of the <sup>13</sup>C solid state NMR spectra, obtained



**Figure 5.** The effect of dihedral angle on  $^{13}\text{C}$  chemical shift for  $\text{C}_9$ .



**Figure 6.** The effect of dihedral angle on  $^{13}\text{C}$  chemical shift for  $\text{C}_{20}$ .

in order to investigate the temperature dependency, of **12-4** oligomer.

Figure 5 and 6 show the dihedral angle effect on  $^{13}\text{C}$  chemical shift for  $\text{C}_9$  and  $\text{C}_{20}$ , respectively. The chemical shift of  $\text{C}_9$  were very affected by both  $\alpha$  and  $\beta$ . The changes of  $\pi$  conjugation between carbonyl group, especially  $\text{C}=\text{O}$ , and phenyl ring influence the chemical shift of  $\text{C}_9$ . Figure 5 shows that  $\text{C}_9$  is mostly deshielded when it has planar conformation and mostly shielded when it has orthogonal conformation in which the  $\pi$  conjugation between  $\text{C}=\text{O}$  and phenyl ring is not totally extant. This result indicates that the electron necessary for the  $\pi$  conjugation between  $\text{C}=\text{O}$  and phenyl ring is supplied from the phenyl ring. Because the  $\text{C}_4$  is not affected by  $\alpha'$  and  $\beta'$  as expected, the conformational change of the biphenyl groups, which are not adjacent, dose not have influence on the chemical shifts, which is consistent with the result as seen in Figure 6. Because the chemical environment of  $\text{C}_{20}$  is very similar to that of  $\text{C}_4$ , the effect of the dihedral angle on the chemical shift of  $\text{C}_{20}$  is very close to that of  $\text{C}_4$  (Figures 5 and 6).

## Conclusions

We have presented the energies and molecular geometries for the stable conformer of **12-4** oligomer calculated with Hartree-Fock and density functional theory (DFT) of B3LYP using the 6-31G\* basis. Also, in order to understand the conformation change for **12-4** oligomer in more detail, the relaxed PES scan as a function of a dihedral angles, generated ring-ester and ring-ring linkages, has been calculated. The calculated results show that the phenyl ring-ester linkages are coplanar with the dihedral angle about  $0^\circ$  and ring-ring linkages and the dihedral angle of ring-ring linkages is  $43\text{--}44^\circ$  at the HF/6-31G\* level and the biphenyl ring has a comparatively lower energy barrier of internal rotation potential in the ring-ring linkage than that of ring-ester linkage.

In addition, to investigate the direct effect of the dihedral angles on the  $^{13}\text{C}$  chemical shifts, GIAO NMR chemical shifts have been calculated for each conformer at the B3LYP/6-31G\* level of theory. The calculated  $^{13}\text{C}$  chemical shifts of carbonyl carbons were found to move to upfield due to  $\pi$ -conjugation with the phenyl ring and the  $^{13}\text{C}$  chemical shift changes caused by the conformational change between the phenyl groups were about 0.5 ppm. This result will be very useful for interpreting of the  $^{13}\text{C}$  solid state NMR spectra, obtained in order to investigate the temperature dependency, of **12-4** oligomer.

## References

- Lee, M.; Oh, N. K. *J. Mater. Chem.* **1996**, *6*, 1079.
- Yu, S. C.; Choi, Y.; Yu, K. H.; Yu, J.; Choi, H.; Kim, D. H.; Lee, M. *Macromolecules* **2000**, *33*, 6527.
- (a) Lee, M.; Cho, B. K.; Kim, H.; Yoon, J. Y.; Zin, W. C. *J. Am. Chem. Soc.* **1998**, *120*, 13258. (b) Lee, M.; Cho, B. K.; Oh, N. K.; Zin, W. C. *Macromolecules* **2001**, *34*, 1987.
- Birner, P.; Kugler, S.; Simon, K.; Naray-Szabo, G. *Mol. Cryst. Liq. Cryst.* **1982**, *80*, 11.
- Hummel, J. P.; Flory, P. J. *Macromolecules* **1999**, *13*, 479.
- (a) Lesien, J.; Boeffel, C.; Spiess, H. W.; Yoon, D. Y.; Sherwood, M. H.; Kawasumi, M.; Percec, V. *Macromolecules* **1995**, *28*, 6937. (b) Ishida, H.; Kaji, H.; Horii, F. *Macromolecules* **1997**, *30*, 5799.
- Kurusu, H.; Ookubo, T.; Tuchiya, H.; Ando, I.; Watanabe, J. *J. Mol. Struct. (Theochem)* **2001**, *574*, 153.
- Kim, D. H.; Pang, S.; Lee, S. H.; Yu, S. C.; Choi, H. S.; Han, O. H. *Bull. Korean Chem. Soc.* **2001**, *22*, 1289.
- (a) Kim, D. H.; Eun, H. M.; Choi, H. S. *Bull. Korean Chem. Soc.* **2000**, *21*, 148. (b) Wang, B.; Fleischer, U.; Hinton, J. E.; Pulay, P. *J. Comput. Chem.* **2001**, *22*, 1887. (c) Wang, B.; Hinton, J. E.; Pulay, P. *J. Comput. Chem.* **2002**, *23*, 492.
- Fisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.;

- Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
11. Becke, A. *J. Chem. Phys.* **1993**, 98, 5648.
  12. Cacelli, I.; Prampolini, G. *Chem. Phys.* **2005**, 314, 283.
  13. Ditchfield, R. *Mol. Phys.* **1974**, 27, 789.
  14. Imase, T.; Kawauchi, S.; Watanabe, J. *J. Mol. Struct.* **2001**, 560, 275.
  15. Almenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, S. J.; Smadal, S. *J. Mol. Struct.* **1985**, 128, 59.
  16. Eaton, V. J.; Steele, D. *J. Chem. Soc., Faraday Trans.* **1973**, 2, 1601.
  17. Tashiro, K.; Hou, J.; Kobayashi, M.; Inoue, T. *J. Am. Chem. Soc.* **1990**, 112, 8273.
  18. Carreira, L. A.; Towns, T. G. *J. Mol. Struct.* **1977**, 41, 1.
  19. Akiyama, M.; Watanabe, T.; Kakihara, M. *J. Phys. Chem.* **1986**, 90, 1752.
  20. Karpfen, A.; Choi, C. H.; Kertesz, M. *J. Phys. Chem.* **1997**, 101, 7426.
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