

Theoretical Study of Conformation-dependent Spectroscopic Property of Helical conjugated Polyisocyanide derived from L-phenylalanine

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Abstract: In order to understand the relationship between the UV-vis spectrum and helical conformation of polyisocyanide, the geometry optimization, orbital energy and UV-vis spectral simulation of butane-2,3-dione and butane-2,3-diimine as the model compound of polyisocyanide are investigated by semi-empirical AM1 method and ab initio at HF/6-31G* level. Dihedral angle of N=C-C=N (ϕ) is adopted as the parameter to describe a series of the helical conformation of polyisocyanide. While the energy level of HOMO, n orbital, is almost independent of the dihedral angle ϕ , that of LUMO, π^* orbital, becomes unstable with the angle approaching to 90 ° from either 0 ° or 180 °. Because the LUMO has bonding character over two inner carbons at 2- and 3-position which should be sensitive to the angle ϕ , in comparison with the HOMO delocalizing on O or N atoms. As the result, the HOMO to LUMO transition, *i.e.* $n\text{-}\pi^*$ transition, is red-shifted with the angle deviating from 90 °. The red-shift of the absorption edges is known in vicinal diketone compounds with dihedral angles of O=C-C=O deviating from 90 °. Polyisocyanide bearing bulky side chains are known to take 4_1 helix with about 65 ° of dihedral angle in the most stable conformation. The red-shift of the absorption edge observed by thermal treatment of L-phenylalanine-derived polyisocyanide indicates some contribution of conformational change with decreasing dihedral angle.

Key words: polyisocyanide, helix, conformation, UV-spectrum, Configuration Interaction

1. INTRODUCTION

Synthetic helical polymers, composed of ordered coiled main chains as the secondary conformation, have been studied so far in view of biologically important structure and function with its large chirality. Remarkable progress has been made on recent studies of the screw-sense-polymerization,¹ chiral molecular recognition² and so on. In recent years, considerable attention has been drawn to studies on the stimuli-induced changes in helical conformation³ since the helical structure play important roles in biological dynamic processes in DNA, protein, and so on. Polyisocyanide, one of the synthetic helical polymers, consists of regularly twisted sp^2 carbons as the main chain. Overlap of the adjacent p_z orbitals along the twisted main chain is more or less limited. Therefore, the electronic structure of the tilted π -conjugated system should be strongly coupled with the helical conformation of the main chain. On the other hand, several approaches by theoretical studies,⁴ NMR,⁵ light scattering,⁶ and AFM studies⁷ and so forth have been done so far for polyisocyanide to illustrate more real pictures on the conformation of the helical main chain. Now, it is well accepted that the main chain of polyisocyanide takes helical conformation with 4 repeated units per one turn, *i.e.* 4_1 helix, when the size of the side chain is enough bulky like

t-butyl group. However, it has not yet been understood how the changes of helical conformation can be induced by the external stimuli. In our previous work,⁸ the polyisocyanide derived from L-phenylalanine shows a large negative circular dichroism around 240-400 nm absorption to the transition of the main chain, indicating one-handed helical conformation. Fig. 1 shows UV and CD spectra of polyisocyanide derived from L-phenylalanine in 1,2-dichloropropane. Broad absorption bands in a >300 nm region were assigned to $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transitions of the main chain conjugated with C=N groups. Judging from their low ϵ values, these absorption bands around over 400 nm region may be assigned to the $n\text{-}\pi^*$ transition of the conjugated C=N groups.⁹ When the 1,2-dichloropropane solution was kept at 70 °C for 3 hours, the magnitude of the circular dichroism was decreased gradually down to 30 % of the original value. When the solution temperature was cooled down to room temperature, the decreased value of circular dichroism was recovered to the original value for 0.5 h. In UV-vis spectrum, the absorbance was increased over whole the UV-vis spectrum and the absorption edge around 750 nm was extended to a longer wavelength region up to 850 nm. Simultaneously, the UV-vis absorption spectrum was also reversibly changed as a function of the

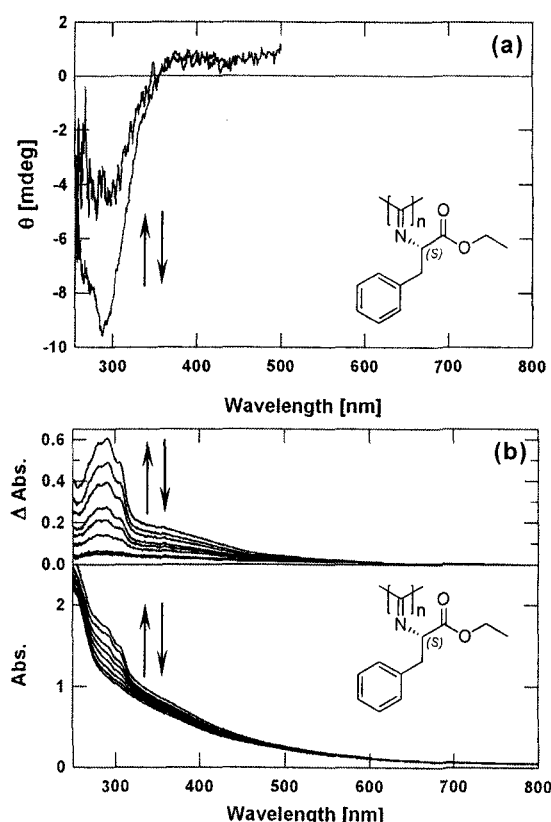


Figure 1 (a) CD, (b) UV and Δ UV spectral change of polyisocyanide derived from L-phenylalanine in 1,2-dichloropropane at 70 °C.

solution temperature. These reversible spectral changes suggest some conformational changes in the helical main chain induced by the thermal fluctuation of the side chain movements. However, it is still difficult to draw real pictures of the helical conformation from the decreasing magnitude of the circular dichroism. In this paper, we try to investigate the helical conformational changes as the result of the increasing and decreasing magnitude of the circular dichroism by the simulation of the UV-vis absorption spectra, so as to illustrate a picture representing how the helix changes. In order to understand UV-vis spectra of polyisocyanide, the dimer models based on two conjugated double bonds were introduced, *i.e.* butane-2,3-dione, and butane-2,3-diimine. The electronic structures of these dimers can be regarded as the minimal π -conjugated system with various dihedral angles, reflecting in the intrinsic electronic structures of polyisocyanides. These spectral considerations, although the simplest model was assumed, would help to understand the complicated spectral change of polyisocyanide.

2. COMPUTATIONAL METHODS

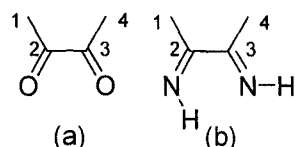
The optimized geometry was performed under the fixed dihedral angles of the π -conjugated system by both semi-empirical quantum AM1 method and Hartree-Fock (HF) with the 6-31G* basis set. Configuration Interaction (CI) was

performed to obtain an electronic absorption spectrum by semi-empirical ZINDO/S method. Semi-empirical calculation was provided with the HyperChem molecular modeling package (version 7.5).¹⁰ The *ab initio* calculation was provided in the Gaussian03 (Gaussian Inc.).¹¹

3. RESULT AND DISCUSSION

Butane-2,3-dione and butane-2,3-diimine were introduced as the model compounds of the polyisocyanide. Both compounds have two adjacent double bonds at 2- and 3-positions. Spectroscopic and theoretical study of such model compounds should be helpful to understand the electronic structure and transition of the concerned polymer. Butane-2,3-diimine has been considered as the minimal model of polyisocyanides so far since Salvadori et al. analyzed the conformation.^{4(c)} They reported that the main chain conformation of polyisocyanide can be equivalently described by the dihedral angle of $N=C-C=N$ (angle ϕ). Actually, because of the twisted main chain, it is easily accepted from the result of the semi-empirical MO calculation of an imine decamer methylated at both ends, $Me(-C=NH-)_{10}-Me$, that the delocalization of π conjugated system along the main chain is limited over at most 4 repeated units. Therefore, the dimer or trimer model would be enough to describe the behavior of the electronic spectrum of polyisocyanide under the first approximation. Butane-2,3-dione has an analogous electronic structure of butane-2,3-diimine including n orbitals. Additionally, the electronic structures of a series of vicinal oligoketones consisting of consecutive $C=O$ units bearing the n orbitals can be regarded as the similar electronic structures of polyisocyanide consisting of $C=N$ units. There have been several reports on the relationship between the conformation and the UV spectrum of vicinal oligoketones.¹² Their conformations can be described by the dihedral angle between the adjacent carbonyl units. Along this line, we are discussing the conformation-dependent electronic structures of the model compounds.

At first, geometry optimizations of the models were carried by the semi-empirical AM1 method under controlled dihedral angles of the adjacent double bonds. Geometry optimized by both semi-empirical (AM1) and *ab initio* (HF/ 6-31G*) methods gave a consistent molecular structure. Figure 2 shows the Walsh diagrams of the models. In case of butane-2,3-dione and butane-2,3-diimine, HOMO is n orbital resulting from lone pair electrons of nitrogen or oxygen. The n orbital is localized on O or N atom, respectively. Therefore, energy level of the n orbital is scarcely affected by the angle ϕ . LUMO has bonding character over two inner carbons at 2- and 3- positions and two nodes in the middle of two double bonds, $C=O$ or $C=N$ units. As the dihedral angle approaches to 90 ° from 180 ° or 0 °, the bonding orbital is torn up, so that the LUMO level becomes unstable.



Scheme 1 Structure of the model compounds. (a) butane-2,3-dione and (b) butane-2,3-diimine.

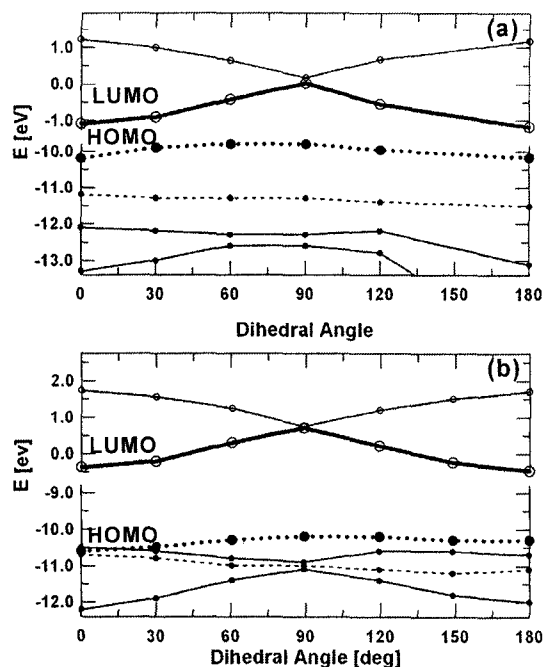


Figure 2 Walsh plots Calculated by ZINDO/S of (a) butane-2,3-dione and (b) butane-2,3-diimine. HOMO, HOMO -1, -2 and -3 were showed as the closed circle, and LUMO and LUMO +1 were showed as the open circle, respectively. The π and π^* orbital energy levels were linked by the solid line and n orbital energy levels were linked by the dotted line.

Configuration Interaction (CI) of the model compounds was performed by ZINDO/S method, followed by the geometry optimization. Space of CI was set to 10 (occupied) and 10 (unoccupied) orbitals. In case of butane-2,3-dione, consistent results with the spectral change depending on the dihedral angle ϕ were obtained. As the angle decreases to 0° , the $n-\pi^*$ transition energy was shifted to a longer wavelength region from 397 nm to 526 nm. As the angle increases from 90° to 180° , the transition energy was also red-shifted from 397 nm to 497 nm. Because the energy of the $n-\pi^*$ transition from HOMO to LUMO became smaller in either increasing or decreasing angles. As a whole of UV-vis spectrum, the absorption edge shifted to a longer wavelength region as the angle becomes apart from 90° . In the case of the butane-2,3-diimine, the similar transition shifts depending on the dihedral angle were obtained in the simulation of UV spectra. The HOMO-LUMO transition, characterized by $n-\pi^*$ transition, was red-shifted as the angle went away from 90° . The $n-\pi^*$ transition of butane-2,3-diimine shifted from 288 nm to 327 nm at 0° and to 334 nm at 180° .

Maurer and co-workers reported the UV-vis

spectra of a series of *vicinal* oligoketone, *i.e.* *tert*-butyl capped monoketone, diketone, triketone, and tetraketone.^{12(c)} These spectra showed that the number of the absorption band increased with increasing the number of the carbonyl group and that the absorption edge was red-shifted up to 650 nm region, in which the tetraketone shows the absorption bands. However, these linear ketones have several conformers with various dihedral angles of $O=C-C=O$. So it could not show the real tendency of the UV-vis spectrum to the conformation. Leonard and co-workers found that the dihedral angle and absorption edge are strongly correlated by comparing UV-vis spectra of several cyclic vicinal diketones.^{12(a)} The dihedral angle, fixed by the cyclic structure with bulky dimethyl groups at both α -carbons, spans from 0° to 150° , depending on the number of cycle member. The dihedral angles of the cyclic diketones were determined by semi-empirical MO calculations (AM1). The wavelength of the observed absorption edges are plotted against the obtained dihedral angle. (Figure 3, solid circle) The relationship indicates the $n-\pi^*$ transition moves toward shorter wavelength as the angle increases from 0° to about 90° and shifts back again toward longer wavelength as the angle increases beyond 90° . It should be noticed here that this tendency is consistent with our AM1 MO calculation result of butane-2,3-dione and butane-2,3-diimine models. On the other hand, Hoffman and co-workers estimated about 65° of the dihedral angle of $N=C-C=N$ in the most stable helical conformation of polyisocyanide bearing bulky side chain by using extended Hückel calculation.^{4(a)} This conformation takes 4_1 helix. If the 4_1 helix is accepted as the conformation of the as-prepared polyisocyanide, the reversible UV spectral changes observed in our thermal

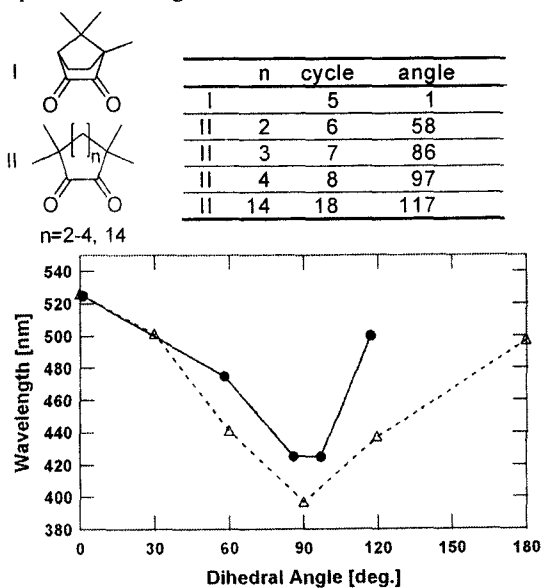


Figure 3 Wavelength vs dihedral angle of cyclic α -diketone. (solid line) and calculated wavelength of $n-\pi^*$ transition of butane-2,3-dione by ZINDO/S (dotted line).

treatment could be explained as follows. The red-shift of the absorption edge observed by thermal treatment of L-phenylalanine-derived polyisocyanide indicated some contribution of conformational change with decreasing dihedral angle, although we should accept non-uniform dihedral angle along the main chain. As a more real picture, the decreasing dihedral angle means that the main chain helix becomes looser, approaching to 5_1 or 6_1 helix, *i.e.*, the diameter of the helix being expanded.

4. CONCLUSION

The conformational study of helical polymers is often complicated for many factors. We should compare only about difference in conformation itself. Fortunately, CD magnitude of L-phenylalanine-based polyisocyanides could be changed reversibly by heating and cooling the solution, reflecting different helical conformations. It is concluded that the different magnitude of circular dichroism and UV-vis spectral change of the polyisocyanide should arise from only the difference of the conformation. At high solution temperature, the absorbance over the whole spectrum increased and absorption edge shifted to longer wavelength region. Based on the UV-vis spectrum of *vic*-oligoketone compounds and semi-empirical MO calculation of butane-2,3-diketone and butane-2,3-diimine as the model, the temperature-dependent CD changes indicate the contribution of the decreasing the dihedral angle. Although it is necessary to clarify how the polymer changes in order to illustrate more concrete conformation, the L-phenylalanine-based polyisocyanide with temperature-dependent conformation will provide important information to understand experimentally the relationship between the helical conformation and UV-vis spectrum depending on the electronic structure along the helical main chain. UV-vis spectral change could be additional tool for conformation-dependent electronic structures of such conjugated helical polymers.

5. REFERENCES

- [1] Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada, H. Yuki, *J. Am. Chem. Soc.* **101**, 4763-4765 (1979); R. J. M. Nolte, A. J. M. van Beijnen, W. Drenth, *J. Am. Chem. Soc.* **110**, 6818-6825 (1988); Y. Ito, E. Ihara, Y. Murakami, M. Sisido, *Macromolecules*, **25**, 6810-6813 (1992); M. Fujiki, *J. Am. Chem. Soc.* **116**, 11976-11981 (1994).
- [2] E. Yashima, J. Noguchi, Y. Okamoto, *Macromolecules*, **28**, 8368-8374 (1995); S. R. Lustig, G. J. Everlof, G. D. Jaycox, *Macromolecules*, **34**, 2364-2372 (2001); Y. Okamoto, S. Honda, I. Okamoto, H. Yuki, *J. Am. Chem. Soc.* **103**, 697-6973 (1981).
- [3] M. M. Green, C. Andreola, B. Munoz, M. P. Reidy, K. Zero, *J. Am. Chem. Soc.* **110**, 4063-4065 (1988).
- [4] (a) C. Kollmar, R. Hoffmann, *J. Am. Chem. Soc.*, **112**, 8320-8328 (1990). (b) C. J. M. Huige, A. M. F. Hezemans, R. J. M. Nolte, W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **112**, 33 (1992). (c) M. Clericuzio, G. Alagona, C. Ghio and P. Salvadori, *J. Am. Chem. Soc.* **119**, 1059-1071 (1997).
- [5] M. M. Green, R. A. Gross, F. C. Schilling, K. Zero, C. Crosby, III, *Macromolecules* **21**, 1839-1846 (1988); J. -T. Huang, J. Sun, W. B. Euler, *J. Polym. Sci., Part A: Polym. Chem.* **35**, 439-446 (1997).
- [6] A. Teramoto, K. Terao, Y. Terao, N. Nakamura, T. Sato, M. Fujiki, *J. Am. Chem. Soc.* **123**, 12303-12310 (2001).
- [7] K. Furukawa, Ebata, K.; Fujiki, M. *Adv. Mater.* **12**, 1033-1036, (2000); Nishimura, T.; Takatani, K.; Sakurai, S.; Maeda, K.; Yashima, E. *Angew Chem Int Ed*, **41**, 3602-3604 (2002); Li, B. S.; Cheuk, K. K. L.; Ling, L.; Chen, J.; Xiao, X.; Bai, C.; Tang, B. Z. *Macromolecules* **36**, 77-85 (2003); Kiriy, N.; Ja'hne, E.; Adler, H.-J.; Schneider, M.; Kiriy, A.; Gorodyska, G.; Minko, S.; Jehnichen, D.; Simon, P.; Fokin, A. A.; Stamm, M. *Nano Lett.* **3**, 707-712 (2003); Li, B. S.; Cheuk, K. K. L.; Yang, D.; Lam, J. W. Y.; Wan, L. J.; Bai, C.; Tang, B. Z. *Macromolecules*, **36**, 5447-5450 (2003); S. Sakurai; K. Kuroyanagi; K. Morino; M. Kunitake; E. Yashima, *Macromolecules*, **36**, 9670-9674 (2003).
- [8] Y. Yamada, T. Kawai, J. Abe, T. Iyoda, *J. Poly. Sci. Part A: Polym. Chem.* **40**, 399-408 (2002)
- [9] R. J. M. Nolte, *Chem. Soc. Rev.* **23**, 11-19 (1994).
- [10] HyperChem v.7.5 is available from HyperCube Inc., 1115 N. W. 4th Street, Gainesville, FL, 32601.
- [11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria; M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven; K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi; V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega; G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota; R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao; H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross; C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev; A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala; K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg; V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain; O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari; J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford; J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz; I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham; C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill; B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople; Gaussian, Inc., Wallingford CT, 2004.
- [12] (a) N. J. Leonard and P. M. Mader, *J. Am. Chem. Soc.* **72**, 5388-5397 (1950). (b) C. Sandris and G. Ourisson, *Bull. Chim. Soc. France*, **25**, 350 (1958). (c) L. Horner and F. Maurer, *Chem. Ber.* **101**, 1783-1798 (1968).

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