Macromolecules

Volume 41, Number 18 September 23, 2008

Communications to the Editor

Optically Active Poly(phenylacetylene) Film: Chirality Inversion Induced by Solvent Vapor and Heating

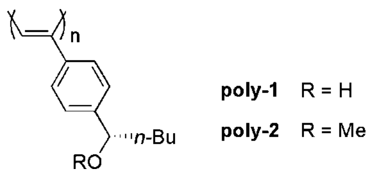
Toshiyuki Fukushima, Kiyohiro Takachi, and Kenji Tsuchihara*

Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba 305-8565, Japan

Received July 3, 2008
Revised Manuscript Received August 14, 2008

Synthetic helical polymers have been studied aiming at the application to asymmetric catalysts or chiral recognition materials including chiral stationary phase for HPLC and enantioselective separation membrane.[1] Chirality control of helical polymer by external stimuli is considered to be important because of the potentiality for controlling the enantioselectivities. Monosubstituted *cis*-poly(acetylene) derivatives prepared with Rh catalyst are one of the most studied helical π-conjugated polymers. Their dynamic helical structure in solution can be controlled by temperature and solvent.[2] However, the chiroptical studies of *cis*-poly(acetylene)s in the solid state are still limited. Percec et al. reported that thermal reduction of ellipticity of helical *cis*-poly(phenylacetylene) films.[3] Yashima et al. visualized by AFM irreversible helical inversion of *cis*-poly(phenylacetylene) bundle which was self-assembled on highly oriented pyrolytic graphite (HOPG) by exposing to specific organic solvent vapor for several hours.[4] We previously reported that color-changeable *cis*-poly(phenylacetylene) film having alkoxyl and chiral OH group at the para position and succeeded to control a sign of the novel Cotton effect which appeared with the color change from yellow to red by exposing to organic solvent vapor and/or by heating, though a sign of the original Cotton effect remained.[5] Hence, aiming to the complete and reversible chirality inverstion, we synthesized a novel optically active poly(phenylacetylene) (**poly-1** in Scheme 1) having alkyl and chiral OH group which should form hydrogen bond to affect the helical structure. Furthermore, **poly-2** which has no OH group was also prepared to study hydrogen bond effect of **poly-1** on helical conformation. Here we demonstrate with circular dichroism (CD) spectroscopy the rapid, repeatable, and reversible chirality inversion of **poly-1** thin film by using the simple methods, namely, by exposing to organic solvent vapor and/or by heating.

Scheme 1. Chemical Structures of Optically Active Poly(Phenylacetylene)s Having a Hydroxy Group (poly-1) and a Methoxy Group (poly-2)



Monomers were prepared according to the literature.[6,7] Polymerization was conducted with the [Rh(norbornadiene)-Cl]$_2$−Et$_3$N catalyst system to afford yellow polymers (**poly-1** and **poly-2**) which had *all-cis* main-chain structure. **Poly-1** was soluble in various organic solvents including acetone, ethyl acetate, CHCl$_3$, Et$_3$N, Et$_2$NH, and MeOH and insoluble in hexane and toluene. **Poly-2** was soluble in ethyl acetate, CHCl$_3$, Et$_3$N, Et$_2$NH, and hexane and insoluble in acetone and MeOH. Polymers in CHCl$_3$ and Et$_2$NH solution ($c = 0.25$ mM) at 20 °C showed intense split-type CD spectra in the conjugated backbone region, which suggested that the polymer main chain takes a helical conformation with an excess of one-handedness.[2] The CD pattern of **poly-1** with an OH group measured in CHCl$_3$ was almost a mirror image of that in Et$_2$NH, indicating that these helicities were opposite handedness to each other. In the case of **poly-2** without an OH group, CD patterns measured in both CHCl$_3$ and Et$_2$NH were same as that of **poly-1** in Et$_2$NH. These results suggested that helicity inversion on backbone was induced by change of interaction between the OH group in the side chain and solvent.

A thin film was made by spin-casting from 4 wt % Et$_2$NH solution of polymers onto a 15 × 15 mm glass substrate at 1000 rpm for 5 s and then 2000 rpm for 5 s. The resulting pale yellow film was amorphous, nondeposit, and transparent, so that CD measurement of the film was reproducible.[8] As shown in Figure 1, **poly-1** film had a very similar CD spectrum to those in the corresponding Et$_2$NH solution, indicating that the helical

---

* Corresponding author. E-mail: k-tsuchihara@aist.go.jp.

10.1021/ma8014849 CCC: $40.75

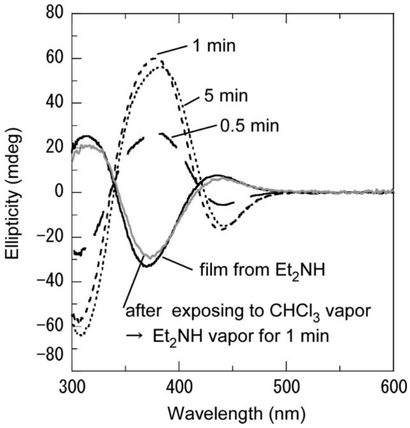


Figure 1. CD spectra of **poly-1** spin-cast film from 4 wt % Et$_2$NH solution before and after exposing to CHCl$_3$ vapor for 0.5, 1, and 5 min and further exposing to Et$_2$NH vapor for 1 min at ordinary pressure and temperature. Spectra were measured at 20 °C. The film was completely dried under reduced pressure before measurement.

conformation in the film was basically the same as that in its casting solution. The CD spectrum in the film was unchanged for at least 3 months. When the film was exposed to CHCl$_3$ vapor at ordinary temperature and pressure for prescribed periods and removed from CHCl$_3$ vapor, CD spectral change was observed. The sign of Cottons was inversed within 30 s of contacting time, and the intensity gradually increased before saturation within 1 min. The CD spectrum was similar after the film was dried under reduced pressure for several hours, indicating that once helix inversion occurred, helix sense remained even after the removal of solvent vapor. The CD spectrum was also inversed by using acetone or ethyl acetate vapor. Toluene, which did not dissolve **poly-1**, was also effective for chirality inversion by solvent vapor, though it took 3 h (Figure 2A). When the film prepared from Et$_2$NH was immersed in toluene for 2 h and was dried under reduced pressure for several hours, CD inversion was also observed though the absorption spectrum was unchanged (Figure 2B). Hence, chirality inversion occurred even by a poor solvent. On the other hand, when hexane whose interaction with **poly-1** is weaker than toluene was used, the CD spectrum remained constant. When this CD inversed film was contacted with a highly polar solvent such as MeOH, Et$_3$N, and Et$_2$NH vapor again for 1 min, the CD spectrum was fully inversed again. This phenomenon was repeatedly observed by using an appropriate set of solvent vapor alternately. The CD inversion was probably due to helicity inversion of polymer backbone as a similar phenomenon observed in solution.[2] This assumption was also supported by the AFM visualized helical inversion of poly(phenylacetylene) molecule by solvent vapor.[4a] These CD inversion phenomena were not observed in **poly-2** film which had no chiral OH group. These results suggested that the chiralty inversion of **poly-1** film should be induced by the change of interaction between polar solvent and chiral OH group in the side chain. However, the intra- and intermolecular hydrogen-bonding effect is still unclear at present because the broad OH stretching vibration around 3500 cm^{-1} by IR measurement was constant irrespective of film chirality. It should be noted that the CD inversion in this film was reversible and relatively rapid than the helicity inversion of poly(phenylacetylene) on HOPG which is irreversible and takes for several hours.[4b] These are probably due to the fact that in our case both polymer and substrate were amorphous during the whole process, which was confirmed by WAXRD.

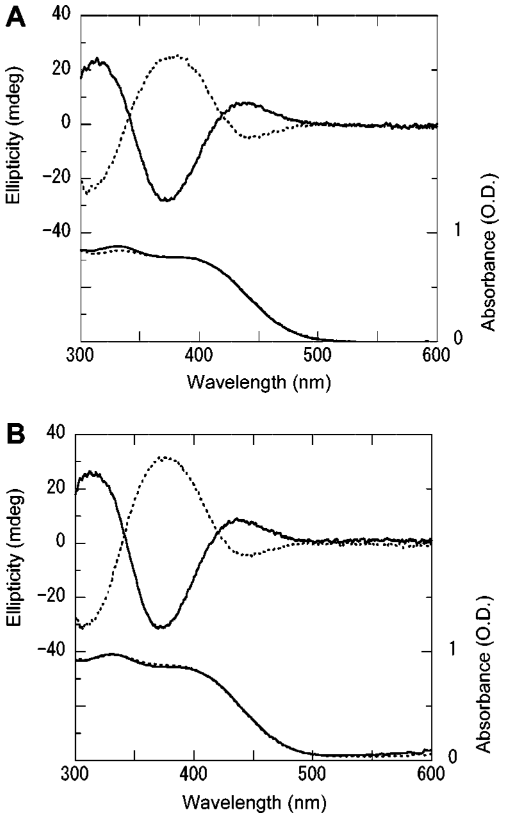


Figure 2. CD (top, left axis) and absorption (bottom, right axis) spectra of **poly-1** spin-cast film from 4 wt % Et$_2$NH solution (A) before (line) and after exposing to toluene vapor for 3 h at room temperature (dot) and (B) before (line) and after immersion in toluene for 2 h at room temperature (dot). The film was completely dried under reduced pressure before measurement. Spectra were measured at 20 °C.

Thermal helix inversion in the solid thin film has been investigated in some helical polymers like poly(L-aspartic acid ester)s,[9] poly(thiophene)s,[10] poly(isocyanate)s,[11] and poly(silane)s.[12] However, chirality inversion of poly(acetylene)s in the solid by heating has never been reported. CD spectral change of **poly-1** film prepared from 4 wt % Et$_2$NH solution was examined (Figure 3). The CD spectrum at 110 °C was fully opposite to those at 20 °C, and the resulting CD spectrum was unchanged upon cooling to 20 °C. This thermal chirality inversion was irreversible; namely, chirality inversion once occurred, it was constant irrespective of temperature. This is in marked contrast to other helical polymers in the film state[9−11] and to helical poly(acetylene)s in solution[2] in which chirality change is reversible corresponding to temperature. CD change of **poly-1** film at 110 °C was finished within 5 min. It is noteworthy that this phenomenon carried out rapidly even in the solid state. If this **poly-1** film was further exposed to Et$_2$NH vapor for 1 min, the CD spectrum was inversed. During this short heating process only negligible thermal decomposition occurred, though *all-cis* poly(phenylacetylene)s[3] have not so high thermal stability. This was also supported by unchanged absorption spectra on heating process. Neither crystallization nor cis−trans isomerization took place during the heating process, which were confirmed by WAXRD and by laser Raman spectroscopy.[13] Only a broad exothermic peak around 100 °C, whose enthalpy change (ΔH = 1.14 J/g) was relatively small, was observed on the first heating process in differential scanning calorimetry measurement of **poly-1** film prepared from Et$_2$NH solution, while other helicity changeable polymers like poly(L-aspartic acid ester)s[9] and poly(silane)s[12] exhibited an endothermic peak at the helix−helix transition temperature on heating

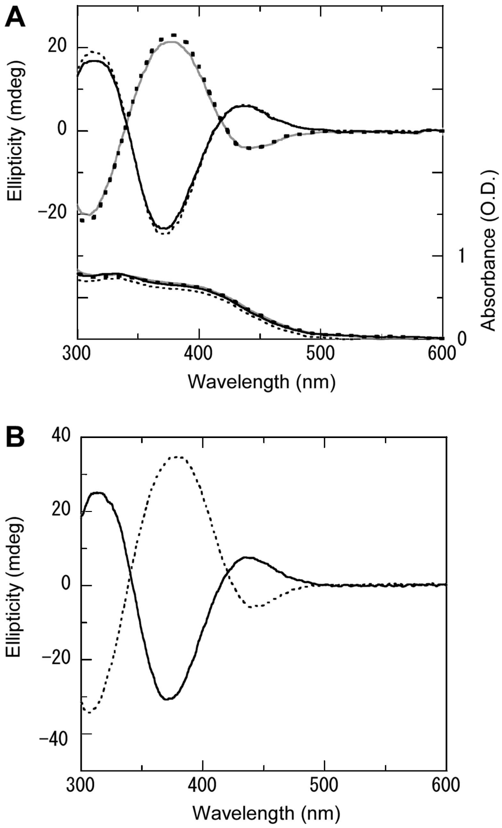


Figure 3. (A) CD (top, left axis) and absorption (bottom, right axis) spectra of the **poly-1** spin-cast film from 4 wt % Et$_2$NH solution measured at 20 °C (dash), 110 °C (gray line), and cooling from 110 to 20 °C (dot) and further exposing to Et$_2$NH vapor (black line) for 1 min at ordinary pressure and temperature. The film after exposing to solvent vapor for the measurement was completely dried under reduced pressure for several hours. (B) CD spectra of the **poly-1** spin-cast film from 4 wt % Et$_2$NH solution before (line) and after heating at 110 °C for 1 min (dash). Spectra were measured at 20 °C.

process. The reason for this difference is not clear at present, but one possibility is as follows: unlike other helicity changeable polymers, in **poly-1** film, the helical state which is induced by polar solvent and shows negative Cotton around 375 nm is only quasi-stable. If mobility of the polymer molecule is enhanced by heating without polar solvent, helical inversion to thermally stable state, which shows positive Cotton around 375 nm, takes place by self-organization.

In summary, reversible and repeatable chirality inversion of optically active *cis*-poly(phenylacetylene) film could be achieved by exposing to appropriate organic solvent vapor for several minutes. Thermal chirality inversion of the film prepared from polar solvent was also achieved by heating. It is noteworthy that all of the chirality inversion can be completed rapidly, within several minutes, even in the solid state probably because the film is amorphous and the polymer molecule has high mobility. The resulting film chirality was kept for at least 3 months even after the removal of these external stimuli. The current study therefore presented that chirality of poly(phenylacetylene) thin film is successfully controlled rapidly by simple methods.

Supporting Information Available: Experimental procedures for synthesis and analytical data of polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893. (b) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013. (c) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039. (d) Fujiki, M. *Macromol. Rapid Commun.* **2001**, *22*, 539. (e) Hoeben, F. J. M.; Pascal Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491. (f) Lam, J. W. Y.; Tang, B.-Z. *Acc. Chem. Res.* **2005**, *38*, 745. (g) Masuda, T. *J. Mol. Catal. A* **2002**, *190*, 197. (h) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.—Eur. J.* **2004**, *10*, 42.

(2) (a) Hasegawa, T.; Morino, K.; Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E. *Macromolecules* **2006**, *39*, 482. (b) Yashima, E.; Maeda, K.; Okamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 8159. (c) Nakako, H.; Nomura, R.; Masuda, T. *Macromolecules* **2001**, *34*, 1496. (d) Sanda, F.; Nishimura, S.; Shiotsuki, M.; Masuda, T. *Macromolecules* **2005**, *38*, 3075. (e) Cheuk, K. L.; Lam, J. W. Y.; Chen, J.; Lai, L. M.; Tang, B.-Z. *Macromolecules* **2003**, *36*, 5947. (f) Cheuk, K. K. L.; Lam, J. W. Y.; Lai, L. M.; Dong, Y.; Tang, B.-Z. *Macromolecules* **2003**, *36*, 9752. (g) Schenning, A. P. H. J.; Fransen, M.; Meijer, E. W. *Macromol. Rapid Commun.* **2002**, *23*, 265. (h) Teraguchi, M.; Mottate, K.; Kim, S.-Y.; Toshiki Aoki, T.; Kaneko, T.; Hadano, S.; Toshio Masuda, T. *Macromolecules* **2005**, *38*, 6367.

(3) (a) Percec, V.; Rudick, J. G.; Aqad, E. *Macromolecules* **2005**, *38*, 7205. (b) Percec, V.; Rudick, J. G.; Peterca, M.; Wagner, M.; Obata, M.; Mitchell, C. M.; Cho, W.-D.; Balagurusamy, V. S. K.; Heiney, P. A. *J. Am. Chem. Soc.* **2005**, *127*, 15257.

(4) (a) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1245. (b) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *12*, 5650. (c) Okoshi, K.; Sakurai, S.-i.; Ohsawa, S.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 8173.

(5) Fukushima, T.; Takachi, K.; Tsuchihara, K. *Macromolecules* **2006**, *39*, 3103.

(6) (a) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627. (b) Bergen, M.; Gais, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 4321.

(7) (a) Furlani, A.; Napoletano, C.; Russo, M. V.; Feast, W. *Polym. Bull.* **1986**, *16*, 311. (b) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *22*, 1105.

(8) The exact CD spectrum of a macroscopically anisotropic film is difficult to obtain because the apparent CD often accompanies a contribution from the linear dichroism signal. We used only homogeneous and transparent films to get the exact CD spectrum and checked that the apparent CD spectrum was not affected by the rotation angle and by the side of the sample.

(9) (a) Watanabe, J.; Okamoto, S.; Satoh, K.; Sakajiri, K.; Furuya, H.; Abe, A. *Macromolecules* **1996**, *29*, 7084. (b) Sakajiri, K.; Satoh, K.; Kawauchi, S.; Watanabe, J. *J. Mol. Struct.* **1999**, *476*, 1.

(10) Bouman, M. M.; Meijer, E. W. *Adv. Mater.* **1995**, *7*, 385.

(11) Cheon, K. S.; Selinger, J. V.; Green, M. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1482.

(12) (a) Ohira, A.; Okoshi, K.; Fujiki, M.; Kunitake, M.; Naito, M.; Hagihara, T. *Adv. Mater.* **2004**, *16*, 1645. (b) Ohira, A.; Kunitake, M.; Fujiki, M.; Naito, M.; Saxena, A. *Chem. Mater.* **2004**, *16*, 3919. (c) Kim, S.-Y.; Fujiki, M.; Ohira, A.; Kwak, G.; Kawakami, X. *Macromolecules* **2004**, *37*, 4321.

(13) Tabata, M.; Tanaka, Y.; Sadahiro, Y.; Sone, T.; Yokota, K.; Miura, I. *Macromolecules* **1997**, *30*, 5200.

MA8014849