Macromolecules **2002,** *35,* 941−944 **941**

Chiroptical Properties of Poly{3,4-bis[(*S*)-2-methyloctyl]thiophene}

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Received February 23, 2001; Revised Manuscript Received October 1, 2001

ABSTRACT: The circular dichroism (CD) of a polythiophene in the molecularly dispersed state was observed for the first time. The polythiophene possesses two chiral alkyl side chains (poly{3,4-bis[(*S*)-2-methyloctyl]thiophene}, PDMOT). The chiroptical properties of this polymer in solution, aggregate, and thin solid film states were investigated. A chirally distorted main-chain conformation in a single molecule of PDMOT accounts for the observed CD spectra in solution and could also be considered as a novel chiral motif in an optically active polymer, besides the highly ordered, intramolecular helical structure and the chiral superstructure resulting from intermolecular $\pi-\pi$ stacking. Significant temperature and solvent effects on the CD were also observed in the spectra.

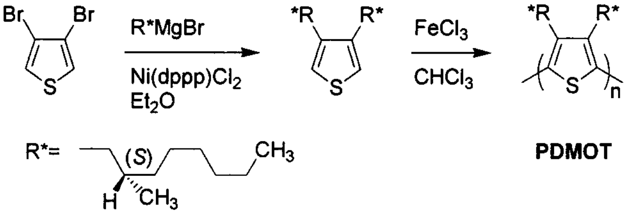
Introduction

Optically active π-conjugated polymers have received much interest due to their potential application in circularly polarized luminescent and enantiosensor materials.[1] The polythiophenes, as important members of the conjugated polymer family, have been extensively investigated, including those bearing chiral monoalkyl and dialkoxy moieties.[2] However, circular dichroism (CD) in the $\pi-\pi^*$ transition region has been observed only when the polymer is in aggregated and solid film states, due to chiral supramacromolecular ordering resulting from intermolecular $\pi-\pi$ stacking. Recently, Yashima et al. reported the induced circular dichroism (ICD) in the visible region of regioregular poly[(*R*)-3-(4-ethyl-2-oxazolin-2-yl)phenylthiophene] in a good solvent by adding metal ions, in which the induced chirality was assumed to be derived from a predominantly one-handed helical main-chain structure.[3] To further investigate the chiroptical property−structure relationship in various polythiophenes, we synthesized the first dialkyl-substituted chiral polythiophene, poly{3,4-bis[(*S*)-2-methyloctyl]thiophene} (PDMOT). In this paper, we report its unique CD spectra in the near-UV region in solution, aggregate, and solid film states, which showed remarkable temperature and solvent effects. Since this is the first observation of CD in the molecularly dispersed state of a polythiophene, this result could lead to new concepts structure in a polymer.

Experimental Section

Measurements. Molecular weights were estimated by size exclusion chromatography (SEC) on a Shodex KF806M column (eluent THF, 30 °C) using a Shimadzu liquid chromatograph equipped with a photodiode array detector and calibrated using polystyrene standards. Variable temperature CD and simultaneous UV−vis spectra were recorded using a JASCO J-725 spectropolarimeter with a Peltier controller for temperatures from 80 to −10 °C (1 cm path length cell; sample concentration $= 1.0 \times 10^{-4}$ mol/L of the thiophene repeating units). The variable temperature solid CD spectra were recorded on the same spectropolarimeter using a Mettler Toledo FP 82 HT hot stage at temperatures ranging from 25 to 145 °C. Intrinsic viscosity as a function of molecular weight was determined at the Toray Research Center (Shiga, Japan) using a Waters 1500 SEC apparatus with a Viscotec H502a viscometer. NMR spectra were recorded on a Varian Unity 300 spectrometer relative to tetramethylsilane as internal standard in CDCl$_3$.

Scheme 1. Synthesis of PDMOT



Preparation of Monomer and Polymer. The preparation of PDMOT is shown in Scheme 1. The monomer (DMOT) was prepared by coupling 17.0 g (0.07 mol) of 3,4-dibromothiophene with (*S*)-2-methyloctylmagnesium bromide (0.145 mol in 150 mL of diethyl ether solution) in the presence of Ni(dppp)Cl$_2$ ([1,2-bis(diphenylphosphino)propane]dichloronickel(II)).[4] (*S*)-2-Methyloctyl bromide was synthesized by the Chemical Soft Co. (Kyoto, Japan) by bromination of (*S*)-2-methyl-1-octanol (Japan Energy, Tokyo, Japan, $[\alpha]_D^{25} = -9.6°$ (neat), ≥89% e.e. (noted *in Chiral Reagents* 1600, p 213)) and was used directly without further purification. Yield of DMOT was 5 g (21%); bp 160−165 °C/0.8 mmHg; $[\alpha]_D^{25} = 5.8°$ (neat). ^{13}C NMR (CDCl$_3$, ppm): 14.12, 19.76, 22.71, 27.19, 29.62, 31.96, 33.58, 36.57, 37.14, 120.83, and 141.01. The ferric chloride oxidation method was used to synthesize PDMOT based on the reported procedure[5] with a yield of 60%. PDMOT is readily soluble in organic solvents such as hexane, isooctane, toluene, THF, and chloroform but is only sparingly soluble in *N,N*-dimethylformamide (DMF), cold 1-octanol, and methanol. ^{13}C NMR (CDCl$_3$, ppm): 14.05, 19.69, 22.73, 27.19, 29.75, 31.97, 33.90, 36.50, 37.27, 130.89, and 140.52. The weight-average molecular weight (M_w) was 31 600, and the polydispersity index (M_w/M_n) was 2.8.

Results and Discussion

Compared to the monoalkyl-substituted polythiophenes,[2,6] PDMOT absorbs at a shorter wavelength (λ_{max} = 318 nm in chloroform) in the UV−vis spectra, due to the steric demands of the two alkyl side chains. On the other hand, compared to the dialkoxy-substituted polythiophenes,[2,6] the blue shift of the λ_{max} of PDMOT may be due to the electronic effects of the weaker electron-

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10.1021/ma010330j CCC: $22.00

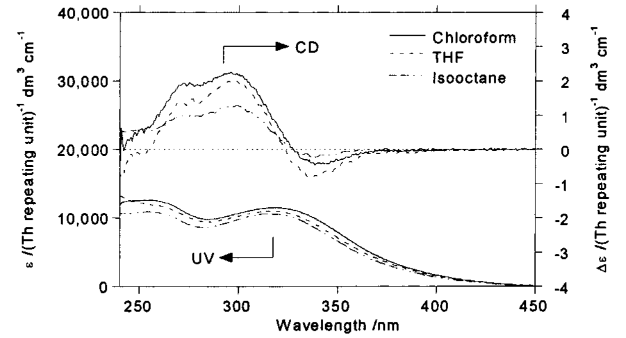

Figure 1. UV−vis and CD spectra of PDMOT ($M_w = 31\,600$, $M_w/M_n = 2.8$) in three good solvents at 21 °C.

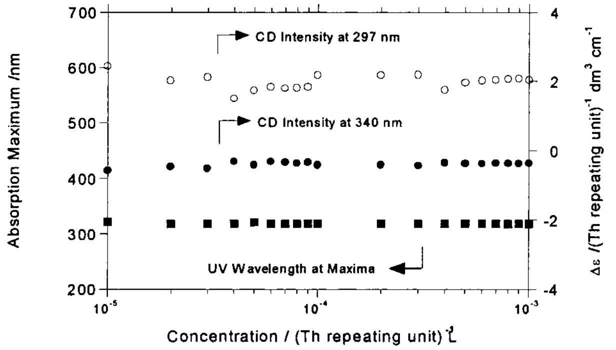

Figure 2. Concentration dependent UV−vis and CD spectral analyses of PDMOT in chloroform at 21 °C.

donating alkyl side chains. Significantly, CD signals were clearly observed in good solvents, such as chloroform, THF, and isooctane (Figure 1), and constitute the first observation of CD in a molecularly dispersed polythiophene. A positive Cotton effect appeared at shorter wavelengths around 272 and 297 nm, and a negative Cotton effect appeared at longer wavelength around 340 nm. Apparently, this bisignate Cotton effect has a different origin from either the effects resulting from chiral aggregation[2] or the single-sign Cotton effect due to a one-handed helical polysilane structure.[7] To elucidate the origin of the observed Cotton effect in the near-UV region, the polymer concentration dependence of the CD signal was measured in chloroform (Figure 2). The results showed that the CD profiles, including absolute magnitude and sign direction, are independent of the polymer concentration over the broad range from 10^{-5} to 10^{-3} mol/L of the thiophene repeating units, indicating that the contribution of the interchain interaction to the observed Cotton effect is minimal for PDMOT in chloroform, even though the distance between the polymer chains is shortened by the increase in concentration. A chiral structure incorporated in each individual polymer chain appears to be responsible for the unsymmetric bisignate CD signals and thus affording the first polythiophene optically active in the molecularly dispersed state.

To further confirm this idea, the solvent effect on the optical properties of PDMOT was measured. For this purpose, we used 1-octanol as a poor solvent, which may lead to the formation of aggregates at lower temperatures. Initially, PDMOT completely dissolved on gentle heating to give a transparent yellow solution. Variable temperature CD and UV−vis spectra during the cooling run are shown in Figure 3. Remarkable thermo-driven changes in the CD spectra were clearly observed. At lower temperatures (0−20 °C), the bisignate Cotton effect was evident, but at higher temperature (80 °C), a positive-sign CD signal similar to that in chloroform was obtained, while no obvious change in the UV−vis spectra was evident. Similarly, a significant change in the CD spectra was observed in the cosolvent system consisting of chloroform and DMF (a poor solvent) (Figure 4). Clearly, with the increase of the DMF content, the absolute magnitude of the original CD signals at 272 and 297 nm gradually decreased, and the sign at 290 nm changed from positive to negative when the content of DMF reached 90%, while minimal change in the UV−vis spectra was observed.

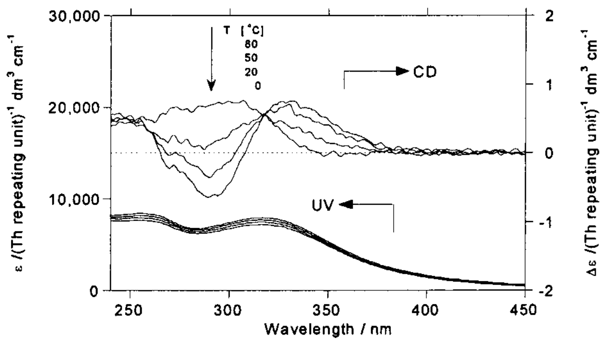

Figure 3. Variable temperature UV−vis and CD spectra of PDMOT in 1-octanol.

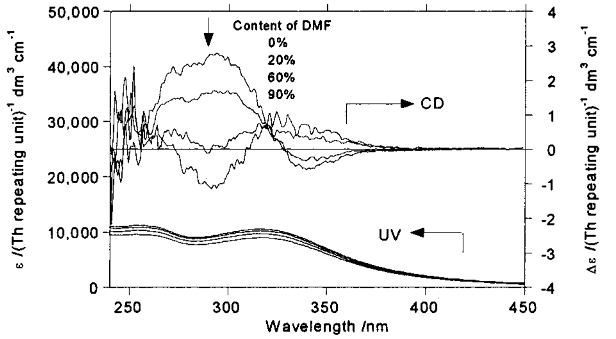

Figure 4. UV−vis and CD spectra of PDMOT as a function of DMF content (vol %) in a mixed DMF/chloroform system at 21 °C.

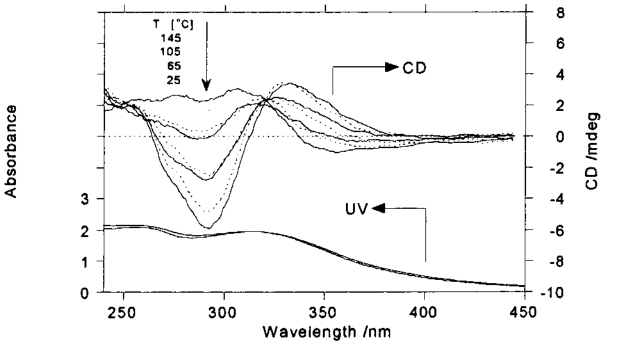

Figure 5. Variable temperature UV−vis and CD spectra of PDMOT in the solid film (solid lines, heating process; dotted line, cooling process).

π-Conjugated polymers bearing chiral side chains are known to exhibit similar bisignate Cotton effects in both aggregate and solid states, due to exciton coupling of the chiral oriented chromophores. For comparison, the variable temperature CD and UV−vis spectra of a solid film prepared by solvent-casting from a chloroform solution of PDMOT were measured (Figure 5). A significant change in the CD spectrum was observed, but minimal change in the UV−vis spectrum was found over

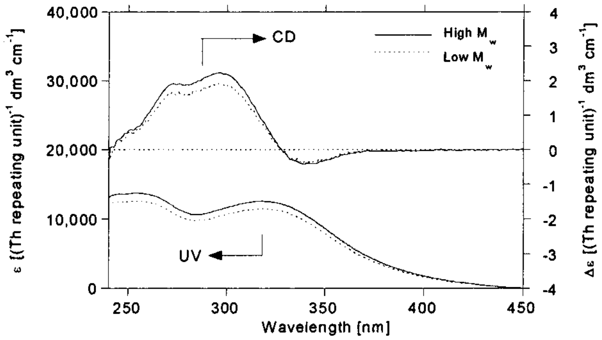

Figure 6. Comparison of UV−vis and CD spectra of different molecular weight PDMOTs in chloroform at 21 °C: solid lines, high M_w, M_w = 46 000 (M_w/M_n = 2.8); dotted lines, low M_w, M_w = 1100 (M_w/M_n = 1.2).

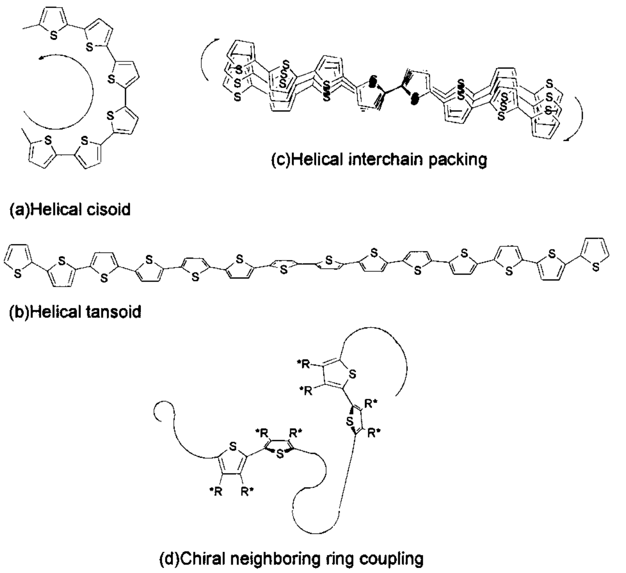

Figure 7. Possible chirally ordered model structures of polythiophenes (a and b, the two types of intramolecular chiral structures postulated by Cui and Kertesz; c, interchain chiral $\pi-\pi$ stacking structure; d, chirally distorted structure in PDMOT).

a range of temperatures. At lower temperatures, a bisignate CD signal, which was similar to PDMOT in 1-octanol at 0 °C and in the chloroform−DMF system containing a high content of DMF, was observed. As the temperature was increased, the absolute magnitude of the CD signal decreased, and the CD signal at 145 °C became similar to that in chloroform. This process was completely reversible in the heating and cooling runs.

The difference between the CD spectra of PDMOT in good and poor solvents, molecularly disperse in solution and in the solid state, at high and low temperatures, together with the CD signal independence of the polymer concentration, suggests the existence of a certain chiral backbone conformation incorporated in each individual chain in addition to any chirally oriented supramolecular structures resulting from intermolecular interactions. The marked thermo- and solvato-driven changes in the CD spectra can thus be interpreted as the transition between the molecularly dispersed and aggregated states.

Cui and Kertesz[8] indicated the theoretical existence of two possible helical backbone conformations (cisoid and transoid) for a polythiophene (Figure 7a,b). To verify whether a chirally ordered structure exists in the PDMOT molecule, the chiroptical properties were measured for both low and high molecular weight fractions. These samples were separated by filtration through a filter with a pore size of 0.02 μm after the polymer had formed aggregates in a mixture of chloroform and DMF at the volume ratio of 1:9. For the low molecular weight sample, $M_w = 1100$ ($M_w/M_n = 1.2$), and for the higher one, $M_w = 46\ 000$ ($M_w/M_n = 2.8$). Almost no difference was observed in either the CD or UV−vis spectra between these two fractions (Figure 6). This result and the low viscosity index value of PDMOT ($\alpha = 0.49$ in THF, 30 °C) support the idea that no higher-order structure of PDMOT is responsible for the observed chiroptical properties.

Compared to the monoalkyl-substituted polythiophenes,[6] the significantly blue-shifted absorption of PDMOT suggests very limited conjugation along the backbone. (The conjugation is likely to be limited within 2−3 thiophene repeating units, according to the results of Brédas et al.[9]) It is also worth noting that, in all the cases when the temperature and solvent were changed, only a small difference in the UV−vis spectra of PDMOT was observed. This behavior is very different from the case of the monosubstituted or dialkoxy-substituted chiral polythiophenes,[2,10] in which a clear red shift in λ_{max} and the appearance of a vibronic fine structure band due to the change in the backbone conformation in the CD and UV−vis spectra can be observed. On the basis of these observations, the backbone of PDMOT seems to be conformationally restricted. Such rigidity presumably arises due to the steric demands of the two side chains, which should cause a restriction of the σ-bond rotation between two neighboring thiophene rings. As a result, polymerization of the monomers proceeds with chiral coupling of the thiophene rings in one predominant direction similar to that in chiral 1,1′-binaphthol. This idea is consistent with the result of the molecular weight dependence experiment which indicated that no second-order helical structure of PDMOT was formed in chloroform.

In the CD spectra of PDMOT at low temperatures in 1-octanol (Figure 3) or in the solid film (Figure 5), the nodes of all the curves around 318 nm do not reach zero, as reported in the literature for the monosubstituted and dialkoxy-substituted chiral polythiophenes.[2] We assume that the observed CD signals in these figures originate from two different structures: one from the chiral intramolecular backbone conformation (Figure 7d) and the other from the $\pi-\pi$ stacked intermolecularly associated chiral structures (Figure 7c). A reevaluation of Figure 3 may support this idea. The CD spectral curve at the highest temperature, e.g., 80 °C, in 1-octanol, was regarded as being due to the purely molecularly dispersed, chirally distorted state of PDMOT. After subtracting this contribution from the CD curves at lower temperatures in Figure 3, the typical bisignate Cotton effects at 292 and 338 nm were obtained with a zero point at around 318 nm, corresponding to the UV absorption maximum (Figure 8). These results indicate that although the temperature and solvent can affect the interchain interaction, the chiroptical properties of the chirally distorted main chain remained almost unchanged in PDMOT.

In summary, we demonstrate the first circular dichroism of a polythiophene in the molecularly dispersed state. The steric effects of the two branched chiral alkyl side chains in the 3- and 4-positions of the thiophene ring in PDMOT were assumed to account for the unique

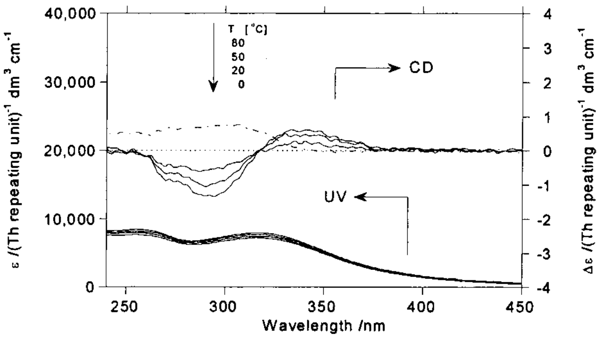

Figure 8. Reevaluated CD and UV−vis spectra of PDMOT in 1-octanol from the original Figure 3 (dashed line, the CD curve at 80 °C; solid lines, CD curves after subtracting the 80 °C CD curve).

CD profile and the significant thermo- and solvato-driven effects on the CD spectra. A predominantly unidirectional coupled conformation of neighboring repeating units or within a very limited length along the backbone may exist, probably generated during the polymerization process due to the chiral side chain effect. The present results should provide new insights into understanding the optical activity of polymers or even producing a chiral structure of interest.

Acknowledgment. The authors thank Hiromi Tamoto-Takigawa for the CD, UV−vis, and GPC measurements. The authors also gratefully thank Prof. Julian R. Koe for fruitful discussion and Drs. Masao Morita and Hideaki Takayanagi for their generous support.

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(10) Poly{[3-(*S*)-2-methyloctyl]thiophene} (λ_{max} = 430 nm in chloroform, 21 °C) was prepared by a similar procedure[4,5] for comparison. No significant optical activity in the UV−vis region was observed in good solvents such as chloroform or THF at room temperature.

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