



## Polymer Communication

## Chain helicity of a poly(phenylacetylene) with chiral centers between backbone and mesogenic groups on side chains

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## ABSTRACT

An optically active poly(phenylacetylene), poly{2-(*R*)-methyl-2-[4'-(tetradecyloxy)biphenyl-4-yloxy]-propyl 4-ethynylbenzoate} (**P1**) is synthesized in a high yield with a high molecular weight ( $1.3 \times 10^6$  g/mol) by [Rh(nbd)Cl]<sub>2</sub> catalyst. The chemical structure of the polymer is characterized by IR and NMR spectroscopies with satisfactory analysis data. The polymer is soluble in many common organic solvents. It shows circular dichroism (CD) band in the absorption region of the polyacetylene backbone, indicating that **P1** is chiroptical owing to the formation of helical conformation with an excess screw sense. Combining the results of CD and light scattering experiments, we find that addition of poor solvent can induce the neighboring helical segments within a single polymer strand to become closer, resulting in exciton coupling prior to polymer precipitation. The exciton coupling can be kept in the solid state after solvent evaporation.

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## 1. Introduction

Because of their potential technological applications as optical polarizing films, chiral stationary phases, asymmetric electrodes, anisotropic molecular wires, fluorescent chemosensors, and so forth, synthesis of helical polymers with  $\pi$ -conjugation along the main chains is under hot pursuits [1–4]. Typical examples of such polymers are optically active polyacetylenes, whose backbones can exist in a one-handed helical conformation when appropriate chiral pendants are incorporated. Taking the advantage of the organorhodium catalyst's high tolerance to the functional groups in the acetylene monomers, many helical polyacetylenes, such as derivatives of poly(phenylacetylene) [5–12], poly(propiolate) [13–16], poly(*N*-propargylamide) [17–21], and poly(1-alkyne) [22], have been designed and synthesized. When the chiral centers are close to the main chains, their asymmetric information can be imposed on the backbones, leading to the generation of polymers with an excess of a single-handed helix with right- or left-handedness. Increasing the bulkiness of the chiral pendants can enhance the

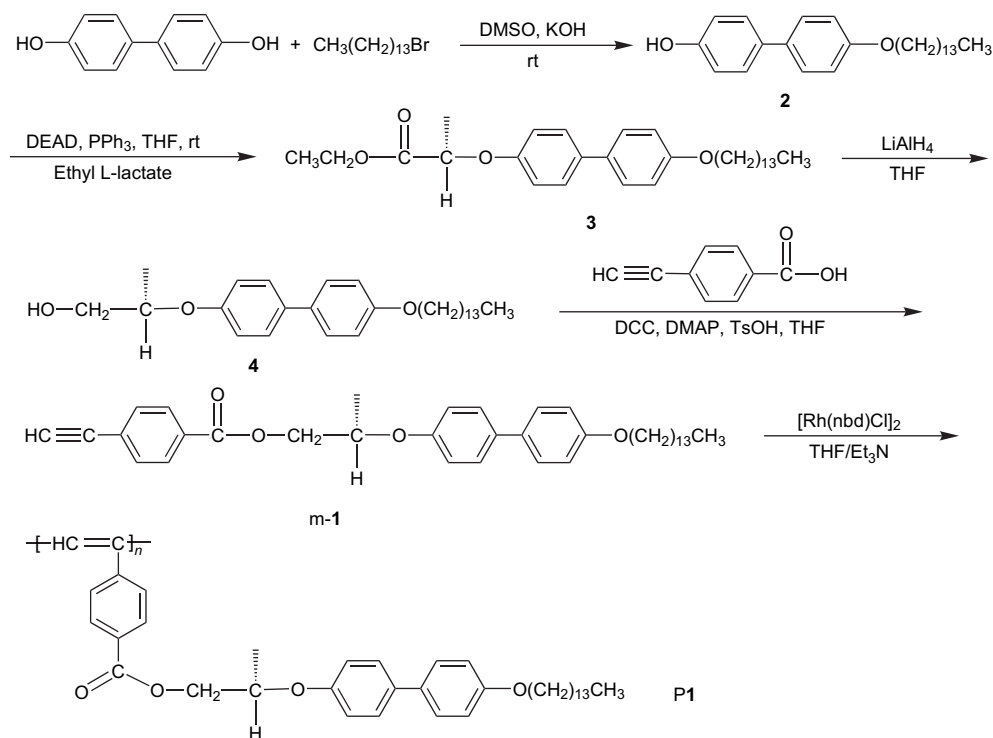
persistence length of the helix and thus increase the Cotton effects and optical rotations [23].

In the present work, we intend to attach chiral liquid crystalline pendants to the polyacetylene skeleton, with an aim to generate polymer with novel electronic and optical properties. Although the chiral mesogenic groups are usually larger in size in comparison with other moieties such as amino acids, whether the chiral information in the side chains can be transferred to the polyacetylene backbone is strongly dependent on the distance between them. Using [Rh(nbd)Cl]<sub>2</sub> catalyst, Akagi and coworkers synthesized a series of polyacetylenes bearing biphenyl side chains with chiral alkyl tails [24]. The chiroptical properties of the pendants were maintained after polymerization but helical backbone conformation was, however, not detected. Masuda et al. synthesized poly(*N*-propargylamide)s containing azobenzene appendages [18]. They found that the polymer main chain took a single-handed helical structure, which is stabilized by intramolecular hydrogen bonding and can be kept when the *trans*-azobenzene is isomerized into the *cis* counterpart upon UV irradiation. Here, we synthesized a poly(phenylacetylene) derivative, poly{2-(*R*)-methyl-2-[4'-(tetradecyloxy)biphenyl-4-yloxy]propyl 4-ethynylbenzoate} (**P1**; Scheme 1), where the chiral carbon atoms are placed between the polyacetylene backbone and the biphenyl groups. As the absorption of the biphenyl moiety is distinguishable from that of the polymer backbone, we can unambiguously prove the existence of helical

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**Scheme 1.** Synthetic routes to monomer **m-1** and polymer **P1**.

structure of **P1** using circular dichroism (CD) measurement. On the basis of the CD and light scattering (LS) experiments, we find that when the solvent polarity becomes poorer due to progressive addition of nonsolvent, the neighboring helical segments within a same polymer strand in solution get closer, leading to exciton coupling prior to polymer precipitation. Furthermore, the exciton coupling can be kept in the solid state after solvent evaporation.

## 2. Experimental section

### 2.1. Synthesis of the monomer and polymer

**Scheme 1** shows the synthetic routes to monomer **m-1** and its polymer **P1** (detailed synthetic procedures and characterization data can be found in [Supporting information](#)). In brief, to obtain the chiral intermediate of compound **3**, the chiral center originally at ethyl L-lactate with *S* configuration was linked to the biphenyl group using Mitsunobu reaction. This reaction is characterized by an  $\text{S}_{\text{N}}2$ -type Walden inversion at the chiral center but with almost no racemization [24], resulting in **3** with *R* configuration. The optical purity of **3** was measured to be 93% (see [Fig. S1](#) in Supporting information), indicating that **3** with the *R* configuration was the main product. After hydrogenation of **3** using  $\text{LiAlH}_4$  in THF, the hydroxyl group in **4** was reacted with 4-ethynylbenzoic acid in the presence of 1,3-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), and *p*-toluenesulfonic acid (TsOH), giving **m-1** as a white solid. Polymerization of the monomer was carried out in THF using  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  as catalyst and  $\text{Et}_3\text{N}$  as cocatalyst. The polymer was purified by precipitation its THF solution into acetone.

Polymer **P1** was characterized by standard spectroscopic methods, which gave satisfactory data corresponding to its expected molecular structure. As can be seen from the  $^1\text{H}$  NMR spectra shown in [Fig. S2](#) (Supporting information), **P1** in  $\text{CDCl}_3$  shows no resonance peak of  $\text{HC}\equiv$  of **m-1** at  $\delta$  3.32, whereas a new absorption peak corresponding to the absorption of *Z* olefin backbone proton appears at  $\delta$  5.66 [1], indicating that **m-1** is successfully transformed

into **P1** by the polymerization reaction. This prediction is further supported by the IR and  $^{13}\text{C}$  NMR measurements ([Figs. S3 and S4](#)). Based on the  $^1\text{H}$  NMR spectra of **P1** in  $\text{THF-}d_8$  ([Fig. S5](#)), the *Z* content of **P1** was determined to be 76%, confirming that the polymerization of **m-1** using  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  catalyst resulted in a *Z*-rich stereostructure. The weight-average molecular weight ( $M_w$ ) of **P1** is determined to be  $1.3 \times 10^6$  by static LS ([Fig. S6](#)) and its polydispersity measured by gel permeation chromatography (GPC, Waters 150C) using polystyrene standards is 1.3.

### 2.2. Equipment and experiments

As the radius of gyration of **P1** was measured to be  $\sim 55$  nm, its critical concentration of overlap limit ( $C^*$ ) is estimated to be  $\sim 3$  mg/mL (i.e. 5.3 mM in terms of repeating unit). We prepared solutions with concentrations usually one order of magnitude lower than the  $C^*$  value. The polymer solutions were obtained by dissolving the polymer in pure solvents such as chloroform, THF, or toluene, and were stored overnight. When using chloroform/hexane mixtures as the solvent, the polymer was first dissolved in chloroform followed by dropwise addition of hexane to the desired volume ratio and concentration.

Specific rotations ( $[\alpha]_D^{23}$ ) were measured by a JASCO model P-1030 polarimeter. The optical purity of **3** determined by chiral HPLC was performed on Agilent 1100, using chiralcel OD-H column ( $4.6 \text{ mm} \times 250 \text{ mm}$ ). UV spectra were measured on a PE-Lambda 35 spectrophotometer with the slit width of 1 nm. CD spectra were taken on a Jasco-810 spectropolarimeter using 1 cm quartz cell. Each spectrum was the average of 3 scans. For the measurements, the solvent was used as the reference. Molar extinction coefficient ( $\epsilon$ ) and molar ellipticity ( $[\theta]$ ) of **P1** were calculated on the basis of its repeat unit.

Dynamic and static LS measurements were performed on Brookhaven Instruments BI-200SM Goniometer with a BI-Turbo-Corr Digital Correlator. The vertical polarized laser was supplied by a solid-state Laser source (CNI Changchun GXL-III, 532 nm,

100 mW). To determine the absolute  $M_w$ , the THF solutions of P1 with different concentrations were filtered through Millipore 0.22  $\mu\text{m}$  PTFE filter into dust-free vials, and the static LS measurements were performed in the angle range of  $20^\circ$ – $90^\circ$ . For P1 in chloroform/hexane mixtures, the chloroform solution was first filtered into a dust-free vial, and then diluted with filtered hexane to a desired hexane/chloroform volume ratio and a concentration of 0.2 mg/mL. To measure the dynamic LS data, the autocorrelation function was collected at  $30^\circ$ ,  $60^\circ$ , and  $90^\circ$  in the homodyne mode using Brookhaven Instrument software (9KLD SW). Time correlation functions were analyzed with a Laplace inversion program CONTIN. The value of  $dn/dc$  of the polymer in THF was determined to be 0.1793 mL/g. Viscosities of the mixed solvents at  $25^\circ\text{C}$  were measured using a Ubbelohde viscometer, and their refractive indexes were calculated as the volume-weighted average of each solvent component.

### 3. Results and discussion

Polymer P1 is soluble in many common organic solvents, allowing us to investigate its properties by “wet” spectroscopic methods. Fig. 1 shows the UV and CD spectra of P1 in chloroform, THF, and toluene at room temperature ( $\sim 23^\circ\text{C}$ ). All the spectra exhibit a broad band from 350 to 550 nm, which is well separated from the absorption band of biphenyl group and shall be attributed to  $\pi$ - $\pi^*$  electronic transition of the polyene backbone. The strong Cotton effect observed at  $\sim 385$  nm clearly indicates the existence of backbone containing a helical conformation with an excess of single-handedness. This confirms that the asymmetric force field generated by the chiral centers indeed affects the secondary structure of P1. Compared with those in THF and toluene, the absorption of P1 in chloroform is red shifted with a larger  $\epsilon$ . The red shift occurred in chloroform may be due to the longer conjugate length of the backbone with more extended conformation. Consequently, P1 in chloroform may possess helical pitch longer than that in THF and toluene, resulting in a weaker CD band at  $\sim 385$  nm [12,14].

It is intriguing to note that P1 shows different chiroptical properties in solvent mixtures containing chloroform as good solvent and hexane as poor solvent. Fig. 2 depicts the CD spectra of P1 in chloroform/hexane mixtures with different hexane fractions but fixed concentration of 0.45 mM. The CD spectra in mixtures with hexane contents below 70 vol% are almost identical to that in pure chloroform, exhibiting only a negative CD band with a minimum at  $\sim 385$  nm. However, once the hexane content reaches 75 vol%, the CD band splits into two intense ones with opposite signs, with the

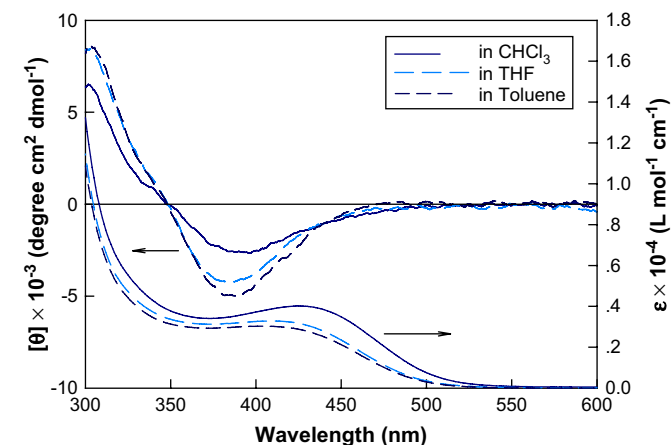


Fig. 1. CD and UV spectra of P1 in different solvents at  $23^\circ\text{C}$ . Polymer concentration (mM): 0.21 (CD), 0.063 (UV).

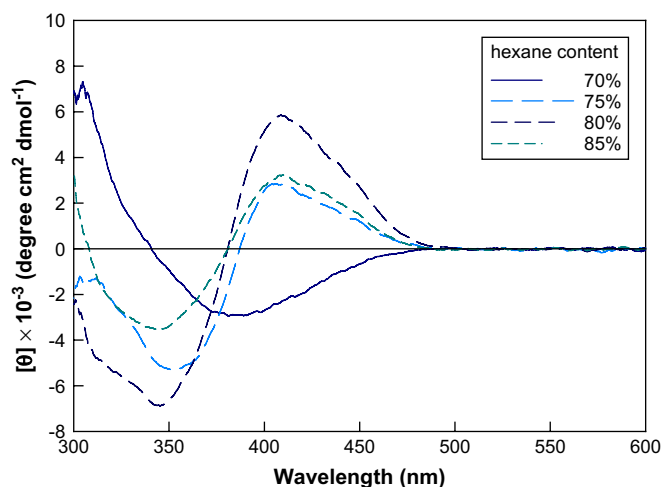


Fig. 2. CD spectra of P1 in chloroform/hexane mixtures with different hexane contents at  $23^\circ\text{C}$ . Polymer concentration: 0.45 mM.

zero intensity at  $\sim 385$  nm. This bisignated CD spectrum reflects the characteristic of exciton coupling between closely situated transition dipole moments in neighboring chiral segments. The exciton coupling is preserved with further increasing the amount of hexane. Because the CD spectra show positive first and negative second Cotton effects (from longer to shorter wavelength), the screw sense of the two transition dipoles is right-handed.

The exciton coupling can originate from either intermolecular or intramolecular interactions. Polythiophene [25–28] and polysilane [29,30] have been found to form helical aggregates with induced exciton coupling, wherein the intermolecular interaction is dominant. Other researchers have, however, reported that exciton coupling appears when two segments in one polymer strand interact with each other [31,32]. To elucidate whether the exciton coupling arises from chain aggregates or from an isolated strand, we examined the concentration dependence of the CD spectrum in a chloroform/hexane mixture with a hexane content of 75 vol%. As shown in Fig. 3, the ellipticities at 400 and 350 nm, where the opposite signed CD bands exhibit the intensities rather close to maximum, remain almost constant when the concentration is varied from 0.009 to 3.5 mM (i.e.  $5 \times 10^{-3}$  to 2 mg/mL). As the aggregate mechanism relies on the solution concentration but the intramolecular mechanism does not [32,33], the result infers that in

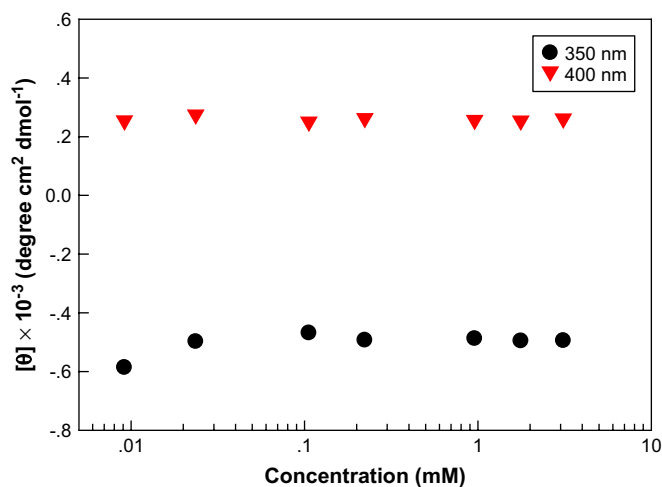


Fig. 3. Concentration dependence of CD intensities of P1 at 400 and 350 nm in a chloroform/hexane mixture with a hexane content of 75 vol%. The measurements were carried out at  $23^\circ\text{C}$ .

this concentration range, the exciton coupling is most likely caused by segmental interaction within a single polymer chain.

More evidences supporting the intramolecular mechanism come from our LS experiments in chloroform/hexane mixtures with fixed concentrations of 0.2 mg/mL. Fig. 4 plots the  $R_g$  (by static LS) and apparent hydrodynamic radius  $R_h$  (by dynamic LS) of P1 as a function of the hexane content at 25 °C. In pure chloroform, the  $R_g$  and  $R_h$  values are measured to be 55 and 35 nm, respectively. The  $R_g$  and  $R_h$  values change little at hexane contents below 80 vol%. It is worth noting that the  $R_g/R_h$  ratio is around 1.5–1.6. This means that in solutions the P1 chain with a rather high  $M_w$  of  $1.3 \times 10^6$  is essentially random coil as a whole. Combining the LS and CD results, we can imagine that at a subchain level the chain segments with helical conformation give the Cotton effect; when they are linked together, an overall coil is formed. The  $R_g$  and  $R_h$  values start to increase at hexane content higher than 80 vol%. At 85 vol%, the  $R_h$  value drastically rises to 360 nm and the  $R_g/R_h$  value drops to 0.5, corresponding to the formation of large solid particles. The change in the scattering intensity with the hexane content is coincided with those of  $R_g$  and  $R_h$ . As shown in the inset of Fig. 4, the scattering intensity at an angle of 90° ( $I_{90^\circ}$ ) keeps almost unchanged at hexane contents below 80 vol%, but dramatically increases afterwards.

On the basis of LS results, we conclude that at the fixed concentration and temperature, the critical condition for the solution phase separation is at a hexane content of ~80 vol%. The obvious larger particle size and stronger scattering at 85 vol% can be ascribed to the formation of aggregates. On the other hand, the P1 chains are well dissolved in dilute solutions when the hexane content is below 80 vol%. When the polymer solution is brought close to the phase separation, we expect that the coil size will decrease when the hexane content becomes higher. However, as the sample shows a rather broad polydispersity of 1.3, our LS experiments cannot unambiguously detect the shrinkage of the coil size in terms of  $R_g$  and  $R_h$ .

It now becomes clear that exciton coupling taken place at a hexane content of 75 vol% is largely initiated by intramolecular interaction, although the intermolecular interaction cannot be completely precluded. According to the theory of exciton coupling, the amplitude and sign of the Cotton effect are functions of the distance as well as the dihedral angle between the two transition dipoles. For two closely placed dipoles, transition to either high or low energy sides is allowed when the dihedral angle is in-between 0° and 180° so that the splitting of Cotton

effect occurs. The amplitude of the bisigned signal reaches its maximum at a dihedral angle of ~70°. For occurrence of coupling between two helical segments belonging to a same chain in solution, we presume that the P1 coil progressively becomes compact with an increase in the hexane content. This process leads the neighboring helical segments to be adequately close with a suitable and more or less settled dihedral angle, and thus induces exciton coupling prior to solution phase separation. In Fig. 2, stronger bisigned CD bands are observed at 80 vol%. This implies that when aggregation starts to occur, the helical segment interaction will become stronger and the dihedral angle will be more close to 70°. The amplitude, however, decreases at 85 vol%, where obvious aggregation is observed [29]. In this case, the chain segments may pack in a more parallel manner in the aggregates and the dihedral angle is deviated from 70°.

We found that the exciton coupling could be maintained in the solid state. As shown in Fig. 5, a thin film of P1 obtained by casting its solution with a hexane content of 75 vol% exhibits strong bisigned CD bands at the wavelengths similar to those in the solution. The solution drying process was completed in a rather short period of time. Since chloroform evaporated relatively faster than hexane due to its higher vapor pressure, the hexane content gradually becomes higher during drying, which can help to freeze the helical structure of the polymer. Moreover, the final solidification shows almost no effect on the chain conformation. The morphology and phase structures of P1 in the solid state are currently under investigation in our laboratories.

#### 4. Summary

In summary, we have synthesized a poly(phenylacetylene) derivative (P1) with chiral centers located between the main chain and the biphenyl mesogenic groups. The chiral centers successfully confer helical conformation on the polyene backbone, inducing it to rotate in a preferred screw sense. Exciton coupling is observed upon addition of nonsolvent of hexane into its chloroform solution. Experimental results reveal that the exciton coupling follows an intramolecular mechanism, namely, the helical chain segments belonging to a same polymer strand can closely interfere with each other to give strong bisigned CD bands, which appear prior to the solution phase separation. The exciton coupling could be maintained in the solid state, offering the opportunity to study the polymer as an optically active material and a chiral stationary phase.

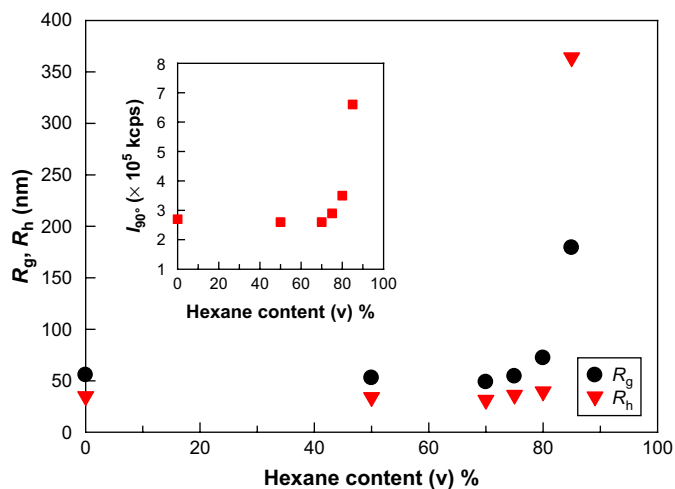


Fig. 4.  $R_g$  and  $R_h$  (apparent) of P1 as a function of hexane content in chloroform/hexane mixtures at 25 °C. The polymer concentrations were 0.2 mg/mL. The inset plots the solution scattering intensity at an angle of 90° vs. hexane content.

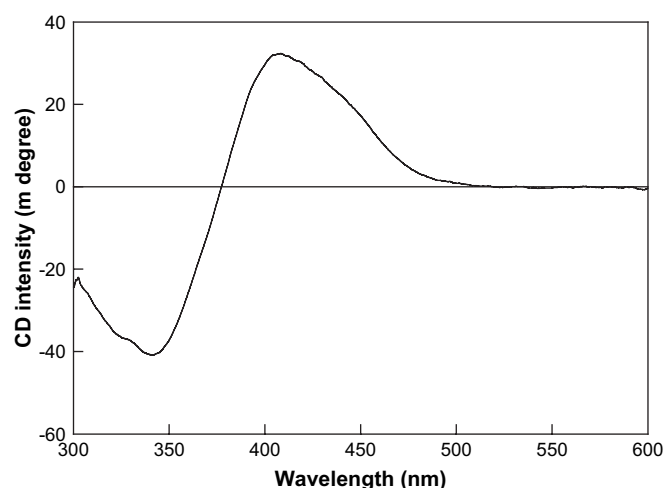


Fig. 5. CD spectrum of a thin film of P1 casted from its chloroform/hexane mixture with a hexane content of 75 vol%.

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## Appendix. Supporting information

Synthetic procedures and characterization data for monomer **m-1** and polymer **P1** and their  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR spectra, and Zimm plot of absolute  $M_w$  determination. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.06.007.

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