4054 *Macromolecules* **2005,** *38,* 4054−4057

Facile Control of Chiral Packing in Poly(*p*-phenylenevinylene) Spin-Cast Films

Andrew Satrijo and Timothy M. Swager*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received December 15, 2004
Revised Manuscript Received March 24, 2005

The control of film morphology is of critical importance in the fabrication of conjugated polymer-based devices such as light-emitting diodes, field effect transistors, photodiodes, and photovoltaic cells.[1] To optimize the performance and efficiency of these devices, it is crucial to obtain a better understanding of the polymer's interchain interactions and aggregation behavior in the solid state. Many groups have recently studied the morphological properties of poly(*p*-phenylenevinylene) (PPV) derivatives, which are among the most extensively investigated conjugated polymers for electronic applications due to their stability, easy processability, and good electrical and optical properties.[1] The morphology and electrooptical properties of conjugated polymer films are highly dependent on the deposition technique,[2] choice of solvent,[3−7] polymer concentration,[5] and annealing process.[4,6,8,9] Notably, Schwartz et al. observed that the degree of aggregation in a poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) solution could be directly transferred into the film state by spin-casting deposition.[6] Generally, PPV films with higher degrees of interchain contact have lower luminescence quantum yields, higher probabilities of exciton−exciton annihilation, lower rates of photobleaching, and greater charge carrier mobilities.

Currently, the nature of polymer aggregation in spin-cast films is still unclear. One method to monitor aggregation behavior both in solution and in the solid state is by employing circular dichroism (CD) spectroscopy, a widely used technique for the conformational analysis of chiral molecules and materials.[10] In this study, we used CD spectroscopy to demonstrate that films spin-cast from a chiral π-conjugated polymer can be easily and selectively fabricated from different solvents to have correspondingly different chiral architectures with opposite handedness.

Fujiki et al. recently reported that σ-conjugated polysilane films can be selectively prepared to contain either *P*- or *M*-helices by drop-casting from isooctane or hexane solutions above or below the helix−helix (*P*−*M*) inversion temperature.[7] In another account, Meijer et al. reported that the cooling rate of a heated chiral polythiophene film determined its chiral organization.[11] By immersing the hot film into a cold water bath, they were able to freeze-in a metastable assembly that possessed a chirality that was opposite to that of a film that was slowly cooled.

The chiral PPVs synthesized for this study are shown in Scheme 1. To induce optical activity in the conjugated backbone, enantiomerically pure chiral side chains were incorporated into the polymers.[12]

By adding a poor solvent (e.g., polar acetonitrile) to a solution of PPV1 dissolved in a good solvent (e.g., nonpolar chloroform), it is possible to study the conformation of the polymer at various degrees of aggregation (Figure 1a).[16−20] The strong bisignate Cotton effects centered at the $\pi-\pi^*$ transition (around 430 nm in the UV−vis absorption spectra) are indicative of exciton coupling[21] between obliquely oriented neighboring polymer backbone chains, suggesting the existence of a chiral supramolecular organization within the aggregates.[22] In 100% chloroform, aggregation of the polymer did not occur, so as expected, no bisignate CD couplets were observed. In relatively nonpolar cosolvent mixtures (70:30 and 60:40 $CHCl_3$:MeCN) a positive CD couplet is observed, whereas in polar cosolvent mixtures (≤50:50 $CHCl_3$:MeCN) a negative CD couplet is observed.[23,24] This solvent-induced inversion of Cotton effects has been previously observed for chiral aggregate solutions of polythiophene[13,19,20,25] and polysilane.[17] Yashima et al. attributed this phenomenon in polythiophene to the formation of two types of π-stacked, chiral supramolecular assemblies: a cholesteric liquid crystalline-type (i.e., helical) assembly of coplanar chains and a stack of twisted backbone chains.[19] Thus, for example, a cholesteric assembly may be dominant in nonpolar solvents (e.g., 60:40 $CHCl_3$:MeCN which exhibited right-handed chirality), while the twisted stack assembly may be dominant in more polar solvents (e.g., 50:50 $CHCl_3$:MeCN which exhibited left-handed chirality). However, it is not known exactly what type of architecture is responsible for each observed handedness.

When the aggregate-free chloroform solution was spin-cast into a thin film, no chiral organization was found to exist in the resulting film (Figure 1b). The disordered assembly in the solid state is a direct consequence of the absence of ordered chiral aggregates in good solvents. Several groups observed that it was important to thermally anneal films in order to develop chiroptical properties in the solid state.[26] Additionally, Liu et al. recently described a method of increasing the degree of interchain interactions in MEH-PPV films by exposing the films to saturated organic solvent vapor,[9] which induces a plasticization effect and reduces the glass-transition temperature of polymers.[27] Consistent with these studies, thermally annealing a film of PPV1 (at 45 °C for 30 min) in the presence of chloroform vapor[28] resulted in a bisignate CD couplet, suggesting that the polymer chains self-assembled from a disordered state to a more thermodynamically favored chiral organization. This CD spectrum has a similar shape to the negative CD couplet observed for the tightly aggregated polymer in poor solvents (≤50:50 $CHCl_3$:MeCN). Thus, the annealed film and the tightly aggregated polymer solutions both consist of a predominantly left-handed chiral organization.

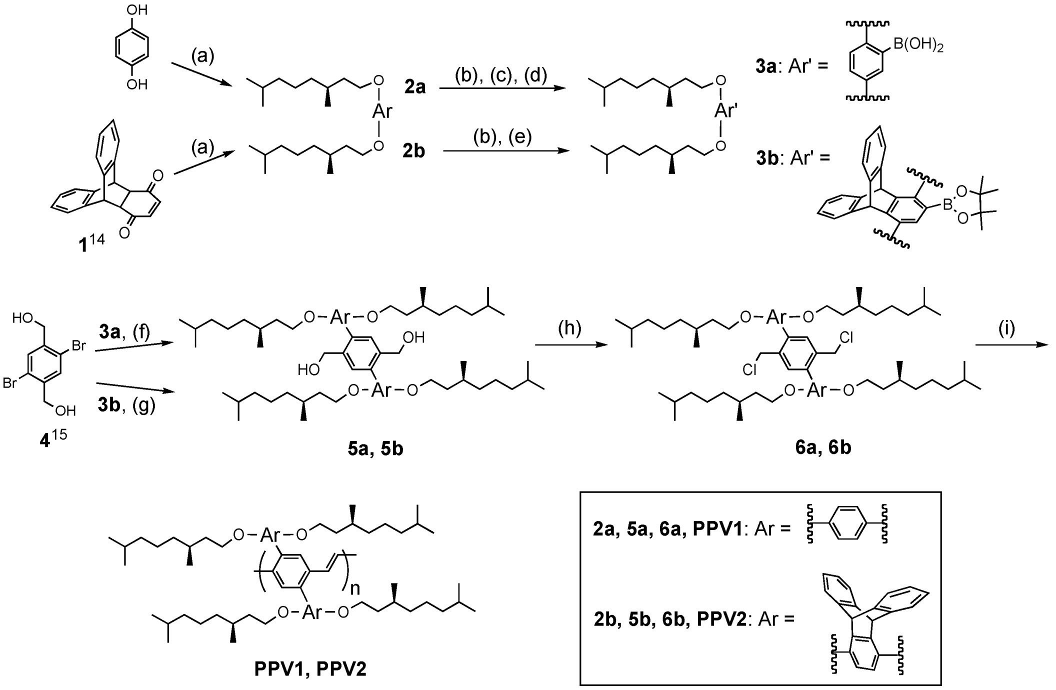
Using the same polymer, we wanted to fabricate a film having a chiral architecture with the opposite handedness. Unfortunately, spin-cast films from good solvent-poor solvent mixtures, such as $CHCl_3$/MeCN or $CHCl_3$/MeOH, exhibited a significant amount of light scattering and inhomogeneity due to precipitation during the spin-coating process. A survey of various solvents revealed that in 1,2-dichloroethane (DCE) the polymer exhibited a strong positive CD couplet (Figure 2a) similar to that observed in 60:40 $CHCl_3$:MeCN. The lower solubility of PPV1 in 1,2-dichloroethane relative to chloroform[29] allowed the formation of stable ag-

---

* Corresponding author. E-mail: tswager@mit.edu.

10.1021/ma047418s CCC: $30.25

Scheme 1. Synthesis of Chiral PPV Derivatives PPV1 and PPV2[a]



[a] (a) (*S*)-3,7-Dimethyloctyl bromide,[13] K_2CO_3, KI, 2-butanone, reflux; (b) *n*-BuLi, TMEDA, hexane, rt; (c) $B(OMe)_3$, 0 °C; (d) aqueous HCl; (e) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 0 °C; (f) $Pd(PPh_3)_4$, K_2CO_3, DMF, PhMe, H_2O, EtOH, 90 °C; (g) $Pd(PPh_3)_4$, Cs_2CO_3, *p*-dioxane, 90 °C; (h) $SOCl_2$, CH_2Cl_2; (i) KO*t*Bu, THF.

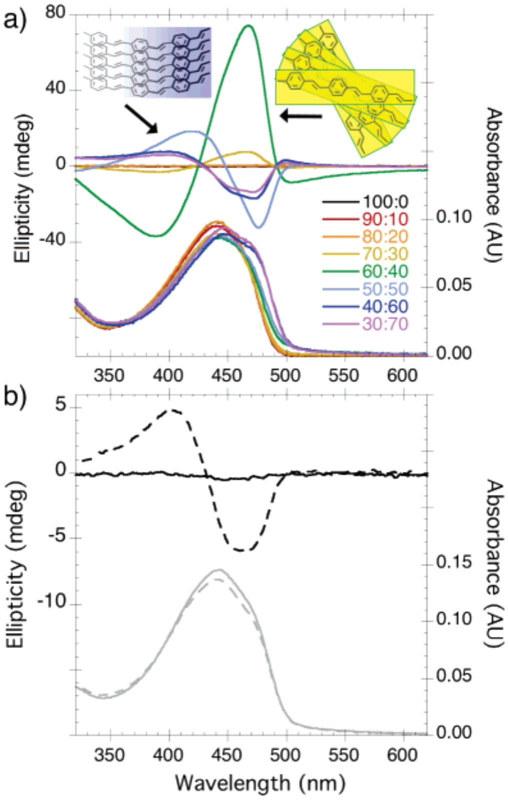


Figure 1. CD and UV–vis spectra of PPV1 as (a) solutions in $CHCl_3$:MeCN (v:v) and (b) a spin-cast film, before (solid line) and after (dashed line) annealing. Insets: proposed packing models of (left) left-handed twisted stack and (right) right-handed cholesteric assembly.

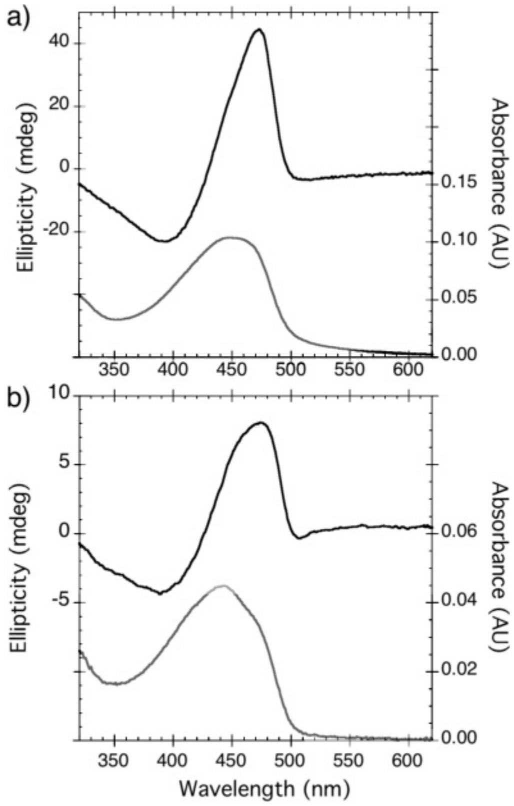


Figure 2. CD and UV–vis spectra of PPV1 as (a) a solution in 1,2-dichloroethane and (b) a corresponding spin-cast film without any annealing.

gregates in solution. The DCE solution, as well as the polar $CHCl_3$:MeCN solutions (Figure 1a), exhibited red-tailing in the UV–vis spectra, signifying the presence of light-scattering aggregate particles.

Similar to the DCE solution, the corresponding spin-cast films also displayed strong positive CD couplets (Figure 2b), indicative of a predominantly right-handed chiral organization. It is apparent that the spin-casting process kinetically traps the polymer chains in their solution conformation.[4–6] Thermal annealing in the

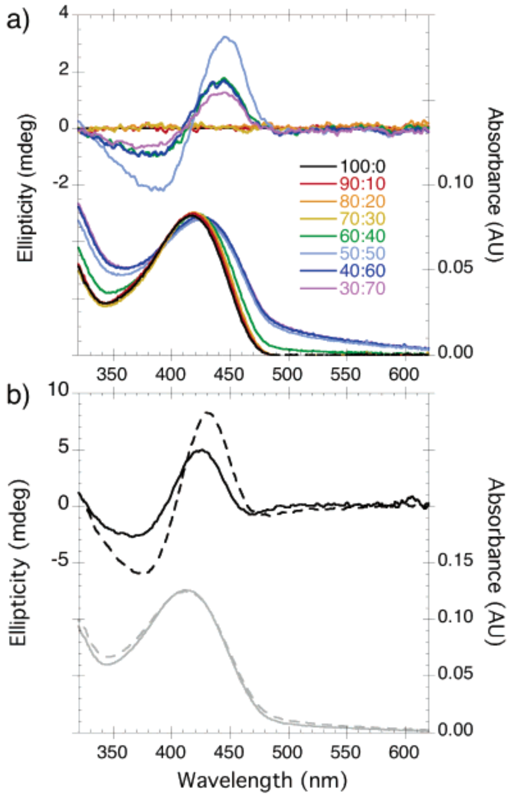


Figure 3. CD and UV−vis spectra of PPV2 as (a) solutions in $CHCl_3$:MeCN (v:v) and (b) a spin-cast film, before (solid line) and after (dashed line) annealing.

presence of $CHCl_3$ or DCE vapor or under an inert nitrogen atmosphere did not considerably alter the CD spectra of these films, which already possessed a significantly ordered architecture. Thus, we have shown that by simply varying the spin-casting solvent (for kinetic control) or annealing conditions (for thermodynamic control), three distinct film architectures can be prepared from the same PPV: a disordered assembly that does not exhibit any chiral packing and two chiral organizations with opposite handedness.

Another chiral polymer, PPV2, was synthesized in order to study the effects of bulky, interlocking side groups on the chiral organizations. In aggregate solutions, only one type of chiral organization was observed: a right-handed chiral assembly exhibiting a positive CD couplet (Figure 3a). The maximum CD signal intensity appeared in 50:50 $CHCl_3$:MeCN, which had a significant amount of aggregation with minimal precipitation. Unlike PPV1, no solvent-induced inversion of Cotton effects was observed. It is possible that the bulky triptycene side groups prevented the formation of tightly associated assemblies, which markedly exhibited a negative CD couplet in the polar solutions of PPV1.

Similar to PPV1, the 100% chloroform solution of PPV2 did not appear to have any chiral organization. However, when the PPV2−chloroform solution was spin-cast onto a glass substrate, the resulting film exhibited a distinct CD couplet even without any thermal annealing (Figure 3b). The iptycene moieties, which have been proposed to help form interlocking structures,[18] may have assisted in securing an ordered, chiral assembly that formed as the solvent evaporated during the spin-coating process. Subsequent thermal annealing in the presence of chloroform vapor did not significantly alter the shape of the positive CD couplet, but it did increase the signal's intensity, suggestive of a minor reorganization of the film's chiral packing.

In conclusion, we have shown that incorporating bulky, interlocking side groups into a chiral π-conjugated polymer can help to assemble ordered, chiral architectures in films spin-cast from a good solvent (e.g., chloroform). Additionally, we have demonstrated that from one chiral PPV, three distinct film architectures can be prepared: a disordered assembly that does not exhibit any chiral packing and two chiral organizations with opposite handedness. This ability to easily control the stacking organization in a π-conjugated polymer film may facilitate the optimization of its electrooptical properties and aid in future studies of luminescence quenching in the aggregated state.

Acknowledgment. We thank the NSF for financial support. A.S. also thanks NSERC Canada and the MIT-DuPont Alliance for graduate fellowships.

Supporting Information Available: Details of experimental procedures and the synthesis and characterization of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Moratti, S. C. The Chemistry and Uses of Polyphenylenevinylenes. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; p 343.
(2) (a) Fiesel, R.; Neher, D.; Scherf, U. *Synth. Met.* **1999**, *102*, 1457. (b) McQuade, D. T.; Kim, J.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 5885.
(3) Díaz-García, M. A.; Hide, F.; Schwartz, B. J.; Andersson, M. R.; Pei, Q.; Heeger, A. J. *Synth. Met.* **1997**, *84*, 455.
(4) (a) Nguyen, T.-Q.; Doan, V.; Schwartz, B. J. *J. Chem. Phys.* **1999**, *110*, 4068. (b) Nguyen, T.-Q.; Martini, I. B.; Liu, J.; Schwartz, B. J. *J. Phys. Chem. B* **2000**, *104*, 237. (c) Nguyen, T.-Q.; Yee, R. Y.; Schwartz, B. J. *J. Photochem. Photobiol. A* **2001**, *144*, 21.
(5) Shi, Y.; Liu, J.; Yang, Y. *J. Appl. Phys.* **2000**, *87*, 4254.
(6) Schwartz, B. J. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141.
(7) Ohira, A.; Kunitake, M.; Fujiki, M.; Naito, M.; Saxena, A. *Chem. Mater.* **2004**, *16*, 3919.
(8) Liu, J.; Guo, T.-F.; Yang, Y. *J. Appl. Phys.* **2002**, *91*, 1595.
(9) Liu, C.; Zou, X.; Yin, S. *Jpn. J. Appl. Phys.* **2004**, *43*, L563.
(10) (a) *Circular Dichroism: Principles and Applications,* 2nd ed.; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley-VCH: New York, 2000. (b) *Materials-Chirality*; Green, M. M., Nolte, R. J. M., Meijer, E. W., Eds.; Topics in Stereochemistry 24; John Wiley & Sons: Hoboken, NJ, 2003.
(11) Bouman, M. M.; Meijer, E. W. *Adv. Mater.* **1995**, *7*, 385.
(12) For a recent review see: Pu, L. *Acta Polym.* **1997**, *48*, 116.
(13) Bidan, G.; Guillerez, S.; Sorokin, V. *Adv. Mater.* **1996**, *8*, 157.
(14) Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc.* **1942**, *64*, 2649.
(15) Lu, S.; Fan, Q.-L.; Xiao, Y.; Chua, S.-J.; Huang, W. *Thin Solid Films* **2002**, *417*, 215.
(16) (a) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Christiaans, M. P. T.; Meskers, S. C. J.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 4908. (b) Fiesel, R.; Scherf, U. *Macromol. Rapid Commun.* **1998**, *19*, 427. (c) Fiesel, R.; Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Scherf, U.; Bunz, U. H. F. *Macromol. Rapid Commun.* **1999**, *20*, 107.
(17) Nakashima, H.; Fujiki, M.; Koe, J. R.; Motonaga, M. *J. Am. Chem. Soc.* **2001**, *123*, 1963.
(18) Zahn, S.; Swager, T. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4225.
(19) Goto, H.; Okamoto, Y.; Yashima, E. *Macromolecules* **2002**, *35*, 4590.
(20) Zhang, Z.-B.; Fujiki, M.; Motonaga, M.; Nakashima, H.; Torimitsu, K.; Tang, H.-Z. *Macromolecules* **2002**, *35*, 941.
(21) Berova, N.; Nakanishi, K. Exciton Chirality Method: Principles and Applications. In *Circular Dichroism: Principles*

and Applications, 2nd ed.; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley-VCH: New York, 2000; p 337.

(22) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W. *J. Mol. Struct.* **2000**, *521*, 285.

(23) A positive CD couplet is defined as having a positive Cotton effect at longer wavelengths and a negative Cotton effect at shorter wavelengths, whereas a negative CD couplet has the opposite.

(24) In the more polar cosolvent mixtures, the polymer started to precipitate out of solution, which explains the decrease in CD signal intensity below 40:60 $CHCl_3$:MeCN.

(25) Langeveld-Voss, B. M. W.; Christiaans, M. P. T.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1998**, *31*, 6702.

(26) (a) Catellani, M.; Luzzati, S.; Bertini, F.; Bolognesi, A.; Lebon, F.; Longhi, G.; Abbate, S.; Famulari, A.; Meille, S. V. *Chem. Mater.* **2002**, *14*, 4819. (b) Wilson, J. N.; Steffen, W.; McKenzie, T. G.; Lieser, G.; Oda, M.; Neher, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2002**, *124*, 6830. (c) Craig, M. R.; Jonkheijm, P.; Meskers, S. C. J.; Schenning, A. P. H. J.; Meijer, E. W. *Adv. Mater.* **2003**, *15*, 1435.

(27) Bicerano, J. *Prediction of Polymer Properties*, 3rd ed.; Marcel Dekker: New York, 2002.

(28) See Supporting Information for annealing conditions.

(29) The dielectric constants (at 20 °C) of the solvents used in this study are: chloroform, 4.81; 1,2-dichloroethane, 10.42; acetonitrile, 36.64; methanol, 33.0. These values were taken from: Lide, D. R. *Handbook of Organic Solvents*; CRC Press: Boca Raton, FL, 1995.

MA047418S