Chem. Mater. **2000,** *12,* 2741−2744

Poly(2,3-diphenylphenylene vinylene) Derivatives Having Liquid Crystalline Side Groups

An-Kuo Li, Sheng-Shinng Yang, We-Yi Jean, and Chain-Shu Hsu*

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050

Bing R. Hsieh

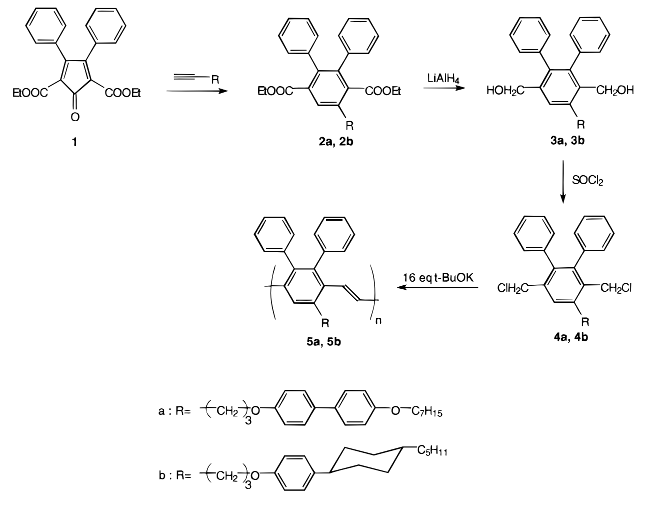
Xerox Corporation, 800 Philips Road, Webster, New York 14580

Received April 11, 2000. Revised Manuscript Received June 12, 2000

Poly(2,3-diphenylphenylene vinylene) (DP-PPV) derivatives with pendant mesogene groups were synthesized. A biphenyoxyl or cyclohexylphenoxy moiety serves as the rigid mesogen core, a methylene chain as the spacer, and a alkyl or alkoxy group as the flexible terminal group. The optical properties of the polymers were investigated by UV−vis and photoluminescent spectroscopies. The polymer films emitted green-blue photoluminescence and electroluminescence. The phase transition behaviors of the polymers were characterized by a polarized optical microscope and a differential scanning calorimeter. The monomers did not show mesophases, while the polymers exhibited a nematic phase around 170−190 °C. The aligned films exhibited dichroism in absorption and emission spectra, implying that the polymers have potential for linearly polarized LED application.

Poly(*p*-phenylene vinylene) (PPV) and its derivatives have attracted a great deal of attention owing to their potential application in organic light emitting diodes (OLEDs).[1] Solvent processability and anisotropic properties are two desirable properties for such polymers. Soluble polymers can be used for both single-layer and multilayer OLEDs by a spin coating process.[2,3] Light emitting polymers with anisotropic properties can provide linearly polarized emission, which is needed for liquid crystal display (LCD) backlight applications. This will simplify LCD manufacturing and reduce cost. A wide range of soluble PPV derivatives have been reported.[4,5] Polarized light emission has been reported for stretch aligned conjugated polymers[6,7] and rubbing aligned functionalized liquid crystal polymers.[8,9] Conjugated polymers with liquid crystalline properties[10] or conjugated polymers having liquid crystal side groups have been reported for polarized OLED application.[11,12] This paper reports two novel poly(2,3-diphenylphenylene vinylene) (DP-PPV) derivatives with liquid crystalline side groups, namely biphenyoxy and cyclohexylphenoxy groups. The polymers were highly soluble, had high molecular weights, and showed liquid crystal behaviors.

Scheme 1



Scheme 1 outlines the overall pathway of preparing the LC substituted monomers and polymers. The monomer synthesis starts with the Diels−Alder reaction

---

* Author for correspondence: Chain-Shu Hsu.

[1] Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holms, A. B. *Nature* **1990**, *347*, 539.

[2] Heeger, A. J.; Braun, D. (UNIAX). WO-B 92/16023, 1992 [*Chem. Abstr.* **1993**, *118*, 157401j].

[3] Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.

[4] Hsieh, B. R.; Yu, Y.; VanLaeken, A. C.; Lee, H. *Macromolecules* **1997**, *30*, 8094.

[5] Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A. *J. Am. Chem. Soc.* **1998**, *120*, 231.

[6] Hagler, T. W.; Pakbaz, K.; Voss, K. F.; Heeger, A. J. *Phys. Rev. B* **1991**, *44*, 8652.

[7] Dyreklev, P.; Berrggren, M.; Inganas, O.; Andersson, M. R.; Wennestrom, O.; Hjertberg, T. *Adv. Mater.* **1995**, *7*, 43.

[8] Hamaguchi, M.; Yoshino, K. *Jpn. J. Appl. Phys.* **1995**, *34*, L712.

[9] Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798.

[10] Lussem, G.; Festag, R.; Greiner, A.; Schmidt, C.; Unterlechner, C.; Heitz, W.; Wendorff, J. H.; Hopmeier, M.; Feldmann, J. *Adv. Mater.* **1995**, *7*, 923. (b) Lussem, G.; Geffarth, F.; Greiner, A.; Heitz, W.; Hopmeier, M.; Oberski, M.; Unterlechner, C.; Wendorff, J. H. *Liq. Cryst.* **1996**, *21*, 903.

[11] Kijima, M.; Akagi, K.; Shirakawa, H. *Synth. Met.* **1997**, *84*, 237. (b) Akagi, K.; Oguma, J.; Shibata, S.; Toyoshima, R.; Osaka, I.; Shirakawa, H. *Synth. Met.* **1999**, *102*, 1287.

[12] Watanabe, Y.; Mihara, T.; Koide, N. *Macromolecules* **1997**, *30*, 1857.

10.1021/cm000295f CCC: $19.00

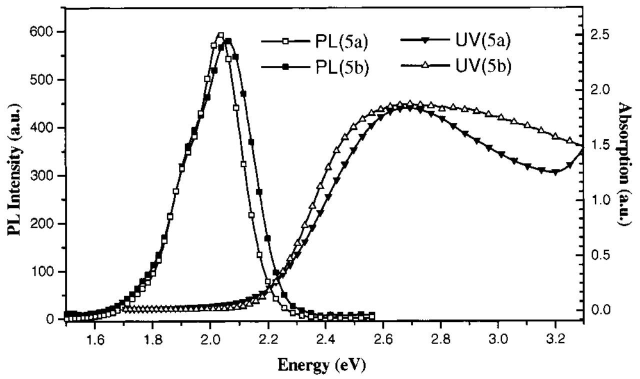


Figure 1. Absorption and photoluminescence spectra of polymer **5a** and **5b**.

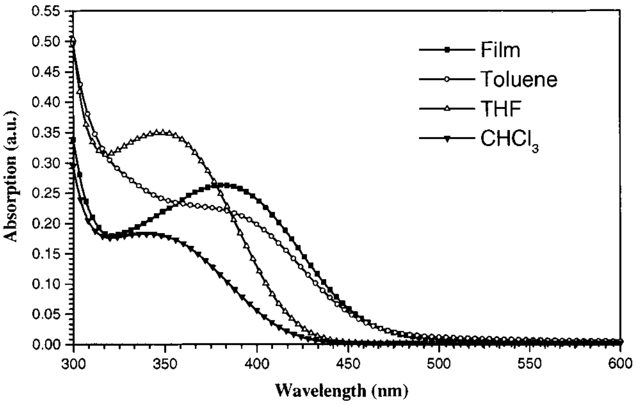


Figure 2. UV–vis absorption spectra of **5a** in various solvents and in the solid state.

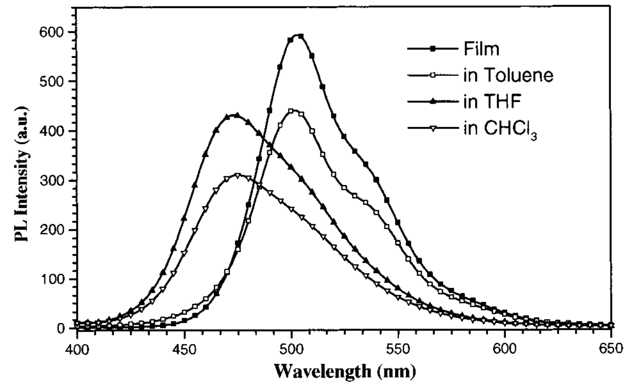


Figure 3. PL emission spectra of polymer **5a** in various solvents and in the solid state.

of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone (**1**) with 4-(*n*-heptyloxy)-4-(4-pentynloxy)biphenyl and 1-(4-pentylcyclohexyl)-4-(4-pentynyloxy)benzene[13] to give **2a** and **2b**, respectively. These are reduced by $LiAlH_4$ to give the corresponding dialcohol **3a** and **3b**. Chlorination of **3a** and **3b** with $SOCl_2$ in methylene chloride gave monomers **4a** and **4b**, respectively. Polymerization of **4a** and **4b** with a large excess of potassium *tert*-butoxide in the absence of chain terminating agents gave the corresponding soluble **5a** and **5b** without gelation.[4,5] Monomers **4a** and **4b** were initially polymerized with 8 equiv of base. The resulting polymer from **4a** contained unconverted chlorine. Fully converted **5a** was obtained using 16 equiv of base.[14]

Both DP-PPV derivatives **5a** and **5b** exhibited strong photoluminescence (PL) and were quite soluble in common organic solvents. The respective weight average molecular weights for **5a** and **5b** obtained by gel permeation chromatography in THF were 225 K (PD = 1.53) and 925 K (PD = 7.69). Both **5a** and **5b** contained *cis* (*Z*) and *trans* (*E*) vinylene groups, as revealed by proton NMR (with the signal for the *Z* form at 6.06 and that for the *E* form at 6.46 ppm) and IR (with *trans*-vinylene out-of-plane bending at 960 cm^{-1} and the *cis* at 868 cm^{-1}).

The optical spectra of thin films of **5a** and **5b** are shown in Figure 1. The LC groups caused small blue shifts in both the absorption edges and the emission peaks. The absorption edges at about 2.0 eV for both polymers were at higher energies than 1.73 eV for DP-PPV.[15] The PL peaks are at 2.0 and 2.05 eV for **5a** and **5b**, respectively. These are similar to those observed for 5-alkyl DP-PPV derivatives.[5] Figure 2 shows the absorption spectra of **5a** in various solvents and in the solid state. The absorption band of **5a** in a poor solvent such as toluene agreed well with that for the polymer film. The absorption band blue shifts in polar solvents such as THF and chloroform. Figure 3 shows a similar shift can also be seen in the PL spectra of **5a** in solution and in films. These results can be explained by different conformations and packing of the polymer chains under different conditions, similar to those reported for poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV).[16] In a good solvent, the polymer chains are extended with little chain aggregation. In a poor solvent or in the solid state, chain aggregates are formed. This is similar to the well-known solvatochromism phenomenon. Similar results have been observed for **5b**. Electroluminescence (EL) for **5a** and **5b** has also been observed in single-layer devices using Al as cathodes. It is possible that one can “design” a chain conformation of a DP-PPV derivative in the solid state by using different casting solvents. This may lead to achieving different colors of EL (green and blue) from a single DP-PPV derivative.

The thermotropic liquid crystalline phases of **5a** and **5b** were investigated by differential scanning calorimetry (DSC) and a polarized optical microscope (POM). Typical mesophase textures of the polymers are shown in Figure 4. A stable mesophase with a threaded texture and large domains was observed for **5a** at 170 °C. The nematic–isotropic transition was observed above 270 °C. The optical texture of the sample was almost unchanged after it was quenched to room temperature. Similarly, a mesophase with a very fine treaded texture was observed for **5b** at 190 °C.

We aligned **5a** and **5b** by a rubbing treatment at a LC state to give polarized optical properties.[17] The UV

---

[13] Oh, S. Y.; Ezaki, R.; Akagi, K.; Shirakawa, H. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2977. (b) Oh, S. Y.; Akagi, K.; Shirakawa, H.; Araya, K. *Macromolecules* **1993**, *26*, 6203.

[14] Synthesis of materials is given in Supporting Information.

[15] Wan, W. C.; Antoniadis, H.; Choong, V. E.; Razafitrimo, H.; Gao, Y.; Feld, W. A.; Hsieh, B. R. *Macromolecules* **1997**, *30*, 6567.

[16] Shi, Y.; Liu, J.; Yang, Y. *J. Appl. Phys.* **2000**, *87*, 4254.

[17] We use a Sigma Koki RM-50 rubbing machine consisting of a rotating roller on top of a moving sample stage. The polymers were spin cast on ITO glass, placed on the stage, and then heated to the thermotropic liquid crystalline phase (190 °C) before rubbing treatment. Rubbing treatment was performed for four times while the roller is moving at 500 rpm.

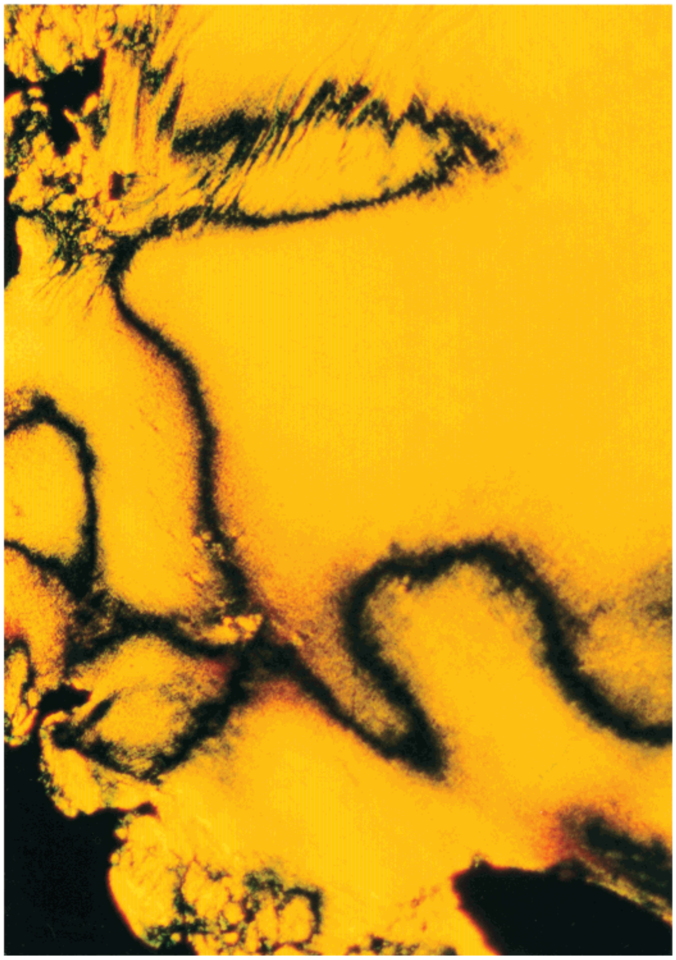


Figure 4. Optical textures of polymer **5a** at 175 °C (top) and polymer **5b** at 195 °C (bottom).

dichroism measurement was performed in the presence of a polarizer inserted between the sample and the light source parallel or perpendicular to the rubbing direction. As shown in Figure 5, a significantly larger absorption ascribed to a $\pi-\pi^*$ transition can be seen at the perpendicular polarized direction for **5a**. Rubbing induced chain alignment of **5a** was also detected by a polarized PL measurement. The dichroic PL spectra of

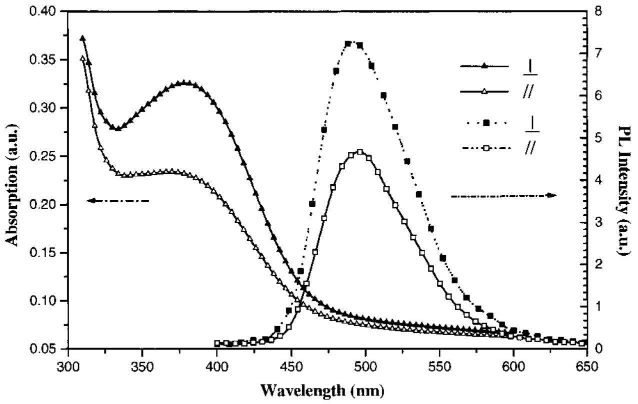


Figure 5. Polarized optical absorption spectra and PL spectra of polymer **5a**.

5a are shown in Figure 5, indicating that the light emitted from the rubbed film was preferentially polarized perpendicular to the rubbing direction. This is because rubbing at the thermotropic liquid crystalline phase induces alignment of the LC side groups along the rubbing direction and alignment of the polymer backbones perpendicular to the rubbing direction (Figure 6). As a result, relatively large absorption and emission are observed in the orthogonal direction with respect to the rubbing direction. The dichroic ratio, defined as the perpendicular to parallel fluorescence intensity, was 2.1, which was better than those for dialkoxy side chain liquid crystalline PPVs (1.2−1.4).[11] However, we did not see a large difference in peak intensity between rubbed and unrubbed films, suggesting that alignment may occur only at the surface.

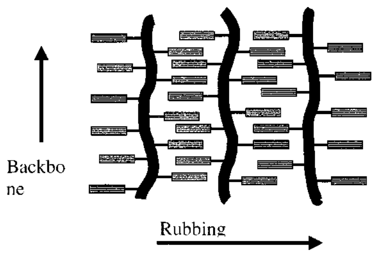


Figure 6. Alignment of LC side groups and polymer backbones due to rubbing treatment.

In summary, two DP-PPV derivatives with mesogenic side groups were synthesized and characterized. The polymers showed green-blue PL and EL. We showed clear evidence of nematic LC phases in these polymers. The polymers can be aligned by traditional rubbing treatment to give linearly dichroic PL with a dichroic ratio of 2.1. Polarized absorption and emission spectra for the rubbed polymers suggest their potential for polarized EL device applications.

Supporting Information Available: Text describing the details of the syntheses (3 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

CM000295F