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Synthesis, liquid crystalline and luminescent properties of trimeric phenylenevinylene with end-groups of (R)-(+)-2-methylbutyric acid ester

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Abstract

The trimeric phenylenevinylene with the symmetrical chiral end-groups (ChTPV) was synthesized. The liquid crystalline and luminescent properties of the ChTPV have been studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM), absorption and photoluminescence spectra. The results indicated that the ChTPV exhibits mesophase over a wide temperature range and a typical optical texture of smectic phase. In contrast with the spectra of the solution, that of the film showed blue-shift in maximal absorption and red-shift in maximal emission due to H-type aggregation with parallel alignment of the TPV transition dipole moment.

Keywords: Trimeric phenylenevinylene; Chiral; Synthesis; Liquid crystalline; Luminescence; H-type aggregation

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The π-conjugated polymers have attracted considerable attention because of their interesting properties such as organic optoelectronics [1]. The nano-scale ordering of π-conjugated polymers plays an important role in enhancing the performance of organic electronic devices [2]. But it has been proven difficult to control the nano-scale structure of rodlike conjugated polymers. One approach to control the nano-scale structure of conjugated polymers was to design molecules that could exhibit thermotropic or lyotropic liquid crystalline (LC) behavior [3]. However, only micron-sized domains are generally obtained because of the viscosity and rigidity of the polymers' extended backbone conjugation.

Use of conjugated, liquid crystalline oligomers can improve ordering, and several LC oligomers with flexible alkyl chains have been reported [4]. However, this introduction of the sterically hindering bulky groups disrupts coplanarity of the π-conjugated system. End-substitution is preferred for this reason; there are few reports about end-substituted OPVs that form LC phases [5]. Thus, development of novel OPVs with end-substituted that form LC phase has an

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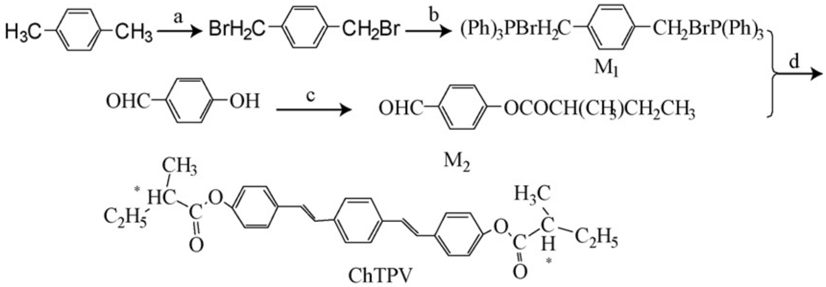

Fig. 1. Synthesis of ChTPV. Reaction conditions: (a) NBS, CCl_4; (b) DMF, PPh_3; (c) (R)-(+)-2-methylbutyric acid, DCC, DMAP, CH_2Cl_2; and (d) BuOK, THF.

important significance. This paper focuses on the synthesis, liquid crystalline and luminescent properties of the trimeric phenylenevinylene with end-groups of (R)-(+)-2-methylbutyric acid ester.

The ChTPV was synthesized by typical witting reaction (see Fig. 1) [6]. Reaction of the p-xylene with *N*-bromosuccinimide yielded 1,4-bis-bromomethylbenzene. Subsequently, the reaction of 1,4-bisbromomethylbenzene with triphenylphosphane yielded compound **M1**. The compound **M2** was obtained by the reaction of 4-hydroxy-benzaldehyde with R-(+)-2-methylbutyric acid. The data of the FT-IR, ^{1}H NMR and elemental analyses for ChTPV are shown as follows: FT-IR (KBr, cm^{-1}) 3024, 2968, 2920, 2850, 1753, 1597, 1514, 1462, 1375, 1203, 1166, 1124, 968, 904, 858,829; ^{1}H NMR ($CDCl_3$, 500 MHz, δ ppm): 7.53–7.50 (t, 8H, Ph–H), 7.13–7.09 (t, 4H, trans –C=C–), 7.07–7.04 (d, 4H, Ph–H), 2.66–2.60 (m, 2H, –OOC–H), 1.88–1.82 (m, 2H, $–CH_2–$), 1.67–1.61 (m, 2H, $–CH_2–$), 1.31–1.30 (d, 6H, $–CH_3$), 1.05–1.02 (t, 6H, $–CH_3$); anal. calcd. for $C_{32}H_{34}O_4$: C, 79.64%; H, 7.10%; found: C, 79.82%; H, 7.14%. On the basis of a detailed analysis of FT-IR, ^{1}H NMR and elemental analyses, the chemical structure was found to be consistent with the structure of ChTPV.

The three-dimensional solid-state packing of small molecules can be understood from the crystallization and melting behavior, therefore, the ChTPV was subjected to thermal analysis by DSC. The DSC thermograms of the ChTPV are shown in Fig. 2. The ChTPV shows transition at 54 °C for crystalline-to-LC and at 101 °C for LC-to-isotropic in the first heating cycle; however, it only showed the crystallization peak in the subsequent cooling cycle.

The ChTPV shows distinctive, strongly birefringent mesophase texture when analyzed by POM. The needle birefringence texture of the ChTPV is shown in Fig. 3. This texture was maintained up to 101 °C at a heating rate of 2 °C/min, indicating the isotropic transition at 101 °C. When the sample was cooled from 120 °C to room temperature, liquid crystal texture of needle shape was also observed between 101 and 50 °C. A needle shape of texture is a typical optical texture of smectic phase [7]. The result indicated that the ChTPV shows the chiral smectic phase between 50 and 101 °C.

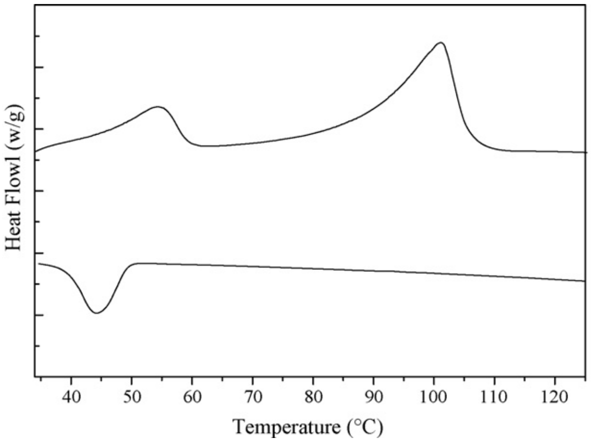

Fig. 2. DSC thermograms of the ChTPV.

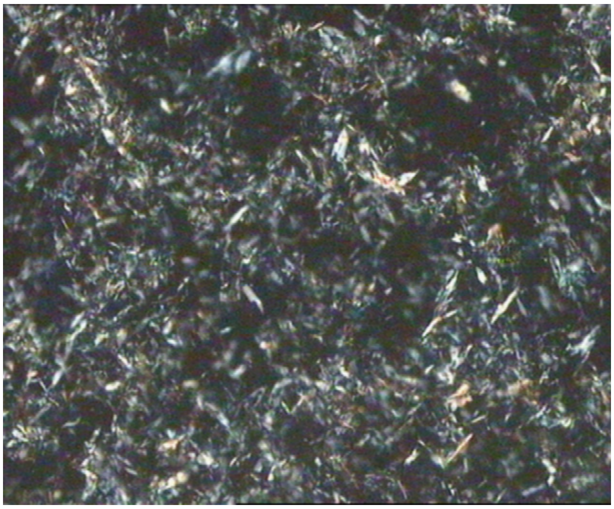

Fig. 3. Polarized optical micrograph of the ChTPV at 70 °C, 200×.

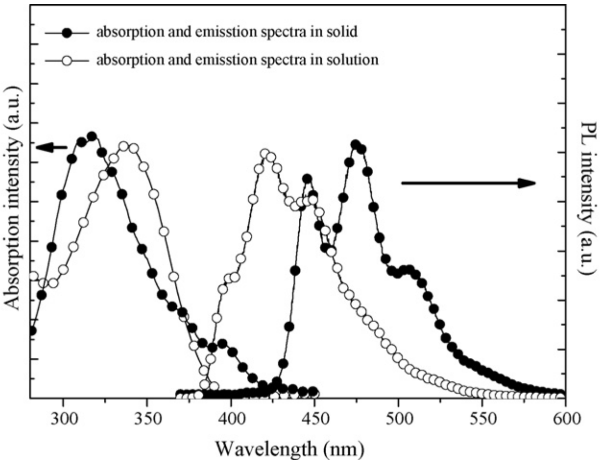

Fig. 4. (a) Absorption spectra and (b) photoluminescence spectra of ChTPV in dilute solution and films (excited wavelength in solution and film are 338 and 310 nm, respectively).

The chiral conjugated molecule from diluted solution or gaseity to solid state, H-type aggregation could formed, which was attributed to the strong intermolecular π–π stacking and the chiral-assembly [8]. Thus, UV–vis absorption and photoluminescence (PL) spectroscopy were used to investigate aggregation in the solution and in the thin film [9]. Fig. 4 shows absorption and photoluminescence of ChTPV in the dilute solution and thin films. Dilute, well-solvated solution of ChTPV in chloroform shows the maximum absorption at 338 nm. Surprisingly, the absorption peaks of the thin film appeared at 310 and 318 nm, which exists 30 and 20 nm of blue-shift compared with its dilute solution. The result is similar with parallel alignment of the TPV transition dipole moments [10]. Furthermore, two PL peaks appeared at 398 and 420 nm, and a shoulder band is located at around 446 nm in chloroform. In contrast with the emission bands in the dilute solution, that of the thin film shows markedly red-shift, the PL peaks appeared at 446, 475 and 505 nm, respectively. In contrast with solution, the thin film shows the enhanced vibronic structure, an absorption peak blue-shift and PL peak red-shift. The result indicates the H-type aggregation with parallel alignment of the TPV molecule in thin film. The driving forces of H-type aggregation for the thin film were attributed to the strong intermolecular π–π stacking and self-assembly.

In summary, the trimeric phenylenevinylene with terminal groups of (R)-(+)-2-methylbutyric acid ester was synthesized. This compound shows smectic phase with heating and cooling. In contrast with diluted $CHCl_3$, the maximal absorption presented distinct blue-shift and the maximal emission presented strong red-shift due to H-type aggregation of ChTPV molecule. We believe that the H-type aggregation was controlled by π–π stacking and chiral-assembly could significantly improve the performance of OPV-based material in the optoelectronic device.

Acknowledgments

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