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Original article

Effects of molecular configuration of a chiral trimeric phenylene vinylene on its liquid crystalline properties

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ABSTRACT

Based on an analysis of the ^{1}H NMR, FT-IR, UV–vis spectra, a chiral trimeric phenylene vinylene derivative (ChTPV) synthesized by a Wittig reaction was determined to have a *trans–cis* configuration, and it could be isomerized to the *trans–trans* isomer when treated with iodine. The melting point of ChTPV with a *trans–trans* configuration increased by 162.1 °C compared to the *trans–cis* isomer, and the ChTPV with *trans–trans* configuration exhibited the typical liquid-crystalline texture of the smectic A in the heating process. The results indicated that the molecular configuration can influence the formation of the liquid crystalline phase of ChTPV.

1. Introduction

Oligo(phenylenevinylene)s (OPVs) have received considerable attention since they can be used to prepare photoelectronic devices [1–3]. The molecular order plays a critical role in photoelectronic device performance, for example, both charge mobility and luminescent efficiency are influenced by molecular aggregation [4,5]. One approach to control the molecular order has been used to design molecules that exhibit thermotropic or lyotropic liquid crystalline (LC) behaviors [6,7]. In addition, new liquid crystals also can have potential applications in the fields other than the photoelectronic devices (separation membrane and heat-resistant materials) [8,9]. ChTPV is a chiral OPVs derivative, which is functionalized on both ends with a *R*-(+)-2-methylbutyric acid ester group. Synthesis of ChTPV and its self-assembly properties in H_2O/THF were studied in our previous work [10,11]. The reaction sequence to prepare ChTPV is illustrated in Scheme 1. However, the ChTPV with a *trans–cis* configuration was found unexpectedly as the major isomer based on a detailed analysis for ^{1}H NMR and FT-IR. The *cis*-configuration disturbs the formation of the liquid crystalline phase because *cis*-configuration generally leads to more non-planarity and exists in a twisted molecular conformation [12]. Furthermore, the *cis*-isomer isomerizes to the *trans*-isomer under refluxing in toluene with iodine as a catalyst [13]. In order to obtain the information of the molecular configuration and its effects on liquid crystalline properties, we report the configurational character and the liquid crystalline properties of ChTPV in this paper.

2. Experimental

The synthesis of the *trans–cis* ChTPV and *trans–trans* ChTPV is outlined in Scheme 1. The detailed procedure of the *trans–cis* ChTPV has been reported elsewhere [10]. The *trans–trans* ChTPV was purified by column chromatography, using silica gel and chloroform/petroleum ether (10:1) as the eluents.

Reagents were purchased from commercial sources (Aldrich) and used without further purification. *N*,*N*-dimethyl formamide (DMF), tetrahydrofuran (THF), carbon tetrachloride and toluene were distilled and purged with argon before use. ^{1}H NMR spectra were measured in $CDC1_3$ solution at 25 °C on an AVANCZ 500 spectrometer with tetramethylsilane (TMS) as the internal standard. FT-IR, UV–vis, and fluorescence spectra were measured, respectively, on an E55-FRA106 FT-IR, UV-3100, and RF-5301PC spectrophotometers. The differential scanning calorimetry (DSC, STA449C) analysis was used with a heating and cooling rate of 10 °C/min under a dry nitrogen purge. The optical textures were observed by polarized optical microscopy (POM, Olympus BX51) equipped with a hot stage calibrated to an accuracy of ±0.1 °C (Linkam THMS600).

3. Results and discussion

The aromatic area of the ^{1}H NMR of the two ChTPV isomers are shown in Fig. 1. The ^{1}H NMR spectrum of the ChTPV shows that the

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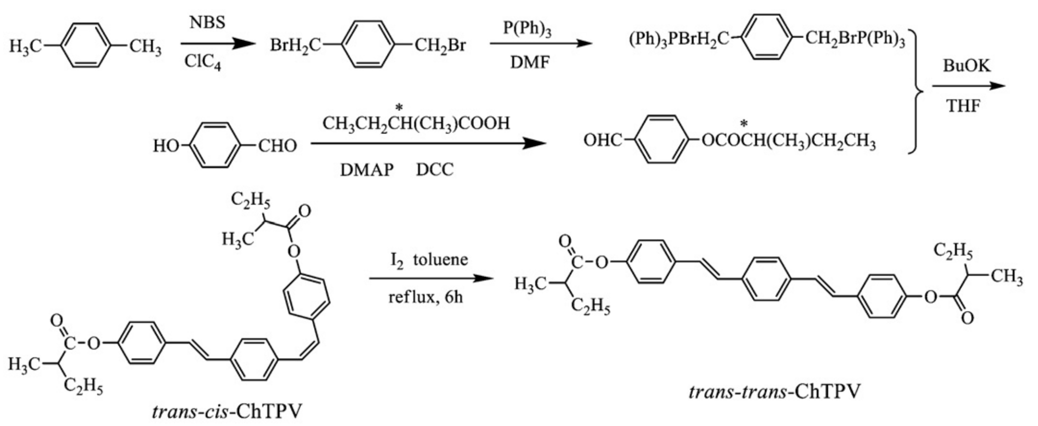

Scheme 1. Synthetic routes of *trans–cis* ChTPV and *trans–trans* ChTPV.

chemical shift of the vinylene protons appear at about 6.5 ppm with a coupling constant of 12 Hz, which is characteristic for the chemical shift and coupling constant of vinylene protons in the *cis*-configuration [12] (Fig. 1a). In addition, the chemical shift of the *trans*-vinylene protons appears also at about 7.1 ppm. Furthermore, the integral area of *cis*-vinylene protons is nearly identical to that the integral area of *trans*-vinylene protons. These results indicate that the *cis*-configuration and *trans*-configuration maybe exist simultaneously in one ChTPV molecule, namely the ChTPV adopts a *trans-cis* configuration. The iodine-treated ChTPV did not have the *cis*-vinylene protons at about 6.5 ppm, which indicates that the iodine-treated ChTPV shows an all-*trans*-configuration. The reason for the signals of the olefinic protons in *trans*-ChTPV shifting downfield compared to those in the *cis*-configuration is the decreased electron cloud density on the olefinic segments, because *trans*-configuration exhibits more planarity and greater conjugated effect in the bisstyryl benzene direction than that of the *cis*-configuration.

Fig. 2 shows the normalized FT-IR spectra with wavenumber of 1754 cm^{-1} as the standard (a), UV–vis and PL spectrum (b) of the ChTPV and the iodine-treated ChTPV. It is well known that the FT-IR spectroscopy is one of the most important analytical means of *cis/trans* configuration of the vinylene bond. The FT-IR spectrum of the ChTPV and the iodine-treated ChTPV shows a same absorption band at about 970 cm^{-1}, which is assigned to the out-of-plane bending mode of the C–H in the *trans*-vinylene [14]. Here, the intensity of the carbonyl stretch at 1754 cm^{-1} is invariant in the isomerization process from *cis*-configuration to *trans*-configuration, because the carbonyl group did not participate in chemical reactions. When FT-IR spectra is normalized using the wavenumber of 1754 cm^{-1} as the standard, the intensity of other absorption peak is proportional to the quantity of the groups. Based on the fact that the intensity of the frequency at 970 cm^{-1} (out-of- plane deformation of the *trans*-vinylene) doubled for the iodine-treated ChTPV compared to the original ChTPV, also indicating that the original ChTPV adopted a *trans–cis* configuration.

The UV–vis spectra of the ChTPV show that the maximal absorption peak at 338 nm with a shoulder peak of 275 nm. The former attributes to the π–π^* transition of the delocalized electron

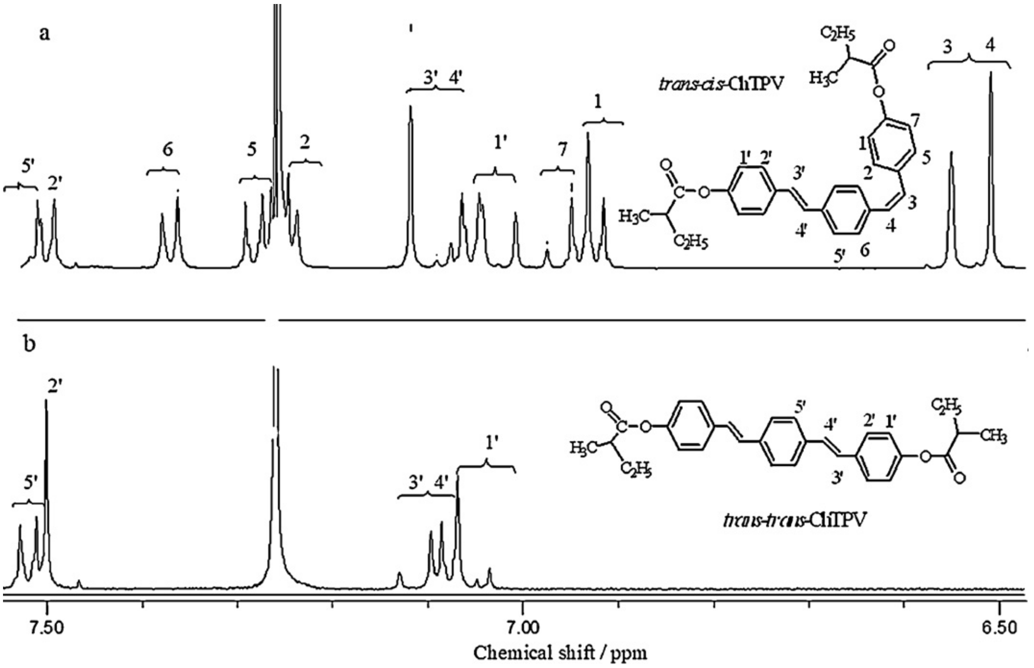

Fig. 1. ^{1}H NMR of the ChTPV (a) and the treated ChTPV with iodine (b).

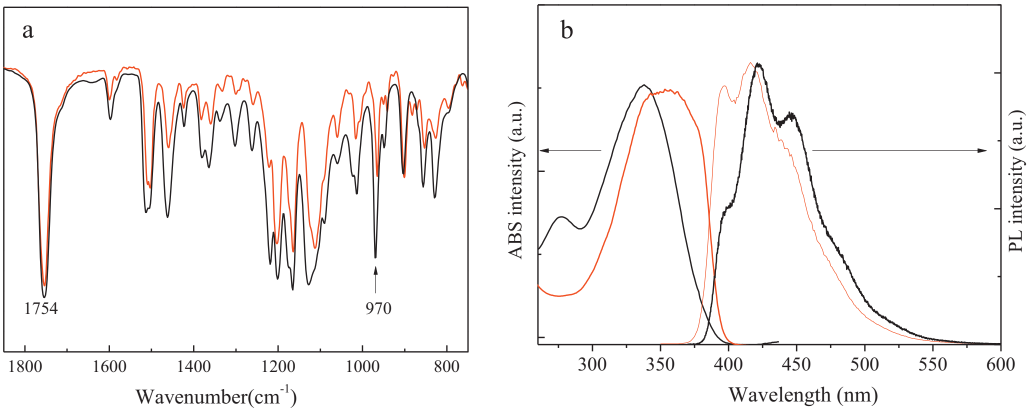

Fig. 2. Normalized FT-IR spectra with wavenumber of 1754 cm^{-1} as the standard (a), UV–vis and PL spectrum (b) of the ChTPV (black line) and the iodine-treated ChTPV (red line). (For interpretation of references to colour in this figure legend, the reader is referred to the web version of this article.)

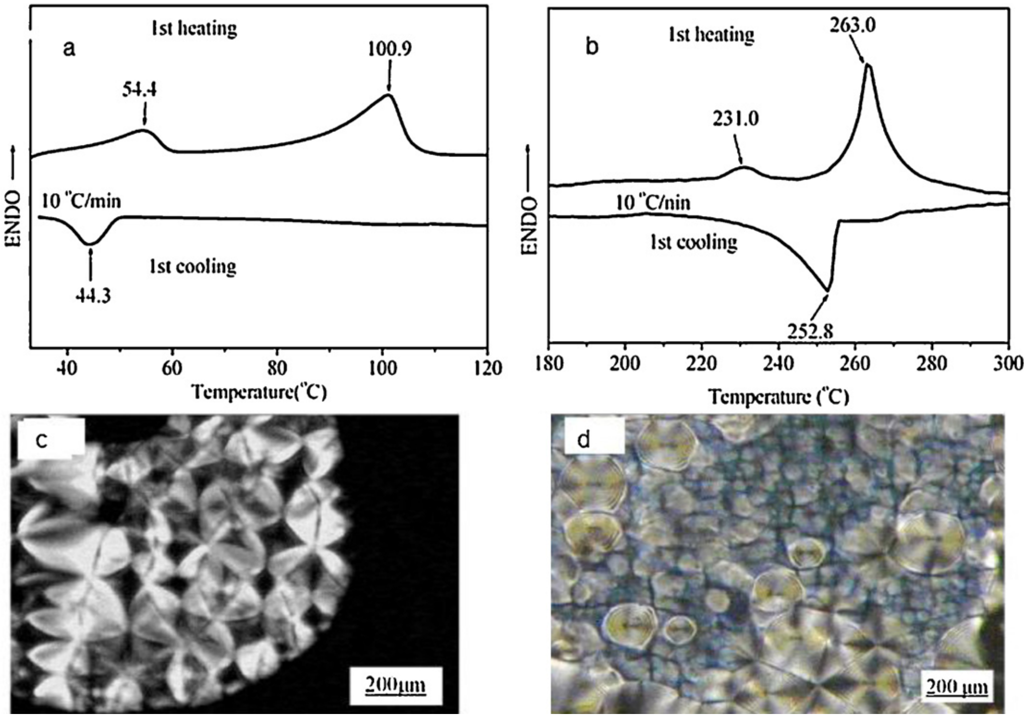

Fig. 3. DSC traces collected from ChTPV with heating and cooling rates of 10 °C/min ((a) ChTPV and (b) ChTPV treated with iodine) and POM photograph of the ChTPV treated with iodine ((c) 293 °C and (d) 298 °C).

and the latter is assigned to the π–π^* transition of the isolated bisstyryl benzene. In contrast to ChTPV, the maximal absorption peak of the iodine-treated ChTPV red shifts from 338 nm to 358 nm, indicating the electron delocalizes in all conjugated system. But their PL spectra show almost the same maximal peak, which is reasonable due to conversion of the configuration in excited state.

The liquid crystal properties of the ChTPV and the iodine-treated ChTPV were investigated using differential scanning calorimetry (DSC, Fig. 3a and b) and hot stage polarized optical microscopy (POM, Fig. 3c and d). Two endothermic peaks of the ChTPV with *trans–cis* configuration could be observed at 54.4 °C and 100.9 °C in the 1st heating process. The endothermic peak at 100.9 °C is consistent with the melting point and the peak at 54.4 °C belongs to the crystal-to-crystal transition. The exothermic peak in the 1st cooling process was found at 44.3 °C, which attributes to the peak temperature of crystallization. The ChTPV with *trans–trans* configuration also showed two endothermic peaks at 231.0 °C and 263.0 °C in the lst heating process. But, clear point was not observed in the heating process. Here, the endothermic peak at 263.0 °C is assigned to the melting point and the peak at 231.0 °C is also for crystal-to-crystal transition. But the ChTPV with *trans–trans* configuration exhibited a typical focal conic sector texture at 293 °C, 298 °C (Fig. 3c and d), which is assigned to smectic A mesophase.

4. Conclusion

In summary, the ChTPV with *trans–cis* configuration was obtained by a Witting coupling reaction, and the isomerization from *cis* to *trans* was realized using iodine as a catalyst. In contrast to *trans–cis* configuration, the ChTPV with *trans–trans* configuration shows higher thermal properties and a typical texture of smectic A mesophase.

Acknowledgments

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