Supramolecular self-assembly nature of a novel thermotropic liquid crystalline polymer containing no conventional mesogens†

Shengtong Sun,a Hui Tang,a Peiyi Wu*a and Xinhua Wanb

Received 19th May 2009, Accepted 29th June 2009
First published as an Advance Article on the web 4th August 2009
DOI: 10.1039/b909914j

Two-dimensional correlation infrared spectroscopy (2DIR) and a newly developed perturbation correlation moving window (PCMW) technique was employed to study the precise supramolecular self-assembly nature of poly[di(butyl)vinyl terephthalate] (PDBVT), a novel thermotropic liquid crystalline polymer which can self-assemble into a two-dimensional hexagonal columnar (2D $\Phi_H$) phase without conventional mesogens. PCMWD had found the weak phase transition temperature to be about 85 °C, and further divided the “S or anti-S” shaped spectral variations into three evolving stages. 2DIF results indicated that carbonyl groups acted as the starting point of molecular motions upon heating, and had a significant influence on the formation of the 2D $\Phi_H$ phase. Based on the additional motion sequence of symmetric and asymmetric C—H stretching vibrations, the whole self-assembly process of PDBVT on the mesoscale, whose backbones experienced “extension—distortion—slight extension” consecutive motions was elucidated.

Introduction

Combining properties of high molecular mass and liquid crystalline phase, liquid crystalline polymers (LCPs) have been well-known for their excellent anisotropic physical properties, easy processing and convenient molecular tailoring.1 In recent years, except for their classical applications in high strength fiber manufacturing, studies of LCPs have been further expanded to current active fields, such as polymer gels,2 thermoplastic elastomers,3 supramolecular assembly,4 information storage5 and template synthesis of nano-materials,6 etc.

Differing from well-known side-chain LCPs, mesogen-jacketed LCPs (MJLCPs), which were firstly proposed by Qifeng Zhou7 in 1987, possess mesogens laterally attached to the main chain with a covalent bond or a short spacer instead of long flexible decoupling spacers according to Finkelmann–Ringsdorf theory.5 This special attachment induces the flexible main chains of MJLCPs to take a relatively extended chain conformation compelled by peripheral high-density mesogens like a “mesogen jacket”, which gives them unique strength properties similar to main chain LCPs. With another advantage of facile radical addition polymerization, MJLCPs have attracted much attention recently, and large numbers of studies have been carried out devoted to the synthesis of new MJLCPs,9,10 the characterization of various self-assembly nanostructures,11,12 the mechanism of liquid crystalline phase development13 and the potential applications to high performance materials.14

However, if the mesogenic side groups of MJLCPs were replaced by flexible chains, novel LCPs which exhibit unexpected thermotropic liquid crystallinity without conventional mesogens can be obtained.9,12 As for Poly[di(alkyl)vinyl-terephthalate]s (PDAVTs) in Scheme 1, the rigidity of the pendant side groups is extremely weakened by incorporating linear alkyl groups into the 1,4-phenylene groups through ester linkages. However, it is especially noteworthy that no obvious mesophase transition of PDAVTs could be observed during DSC heating and cooling experiments except for the glass transition,9c,12 indicating the entropy driven nature of the phase transition. On the other hand, the mechanism of their mesophase development may be largely different from MJLCPs with conventional mesogens, such as poly(2,5-bis[4-methoxyphenyl]oxy carbonyl[styrene]} (PMPCS), which exhibits a molecular motion transferring process between side chains and backbones before and after LC phase transition according to our group’s previous work.13 Further investigation of the effects of side group size and architecture on the mesophase formation of PDAVTs had also been performed. It was demonstrated that PDAVTs could develop into a two-dimensional hexagonal columnar liquid crystalline (2D $\Phi_H$) phase only if the linear alkyl group was in an appropriate range ($m = 3–6$), and too short or too long side groups both resulted in the disruption of liquid crystallinity ($m = 1, 2, 8–12$).12c Recent research on the structure–property relationship of PDAVTs with branched alkyl groups indicated that the methyl

Scheme 1 General chemical structures of PDAVTs.

$\text{R} = C_n\text{H}_{2n+1}, m = 1–6, 8, 10, 12$

a The Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Department of Macromolecular Science and Advanced Materials Laboratory, Fudan University, Shanghai 200433, China. E-mail: peiyiwu@fudan.edu.cn
b College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China
† Electronic supplementary information (ESI) available: Operation details of 2Dcos. See DOI: 10.1039/b909914j
substitution number and position and the size of side groups all have some effect on the temperatures of glass transition and mesophase formation as well as the d-spacing value of the mesophase. Nevertheless, a precise description of the supramolecular self-assembly nature of PDAVTs has not been clarified yet.

Herein, we present our study of the supramolecular self-assembly nature of poly(di(butyl)vinylerethalate) (PDBVT) (\(m = 4\)) during heating, which can develop into an ordered 2D \(\Phi_1\) phase above the LC phase transition temperature, mainly by two-dimensional correlation spectroscopy (2Dcos) as well as a newly developed perturbation correlation moving window (PCMW) technique.

2Dcos is a mathematical method whose basic principles were first proposed by Noda in 1986. Up to the present, 2Dcos has been widely used to study the spectral variations of different chemical species under various external perturbations (e.g., temperature, pressure, concentration, time, electromagnetic, etc.). By spreading peaks along a second dimension, 2Dcos can sort out complex or overlapped spectral features and get an enhanced spectral resolution. Due to the different response of different species to external variables, additional useful information about molecular motions or conformational changes can be extracted which cannot be obtained straight from conventional one-dimensional spectra. Of especial noteworthiness, 2Dcos can discern the specific order occurring under a certain physical variable.

Perturbation correlation moving window (PCMW) is a newly developed technique, whose basic principles can date back to the conventional moving window proposed by Thomas, and later in 2006 Morita improved this technique to give much wider applicability through introducing the perturbation variable into the correlation equation. Except for its original ability in determining transition points as conventional moving window did, PCMW can additionally monitor complicated spectral variations along the perturbation direction.

In this paper, a largely different self-assembly nature of PDBVT from PMPCS is described, which further enriches the theoretical researches on the supramolecular self-assembly behavior of LCPs and may be helpful to provide some bases for molecular tailoring of new LCPs.

**Experimental**

**Materials**

PDBVT was synthesized via an atom transfer radical polymerization method. The number average molecular weight of PDBVT (\(M_n\)) is \(9.4 \times 10^4\), which can develop into a 2D \(\Phi_1\) phase above the phase transition temperature (\(~100 \degree C\) derived from the WAXD measurements). The polydispersity index of PDBVT \(M_w/M_n\) is 1.31 measured by GPC. No obvious mesophase transition can be observed in the DSC experiments except for the glass transition (\(~0.6 \degree C\)).

**FT-IR spectroscopy**

The sample of PDBVT for FT-IR measurements was prepared by a film casting method on a KBr tablet with tetrahydrofuran as the solvent. All time-resolved FT-IR spectra at different temperatures were recorded on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm\(^{-1}\), and 32 scans were available for an acceptable signal-to-noise ratio. Temperature dependent spectra were collected between 35 and 160 \degree C with an increment of 5 \degree C. Raw spectra were baseline corrected by the software Omnic ver. 6.1a.

**Methods**

**2D correlation spectroscopy.** FT-IR spectra collected in the temperature range 35–160 \degree C with a 5 \degree C interval were used to perform a 2D correlation analysis. 2D correlation analysis was carried out using the software 2D Shige ver. 1.3 (\(R\) Shigeaki Morita, Kwansei-Gakuin University, Japan, 2004–2005), and was further plotted into the contour maps by the Origin program ver. 8.0. In the contour maps, red colors are defined as positive intensities, while green colors are negative ones.

**Perturbation correlation moving window.** FT-IR spectra used for 2D correlation analysis were also used to perform perturbation correlation moving window analysis. Primary data processing was carried out with the method Morita provided and further correlation calculation was performed using the same software 2D Shige ver. 1.3 (\(R\) Shigeaki Morita, Kwansei-Gakuin University, Japan, 2004–2005). Similarly, the final contour maps were plotted by the Origin program ver. 8.0, with the same colors defined the same as in the 2D correlation analysis. An appropriate window size (2\(m + 1 = 11\)) was chosen to generate PCMW spectra with good quality.

**Results and discussion**

**A Conventional IR analysis**

Conventional IR spectrum of PDBVT measured at room temperature is presented in Fig. 1. Several spectral regions or isolated bands characteristic for PDBVT can be identified. The region 3100–2800 cm\(^{-1}\) mainly locates the C–H stretching vibrations, including both saturated CH from side alkyl chains and backbones and unsaturated CH from phenylene groups.

![Fig. 1](image)

Conventional IR spectrum (baselined) of PDBVT at room temperature (\(~25 \degree C\)) in the region 3100–650 cm\(^{-1}\) with a break from 2760 to 1770 cm\(^{-1}\).

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The band with the strongest intensity at 1722 cm\(^{-1}\) was contributed from the stretching vibration of C\(=\)O in the ester linkages. The region 1610–1500 cm\(^{-1}\) corresponding to the skeleton stretching vibrations of phenylene was disturbed by background noise due to the relatively weak spectral intensities. Several middle intensity bands between 1470–1380 cm\(^{-1}\) can be assigned to C–H deformation vibrations. Five strong bands at 1282, 1245, 1184, 1118, 1078 cm\(^{-1}\) may come from the stretching vibrations of C–O–C or C–C,\(^6\) while an apparent band at 755 cm\(^{-1}\) has been reported to be the out-of-plane bending vibration of phenylene.\(^{11e}\) In order to trace all the group motions of PDBVT, two regions were focused on to investigate the temperature dependent spectral variations: the region 3100–2800 cm\(^{-1}\) corresponding to C–H stretching vibrations and 1755–1680 cm\(^{-1}\) corresponding to C\(=\)O stretching vibrations.

Due to the weak intensity changes, spectral variations of the regions 3100–2800 and 1755–1680 cm\(^{-1}\) of PDBVT upon heating were presented by 3D representations for clarity in Fig. 2a. For the convenience of discussion, detailed band assignments in these two regions according to conventional IR as well as 2Dcos have been presented together in Table 1.

To further examine spectral variation tendencies, corresponding differential spectra of these two regions were also plotted in Fig. 2b. It is noted that nearly all the stretching vibrations of saturated CH between 2968 and 2800 cm\(^{-1}\) had intensities apparently decreasing with the increasing temperature, while that of unsaturated CH above 3000 cm\(^{-1}\) had intensities slightly increasing (hard to observe in conventional IR spectra for the compared low intensities with saturated CH). Of special noteworthiness, the band at 2985 cm\(^{-1}\) assigned to \(v_{as}(\text{CH}_3)\) (disorder) had intensity increasing intensively, which may result from the relatively free terminal CH\(_3\) largely transforming into the disordered phase with temperature increasing.

From conventional IR spectra, only a strong peak at 1722 cm\(^{-1}\) corresponding to a C\(=\)O stretching vibration can be found with decreasing intensity. However, differential spectra in this region appeared to have two splitting bands at 1736 and 1710 cm\(^{-1}\) respectively. From the perspective of spectroscopy, the band at 1722 cm\(^{-1}\) should be the overlapped band of those at 1736 and 1710 cm\(^{-1}\), and its decreasing intensity should result from the fact that the temperature-induced intensity decreasing effect on the band at 1710 cm\(^{-1}\) was more intense than the temperature-induced intensity increasing effect on the band at 1736 cm\(^{-1}\). That is, a conformation transition from the conformer at 1710 cm\(^{-1}\) to that at 1736 cm\(^{-1}\) might take place during the heating process. It was interesting to find that similar carbonyl band splitting phenomena existed in many chemical systems, sometimes along with a slight band shift.\(^{20}\) As space is limited, detailed investigations about the induced factors of carbonyl band splitting phenomenon as well as its influence on the LC phase formation of PDBVT will be discussed in another paper.

To find the LC phase transition temperature (\(T_{\text{LC}}\)) in order to trace the dynamic process of PDBVT at different LC phase evolving stages, the integral intensity variations as a function of temperature in the regions 3000–2800 and 1745–1700 cm\(^{-1}\) corresponding to the stretching vibrations of saturated CH and C\(=\)O were plotted in Fig. 3. The integral intensities have been normalized for the convenience of comparison between their intensity variation degrees. It is noted that the integral intensities of both regions appeared to exhibit a novel “anti-S-shaped” decreasing, indicating that the LC phase

![Fig. 2](image_url) (a) 3D representation of spectral variations in the regions 3100–2800 cm\(^{-1}\) and 1755–1680 cm\(^{-1}\); (b) the corresponding contour maps of differential spectra in these two regions. The spectrum collected at 35 °C was used as the reference spectrum. Red colors are defined as intensity increasing, while green ones are intensity decreasing.
transition of PDBVT is a weak first order transition. We estimated the integral intensity decreasing degrees of these two regions, and in consequence the region 3000–2800 cm⁻¹ showed a 10% intensity decrease while the region 1745–1700 cm⁻¹ showed a 7% intensity decrease, which are far below those of PMPCS. It is presumed that PDBVT may have a totally different self-assembly nature of LC phase development from that of PMPCS.

For an accurate determination of the transition temperature, Boltzmann fitting (using the Origin program) was employed for these two curves. The corresponding equation is as follows:

\[ y = \frac{A_1 - A_2}{1 + e^{(x-x_0)/\alpha}} + A_2 \]

(1)

In eqn (1), \( A_1 \) is the minimum value of the function; \( A_2 \) is the maximum value of the function; \( x_0 \) is the value on the \( x \) axis corresponding to the inflection of the curve, which also equals the transition temperature; and \( \alpha \) is the domain where this value lies.

The Boltzmann fitted curves are represented as the solid lines in Fig. 3, and the fitting results showed that for the region 3000–2800 cm⁻¹, \( x_0 = 84 \) °C, and for the region 1745–1700 cm⁻¹, \( x_0 = 94 \) °C. The difference is understandable due to the different response of different regions to temperature perturbation, and both the fitting results are close to that derived from WAXD (−100 °C). It demonstrates that the Boltzmann fitting method is a suitable approach to find the transition point for an “anti-S-shaped” curve.

### Table 1: Band assignments of PDBVT in the regions 3100–2800 cm⁻¹ and 1755–1680 cm⁻¹ according to conventional IR and 2Dcos respectively\(^{1,11,13,19}\)

<table>
<thead>
<tr>
<th>Wavenumber/cm⁻¹</th>
<th>Assignment</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3081, 3046</td>
<td>( \nu_{as}(CH) )</td>
<td>( \nu_{as}(CH) )</td>
</tr>
<tr>
<td>2956</td>
<td>( \nu_{as}(CH_3) )</td>
<td>( \nu_{as}(CH_3) )</td>
</tr>
<tr>
<td>2933</td>
<td>( \nu_{as}(CH_2) ) (side chains)</td>
<td>( \nu_{as}(CH_2) ) (side chains)</td>
</tr>
<tr>
<td>2910</td>
<td>( \nu(CH) ) (backbone)</td>
<td>( \nu(CH) ) (backbone)</td>
</tr>
<tr>
<td>2870</td>
<td>( \nu(CH_3) )</td>
<td>( \nu(CH_3) )</td>
</tr>
<tr>
<td>2841</td>
<td>( \nu(CH_2) )</td>
<td>( \nu(CH_2) )</td>
</tr>
<tr>
<td>1722</td>
<td>( \nu(C==O) )</td>
<td>( \nu(C==O) ) (different conformers)</td>
</tr>
</tbody>
</table>

Fig. 3  The integral intensity (normalized) variations as a function of temperature in the 3000–2800 cm⁻¹ and 1745–1700 cm⁻¹ regions. The solid lines were obtained from the Boltzmann fitting method.

B  Perturbation correlation moving window

As mentioned before, PCMW is an available method for determining transition points. The 2D synchronous and asynchronous spectra of PCMW performed in the regions 3100–2800 and 1755–1680 cm⁻¹ were presented in Fig. 4a and b respectively. From synchronous spectra \( T_{LC} \) was obtained to be about 85 °C, which was an approximate to the result derived from Boltzmann fitting on the integral intensities. It is notable that the transition temperatures determined from different bands in the synchronous spectra may give slightly different results, which comes from the different responses of different bands to temperature perturbation.

It is worth noting that for this kind of entropy-driven phase transitions, WAXD, Boltzmann fitting, PCMW approaches could give comparable \( T_{LC} \) of PDBVT, while DSC measurements could not. However, in consideration of testing costs as well as operating convenience, Boltzmann fitting and PCMW, which are both based on IR spectroscopy, are remarkably superior to WAXD.

We could also monitor the spectral variations along the temperature perturbation by combining the signs of synchronous and asynchronous spectra. The rules of PCMW (in the case of linear increment perturbation) proposed by Morita can be summarized as follows: positive synchronous correlation represents spectral intensity increasing, while a negative one represents decreasing; positive asynchronous correlation can be observed for a convex spectral intensity variation while a negative one can be observed for a concave variation.

According to the rules of PCMW, two apparent turning points at about 70 and 110 °C in the region 3100–2800 cm⁻¹ were identified, where a convex decrease and a concave decrease can be observed respectively between 2968 and 2800 cm⁻¹, while a concave increase and a convex increase can be observed above 2968 cm⁻¹. Between the two turning points a nearly linear decrease or increase took place, which appeared in the asynchronous spectra as the correlation intensity close to zero at the temperature range 80–90 °C. It can be described as an “anti-S-shaped” decreasing curve for bands in the region 2968–2800 cm⁻¹ and an “S-shaped” increasing curve for those in the region 3100–2968 cm⁻¹.
The temperature range 80–90 °C should be where the intensity changed fastest—that is, the LC phase transition occurred.

The case for the region 1755–1680 cm\(^{-1}\) was a little different, where three turning points can be observed from the asynchronous spectra. It indicates that the band at 1710 cm\(^{-1}\) appeared to exhibit a convex decrease at the lower and higher temperatures but a concave decrease appeared at the temperature where the LC phase transition occurred, and the situation was the reverse for 1736 cm\(^{-1}\). This phenomenon also contributed to the deviations from anti-S or S shaped dependence and Boltzmann fitted results, which may come from complicated carbonyl conformation transitions of PDBVT during heating.

To further verify the determinations obtained from PCMW, the absorbance intensity variations as a function of temperature at 2956 and 1710 cm\(^{-1}\) are presented in Fig. 5. The absorbance intensities were also normalized for the convenience of comparison. Boltzmann fitting was performed here to calculate \(T_{LC}\), which was 82 °C for 2956 cm\(^{-1}\) and 80 °C for 1710 cm\(^{-1}\), approximate to those derived from PCMW synchronous spectra. Examining the spectral variations at 2956 cm\(^{-1}\) carefully, we find that the temperature dependence of the absorbance intensity appeared to be an “anti-S-shaped” decreasing curve, with the convex decreasing at 70 °C and the concave decreasing at 110 °C as well as the nearly linear decreasing between these two temperatures. This observation was consistent with that determined from PCMW, and the verification at 1710 cm\(^{-1}\) was the same. It indicates that PCMW is a really good method for finding the transition points and greatly simplifies the investigation of complicated spectral variations at different wavenumbers and different external variables.

Two-dimensional correlation analysis

For a more detailed analysis of the supramolecular self-assembly nature of PDBVT, 2D correlation spectroscopy was employed. In 2D correlation analysis, two kinds of correlation maps—synchronous and asynchronous spectra are generated from a set of dynamic spectra.\(^{15}\) Synchronous spectra represent the simultaneous or coincidental changes of spectral intensities measured at two given wavenumbers \(v_1\) and \(v_2\). This spectrum is symmetric with respect to the diagonal line. Correlation peaks in the diagonal line \((v_1 = v_2)\) called

![Fig. 4](image)

**Fig. 4** 2D synchronous (a) and asynchronous (b) spectra of PCMW performed in the temperature range 35–160 °C in the regions 3100–2800 cm\(^{-1}\) and 1755–1680 cm\(^{-1}\). Red colors are defined as positive intensities, while green colors are negative ones.

![Fig. 5](image)

**Fig. 5** The absorbance (normalized) variations as a function of temperature at 2956 and 1710 cm\(^{-1}\). The solid lines were obtained from the Boltzmann fitting method.
Autoppeaks) correspond to the linear evolution of a certain species along the induced perturbation, whose intensities reflect the sensitivity of corresponding species. Asynchronous spectra represent sequential or unsynchronized changes of spectral intensities measured at two given wavenumbers $v_1$ and $v_2$. This spectrum is asymmetric with respect to the diagonal line. An asynchronous correlation peak can develop only if the intensities of two dynamic spectral intensities vary out of phase with each other. Asynchronous spectra can significantly enhance the spectral resolution. On the other hand, combined with synchronous spectra, the signs of asynchronous peaks can provide very useful information about the temporal sequence of events taking place during the studied process. The judging rule can be summarized as Noda’s rule—that is, if the cross-peaks ($v_1$, $v_2$, and assume $v_1 > v_2$) in synchronous and asynchronous spectra have the same sign, the change at $v_1$ may occur prior to that of $v_2$, and vice versa.

Confirmation of segmental modes. From the forementioned conventional IR and PCMW analysis, we concluded that the LC phase transition occurred at the temperature ranging from 80 °C to 90 °C, and an “anti-S-shaped” intensity decrease or “S-shaped” increase can be observed with two apparent turning points at 70 °C and 110 °C. To further investigate the supramolecular self-assembly nature of PDBVT by two-dimensional correlation analysis, a segmental analysis along the temperature perturbation was necessary. What we were mostly concerned with was the process of 2D ΦH phase formation, which mainly occurred between 70 and 110 °C. Therefore this middle temperature section should be emphatically analyzed, while the temperature section below 70 °C corresponding to the preparation for 2D ΦH phase formation was also worth studying. It is noteworthy that the higher temperature section above 110 °C corresponding to the perfection of the 2D ΦH phase cannot provide useful information about the self-assembly nature of PDBVT, and a non-negligible problem should also be considered that the thickness changes induced by the film flowing after the LC phase transition may have a significant influence on the spectral variations, thus the higher temperature section was beyond our discussion. Special attention should be given to the segmental analysis method because different segmental modes may lead to totally different conclusions according to our researches. To this system, a three-segment division based on two turning points seemed to be more reasonable than a two-segment division based on the transition point.

Primary two-dimensional correlation analysis. Fig. 6a and b shows us the synchronous and asynchronous spectra respectively for the regions 3100–2800 cm$^{-1}$ and 1755–1680 cm$^{-1}$ in the temperature range 70–110 °C. The synchronous spectra reflect simultaneous changes between two given wavenumbers. The bands at 2956, 2930, 2898, 2870 and 1712 cm$^{-1}$ (Fig. 6a) all have positive cross-peaks, indicating that they had a similar response in spectral intensity to temperature perturbation— that is, all decreased with increasing temperature determined from the raw spectra. On the other hand, the bands at 2985 and 1736 cm$^{-1}$ have spectral intensities which both increase with increasing temperature. This was consistent with the results derived from differential spectra and PCMW analyses.

The asynchronous spectra (Fig. 6b) had distinguished many subtle bands which could not be observed directly in conventional IR, such as 2985 and 2940 cm$^{-1}$ corresponding to the asymmetric stretching vibration of the disordered phase of CH$_3$ and CH$_2$ respectively. Four splitting bands (1707, 1712, 1731, 1741 cm$^{-1}$) in the region 1755–1680 cm$^{-1}$ had also been identified, which can be assigned to the stretching vibrations of different carbonyl conformers.

The sequence of group motions in the process of 2D ΦH phase formation. Except for enhancing spectral resolution, 2D correlation spectroscopy can also discern the specific order taking place under external perturbation. To simplify Noda’s rule and make it easier, we have proposed a relatively straightforward method. That is, we firstly listed all the signs of cross-peaks in asynchronous spectra, then returned to list the corresponding signs in synchronous spectra. Multiplication was performed in succession on these two signs of each cross-peak. The operational details have been provided in the ESI, and only the final results for the three kinds of correlation in Fig. 6 are presented together in Table 2. To each final sign of cross-peaks, two corresponding wavenumbers can be found on the left and bottom respectively. Because all the signs are above the diagonal line ($v_1 = v_2$) in accordance with our spectral-reading habits, the wavenumber on the bottom is affirmatively larger than the one on the left. Therefore, according to Noda’s rule, if the sign is positive (+), the larger wavenumber or the bottom wavenumber will respond to external perturbation earlier than the smaller wavenumber or the left wavenumber. Similarly, if the sign is negative (−), the left wavenumber will respond earlier than the bottom one. If the sign is zero (or blank), we cannot make an exact judgment.

With this approach, we can easily find out the specific orders in the process of the 2D ΦH phase formation. The sequence is as follows (→ means earlier than): 1731 cm$^{-1}$ → 2841 cm$^{-1}$ → 3041, 2985 cm$^{-1}$ → 1712 cm$^{-1}$ → 2870 cm$^{-1}$ → 2956 cm$^{-1}$ → 2930 cm$^{-1}$ → 2898, 2910 cm$^{-1}$ → 2940 cm$^{-1}$—that is, v(C=O) (1731 cm$^{-1}$) → v$_s$(CH$_2$) → v$_s$(CH$_3$) (disorder) → v(C=O) (1712 cm$^{-1}$) → v$_s$(CH$_2$) → v$_s$(CH$_3$) → v$_a$(CH$_2$) (side chains) → v(CH) (backbone), v$_a$(CH$_3$) (backbone) → v$_a$(CH$_3$) (side chains) (disorder). Without considering the differences in stretching modes, the sequence can be described as: C=O → CH$_3$ → phenylene, CH$_3$ → CH (backbone). It reveals that at the stage of 2D ΦH phase formation carbonyl firstly responded to temperature increasing, and then the adjacent flexible side chains and bulky phenylene started to adjust their conformations with the backbone the slowest response. This motion sequence is largely different from PMPCS with conventional mesogens. It is speculated that the formation of the 2D ΦH phase was contributed from the cooperative movements of these responding groups, and carbonyl played a key role as the starting point of group motions. The influence of carbonyl on the formation of the 2D ΦH phase may be closely related to its conformation
transitions as we mentioned before. And detailed discussion about this influence will also be discussed later in another paper. An intuitive representation of the sequence of group motions has been presented by the directions of dashed arrows in Fig. 8a.

Supramolecular self-assembly nature of PDBVT. A similar operation was performed to the temperature range 35–65 °C corresponding to the 2D Φu phase formation (Fig. 7). Due to the weak spectral variations in this temperature range, all cross-peaks in the synchronous spectra appeared to have lower
correlation intensities than those in the temperature range 70–110 °C (Fig. 6a). We deduced several main specific orders with the forementioned method as follows (operation details are also provided in the ESI): $v_{as}(CH_3)$ (2956 cm$^{-1}$) $\rightarrow$ $v_{as}(CH_2)$ (backbone) (2910 cm$^{-1}$) $\rightarrow$ $v_{as}(CH_3)$ (2870 cm$^{-1}$), $v_{as}(CH_2)$ (side chains) (2930 cm$^{-1}$) $\rightarrow$ $v_s(CH_3)$ (2841 cm$^{-1}$). We discovered an interesting phenomenon that in this temperature range the asymmetric stretching vibration had an earlier response than the symmetric stretching vibration, no matter for methyl or methylene groups in side chains and backbones. It is noted that the direction of asymmetric stretching vibration is parallel to the polymer chain axis while that of the symmetric stretching vibration is vertical to the polymer chain axis (as shown in Fig. 8b). Thus we concluded that there may be such a process occurring in 2D $\Phi_{11}$ phase formation in which the backbone first extended along the polymer main chain axis from the initial random coil state and then distorted laterally into a twist conformation in order to further self-assembly into the final 2D $\Phi_{11}$ phase. 

![Fig. 7](image-url)  

**Fig. 7** 2D synchronous (a) and asynchronous (b) spectra for auto-correlation of the region 3100–2800 cm$^{-1}$ in the temperature range 35–65 °C. Red colors are defined as positive intensities, while green colors as negative ones.

![Table 2](image-url)  

**Table 2** The final results of multiplication on the signs of each cross-peak for the regions 3100–2800 cm$^{-1}$ and 1755–1680 cm$^{-1}$ at the temperature range 70–110 °C

![Fig. 8](image-url)  

**Fig. 8** (a) The sequence of group motions at the stage of 2D $\Phi_{11}$ phase formation in the temperature range 70–110 °C. The asterisk (*) is described as the starting point, while the dashed arrows as the transferring directions of group motions; (b) the scheme of the direction relationship of symmetric and asymmetric C–H stretching vibrations with polymer chain axis; (c) schematic self-assembly process of 2D $\Phi_{11}$ phase formation of PDBVT on the mesoscale during heating. The blue and yellow colors represent different electron densities.
Then we returned to examine the specific orders in the temperature range 70–110 °C when the 2D ΦHI phase was evolving, and considered the orders of C–H stretching modes separately as we did at the lower temperature section. It was noticed that the symmetric stretching vibration had an earlier response than the asymmetric stretching in the temperature range 70–110 °C, which was opposite to the result in the temperature range 35–65 °C. It is understandable that at the 2D ΦHI phase formation stage the backbone of PDBVT had a sight conformation extension due to the close packing of bulky side chains after the continued distortion from its previous stage.

In the previous study, 2D WAXD results of PDAVTs showed an electron density difference between the center and the outside ring of the columns—that is, the polymer chains adopted a somewhat extended conformation with the cylindrical symmetry.12a The self-assembly nature we put forward was consistent with this observation and primarily explained the cause leading to the electron density difference.

The schematic self-assembly process of 2D ΦHI phase formation of PDBVT on the mesoscale during heating is presented in Fig. 8c. At lower temperatures, PDBVT was in its amorphous state, which can be described as a random coil. As temperature increased (35–65 °C), the backbone started to extend along the polymer main chain axis into a relatively stretched conformation, and then distorted laterally into a twist conformation. However, the distortion of backbones consequentially led to close packing of bulky side chains, which was unfavorable to the conformation stability of PDBVT. Thus as the 2D ΦHI phase evolved at higher temperatures (70–110 °C), a slight extension occurred to the backbone to adopt a somewhat extended conformation. These consecutive motions resulted in the final formation of the supramolecular 2D ΦHI phase. As the temperature is increased further, the perfection of this supramolecular structure takes place.

Conclusions

In this paper, we employed two-dimensional correlation infrared spectroscopy (2DIR) and the newly developed perturbation correlation moving window (PCMW) technique to study the supramolecular self-assembly nature of poly(di(butyl)vinyl terephthalate] (PDBVT), a novel thermotropic liquid crystalline polymer which can self-assemble into an unexpected two-dimensional hexagonal columnar (2D ΦHI) phase without conventional mesogens. Although DSC cannot provide any information of its phase transition, Boltzmann fitting and PCMW, which are both based on IR spectroscopy, had figured out the weak phase transition temperature to be about 85 °C, which is comparative to the result of wide-angle X-ray diffraction (WAXD) (~100 °C). PCMW had also been verified to be a good method to greatly simplify the investigation of complicated spectral variations.

In the PCMW analysis, two interesting types of spectral variations—“S-shaped” increasing and “anti-S-shaped” decreasing with two turning points at 70 and 110 °C were identified respectively. Based on these two turning points, a three-segmental analysis was chosen to perform 2DIR analysis.

2DIR results showed the sequence of different species in the process of the 2D ΦHI phase formation as follows: 1731 cm\(^{-1}\) → 2841 cm\(^{-1}\) → 3041, 2985 cm\(^{-1}\) → 1712 cm\(^{-1}\) → 2870 cm\(^{-1}\) → 2956 cm\(^{-1}\) → 2930 cm\(^{-1}\) → 2898, 2910 cm\(^{-1}\) → 2940 cm\(^{-1}\). That is, carbonyl firstly responded to increasing temperature, and then the adjacent flexible side chains and bulky phenylene started to adjust their conformations with the backbone producing the slowest response. As the starting point of molecular motions upon heating, carbonyl may have a significant influence on the formation of the 2D ΦHI phase, which may be closely related to its conformation transitions. Combining the motion sequence of symmetric and asymmetric CH stretching vibrations, we concluded the whole self-assembly process of PDBVT on the mesoscale, whose backbones experienced “extension-distortion–slight extension” consecutive motions.

Acknowledgements

We gratefully acknowledge the financial support of National Science Fund for Distinguished Young Scholars (No. 20425415), National Science Foundation of China (NSFC) (No. 20490220, 20573022, 20774022), the “Leading Scientist Project” of Shanghai (No. 07XD14002), the National Basic Research Program of China (No. 2005CB623800), and Ph.D. Program of MOE (No. 20050246010).

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