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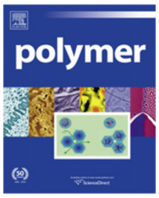

Conformational changes in novel thermotropic liquid crystalline polymer without conventional mesogens: A Raman spectroscopic investigation

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ABSTRACT

Raman spectroscopy was applied to study the conformational changes of poly[di(alkyl) vinylterephthalate] (alkyl = *n*-butyl and *sec*-butyl). Spectral regions assigned to C—H, C—C and ester carbonyl stretching modes were utilized to provide information on the molecular motion, the relative content of *trans* and *gauche* conformers, and the specific interactions existed in the mesophase formation process of these novel thermotropic liquid crystalline polymers. Both the experimental results and the conformational analysis suggested that the aliphatic side groups do have a significant impact on the formation of stable liquid crystalline phase. Based on the van't Hoff relation, the thermodynamic parameters in the phase transition of poly[di(*n*-butyl) vinylterephthalate] were estimated ($\Delta H = 5.52$ kJ mol^{-1}, $\Delta S = 14.02$ J mol^{-1} K^{-1}), which were much smaller than the typical values generally obtained in first-order phase transition. Based on generalized two-dimensional correlation Raman analysis, specific interaction among the phenyl-ring in the mesophase development process was elucidated.

1. Introduction

Materials based on mesogen-containing liquid crystalline polymers have been widely used in numerous technological applications including high performance fibers, structural materials, thermoplastic elastomers, and information storage materials, etc. The desired attributes of liquid crystalline polymers in these systems are application-dependent, which vary substantially from main-chain liquid crystalline polymers to side-chain liquid crystalline polymers. To some extent, the mesogen structure and the mesophase behavior mainly governs the function and the utility of these materials [1].

Differing from conventional liquid crystalline polymers, poly[di(alkyl)vinylterephthalate]s (PDAVTs) is a series of interesting liquid crystalline polymers [2–4]. The rigidity of the pendent side groups is weakened by incorporation of linear alkyl groups into the terephthalate residues. Although there is no conventional mesogen in the polymer, it is capable of forming hexagonal columnar phase at temperature much higher than its glass transition, which is characterized by wide-angle X-ray diffractions [4]. However, it is especially noteworthy that no obvious mesophase transition could be observed during DSC heating experiments, indicating the potential entropy-driven nature during the thermotropic phase transition of PDAVTs.

Recently, the self-assembly nature of poly[di(*n*-butyl)vinylterephthalate] (PDBVT) was studied *via* temperature-variable Fourier transform-infrared spectroscopy (FT-IR) and correlation analysis [5]. Results display that the mesophase formation contributes from the cooperative movements of responding groups, and an "extension-distortion-slight extension" consecutive motion in the backbones was elucidated in the self-assembly process. Further investigation of the architectural effects of pendent side groups on the mesophase behavior of PDAVTs was also carried out, which demonstrated that the mesophase formation depends partly on the presence of suitable length of aliphatic side chains [6]. Nevertheless, a satisfactory model explaining the conformational changes of the pendent alkyl side groups during the amorphous-mesomorphic transition is lacking and the specific interaction in the mesophase formation has not been clarified yet.

It is well-known that hydrocarbon chains are among the most important structural units in organic chemistry [7,8]. In many cases, conformational impact of hydrocarbon chains on the physical and chemical properties of molecular systems are discussed since they are correlated closely to the arrangement of molecules in the systems. Infrared and Raman spectroscopic investigations are of the most importance which has been utilized to study the relationship

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between the hydrocarbon chain conformation and the molecular assembly structure [9–11]. Although infrared spectroscopy can offer direct conformational order information for hydrocarbon chain-containing systems, it is proved to be inadequate for studying subtle molecular changes in conformational order due to the limitation in spectral resolution, activity distinction of alkyl vibrational modes, and experimental sensitivity.

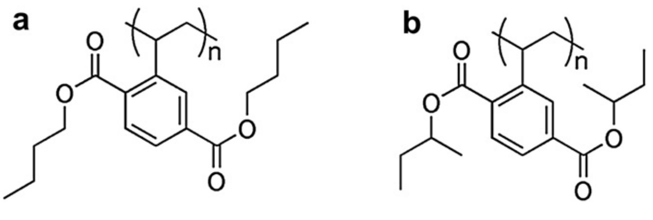
Comparatively, Raman spectroscopy has great advantage to provide information about the conformational change including the molecular motion (chain coupling, twisting and bending), the relative content of *trans* and *gauche* conformers, and the specific interactions [12]. Due to the intimate correlation to subtle molecular structural changes and intermolecular interactions, spectral indicators of conformational order in Raman spectral regions assigned to the ν(C–H), ν(C–C), and δ(C–H) vibrational modes have been widely utilized to examine the conformational order of alkyl chains in polymers and biological systems [10,11,13–17]. Recently, these parameters have also been used to investigate the conformational order of more complex systems [18–21].

In the present study, spectral indicators in the regions assigned to C–H, C–C and ester carbonyl stretching modes were attempted to be utilized to provide information on the polymer conformational change upon heating, and hence, the insight into the mesophase formation process. A comparison was made of the Raman spectra of PDBVT and poly[di(*sec*-butyl)vinylterephthalate] (*sec*PDBVT), so that the band assignment of the polymers were obtained and the conformational impact of hydrocarbon chains on the thermotropic property of polymers were discussed. Based on the van't Hoff relation, thermodynamic parameters in the phase transition of PDBVT sample were estimated. As a supplement of one-dimensional Raman spectra analysis, two-dimensional correlation Raman spectroscopy was applied in this work to discern information about the molecular motion order and the specific interaction occurring upon the temperature variation process.

2. Experimental Section

2.1. Materials

PDBVT and *sec*PDBVT samples were synthesized *via* traditional free radical polymerization method and the chemical structure of the samples was shown in Scheme. 1. For PDBVT sample, the number-average molecular weights (M_n) and the polydispersity distribution index (PDI, M_w/M_n) determined by gel permeation chromatography (GPC) instrument were 4.0×10^4 and 1.86. The thermal transitions of the samples were investigated *via* differential scanning calorimetry (DSC) on a TA Q100 calorimeter at a heating rate of 10 °C min^{-1} under continuous nitrogen flow. The glass transition temperature (T_g) was based on the second heating process after cooling at 2 °C min^{-1} from 200 °C. For the two samples we studied, the DSC curves were featureless except for glass transitions ($T_{g\ \mathrm{PDBVT}} = -12$ °C, $T_{g\ \mathrm{secPDBVT}} = 38$ °C). Two-dimensional hexagonal columnar phase was formed above 90 °C (derived from the polarized light optical microscope observation and wide-angle X-ray diffraction measurement) for PDBVT sample. For *sec*PDBVT sample, M_n and PDI were 3.6×10^4 and 1.72 and the mesophase developing temperature was about 70 °C.



Scheme 1. Chemical structure of a) PDBVT and b) *sec*PDBVT samples.

2.2. Raman spectroscopy

A Ranishaw Raman microscope (Renishaw inVia Reflex) equipped with an energy dispersive CCD detector (resolution better than 1 cm^{-1}) and a diode laser (785 nm) excitation source was used for spectral acquisition. The laser power is 300 mW. Spectra were collected in the spectral region of 4000–100 cm^{-1}. The polymers were heated at a rate of 1 °C min^{-1} and the spectra were collected from 40 to 160 °C at 5 °C intervals. Temperature was controlled *via* a temperature-controlled stage (Linkam, THMS-600) and the raw spectra were baseline corrected by the software Omnic ver. 6.0.

On the data analysis, the Raman intensity ratio was used. However, several bands are heavily overlapped. Therefore, mathematical deconvolution of the superimposed spectra to single bands represented as mathematical function (Gaussian function) were performed and assigned to the analytes before the intensity ratio was calculated.

2.3. Two-dimensional (2D) correlation analysis

Software OMNIC 6.0 programmed by Thermo Nicolet Corporation and Origin 7.5 were used to analyze the spectral data. Baseline correction points are taken at 1660 and 1220 cm^{-1} to overcome baseline shifts. 2D correlation analysis was performed with 2D Shige software (Shigeaki Morita, Kwansei-Gakuin University, Japan). The 2D correlation spectra were plotted into contour maps with Origin 7.5 program in which the white-colored regions were defined as the positive correlation intensities, whereas the gray-colored as the negative ones.

3. Results

3.1. Raman bands associated with liquid crystalline phase

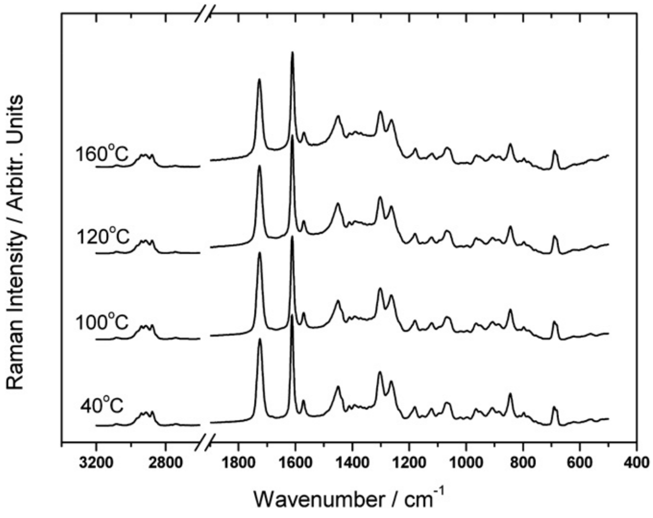


Fig. 1. Raman spectra of PDBVT sample in the 3200–500 cm^{-1} region obtained at 40, 100, 120, and 160 °C.

Temperature-dependant Raman spectra of the samples measured from 40 to 160 °C at 5 °C interval were performed in the 4000–100 cm^{-1} region. Due to the minor spectral variations in the other spectra regions, Fig. 1 only shows the representative Raman spectra of PDBVT sample in the spectral region 3200–500 cm^{-1} at 40, 100, 120, and 160 °C, respectively.

The most striking point about the Raman spectra at various temperatures is their similarity. This fact gives considerable support to the assumption that the side-chains and main-chain of the sample act as a whole to achieve mesophase during the mesophase developing process and no separately ordered structure is formed in the ethylene main-chain and terephthalate residue [2–4]. Similar phenomenon was observed in *sec*PDBVT sample. Table 1 lists the most prominent Raman bands in the spectra of the polymers, together with the suggested assignments [11,22–27].

3.2. *Relative content of trans and gauche conformers*

In the present study, spectral indicators in the regions assigned to the ν(C–H), ν(C–C), and δ(C–H) vibrational modes were used to study the relative content of *trans* and *gauche* conformers of PDBVT sample upon the heating process, respectively.

The experimental observations in the Raman spectra around 3050–2800 cm^{-1} could be classified into two categories: (1) methylene stretching bands peaked at *ca.* 2878 and 2913 cm^{-1} which were assigned to the symmetric and asymmetric CH_2 stretching mode in the side chain, respectively. Since the substituent groups in the phenyl-ring are carbonyl groups and the whole terephthalate residue is stabilized by conjugation [28], the corresponding C–H stretching modes of the alkyl groups in close proximity to the ester carbonyl moiety are of higher energy due to the coupling effects from σ-bonding compared to those in the polymer main-chain [23,25,29]. (2) methyl stretching region involving another two bands peaked at *ca.* 2938 and 2970 cm^{-1}, which correspond to the symmetric and asymmetric CH_3 stretching mode, respectively [11]. Differential spectra of PDBVT sample in the 3050–2800 cm^{-1} region obtained in the temperature region of 40–100 °C is shown in Fig. 2 a and the spectrum recorded at 40 °C was used as the reference. Mode frequencies change little as annealing temperature increase with the intensity increases.

Table 1
Raman band assignments of PDBVT and *sec*PDBVT sample.

Wavenumber (cm^{-1})	Assignment[a]	
	PDBVT	*sec*PDBVT
2975		asymmetric CH_3 str
2970	asymmetric CH_3, str	
2038	symmetric CH_2 str + symmetric CH; str (main chain)	symmetric CH_3 str + symmetric CH_2 str (main chain)
2913	asymmetric CH_2 str (side chain)	
2886	asymmetric CH_2 str (main chain)	asymmetric CH_2 str (main chain)
2878	symmetric CH_2 str (side chain)	
1725	C=O str	
1720		C=O str
1611, 1570	ring C–C str	ring C–C str
1450	CH_2 def	CH_2 def
1410	ring C–C str	ring C–C str
1392	CH_3 symmetric def	CH_3 symmetric def
1356		CH_3 sci
1303	CH_2 twist	CH_2 twist
1264	(ring-carbonyl str) + (O–C str) + (ring C–H in-plane bend)	(ring-carbonyl str) + (O–C str) + (ring C–H in-plane bend)
1120, 1077	skeletal C-C str	skeletal C-C str
1097	C-O str	C-O str
965, 950, 910	C-H rocking mode (*trans* sequence)	
875		CH_3 def
844, 796	ring out-of-plane C-H def	ring out-of-plane C-H def
691	ring C-H out-of-plane bend	ring C-H out-of-plane bend

[a] Key: def deformation; str stretching; bend, bending; wag, wagging; sci, scissor.

Raman ratio η ($I[\nu_{as}(CH_2)]/I[\nu_s(CH_2)]$) is a primary indicator of rotational and conformational order in alkane chains. Upon examining the ratio η in lipid and lipid–protein complexes, Larsson concluded that the ratio is sensitive to subtle changes in order for molecules in both disordered and all-*trans* configuration [14]. Rousseau described the utility of the relative intensity of C–H stretching mode to probe the conformation, environment and dynamics of hydrocarbon chains in triglycerides [25]. Since the mesophase formation of PDBVT sample depends in part on the presence of suitable length of aliphatic side chains and the polymer chains adopt a somewhat extended conformation with peripheral high-density aliphatic side chains [2,4,6], intensity ratio of asymmetric and symmetric CH_2 stretching modes in the temperature-variable Raman spectra were applied here to investigate the alkyl chain coupling effect and the conformational change in PDBVT sample.

Temperature dependence of the ratio η (I_{2913}/I_{2878}) is shown in Fig. 2 b. The ratio η maintains around 1.0 over the amorphous–mesomorphic phase transition boundary, indicating that the aliphatic chains in PDBVT sample were sufficiently decoupled to allow *gauche* conformers to be formed both in the amorphous state and in the mesomorphic state and the relative number of *gauche* conformers remained with increasing thermal energy. In the Raman spectroscopic analysis of octadecane, significant value change of ratio η from crystalline to liquid state has been observed (2.1–0.7) [7,8].

Intermolecular vibrational coupling information could also be investigated *via* the spectral changes in the symmetric CH_2 stretching mode [$\nu_s(CH_2)$], which is sensitive to the subtle chain interactions [10]. However, the $\nu_s(CH_2)$ shifts only 2 cm^{-1} from 40 to 160 °C in PDBVT sample, which is not adequately sensitive to describe the chain coupling effect of the system.

In hydrocarbon chain systems containing methyl groups, band near 2930 cm^{-1} could be assigned to a composite of two overlapped bands, one from the methyl group (2939 cm^{-1}) and the other from the methylene chain (2922 cm^{-1}) [11]. The peak-intensity ratio R (I_{2930}/I_{2878}) can be used to interpret the hydrocarbon chain assembly structure. Snyder compared the Raman spectra of crystalline and liquid polyethylene and investigated the variation in the ratio R from conformational changes [11]. For the crystalline polyethylene, the ratio R is 0.32, and for liquid state it is 0.53. In the present study, the ratio R of PDBVT sample varied from 0.78 to 0.89 in the temperature region between 40 and 160 °C, indicating that with temperature increment, the rotational and vibrational freedom of the terminal methyl groups increased and the intramolecular interactions decreased.

The aliphatic chain mobility reflected by the skeletal C–C stretching was investigated using Raman spectra in the 1220–1020 cm^{-1} region (Fig. 3 a). Both amorphous and mesomorphic state spectra of PDBVT sample produce broad band centered around 1120 and 1077 cm^{-1} due to the existence of *gauche* defects in the aliphatic side chains [22]. Larsson had described the utility of changes in spectral bands around 1100 cm^{-1} for determining alkane chain conformational orders in lipids systems. The relative numbers of *trans* and *gauche* conformers in alkane chains are indicated by the intensity ratio of $\nu(C–C)_G$ (~1080 cm^{-1}) to $\nu(C–C)_T$ (~1130 cm^{-1}) [30]. Unlike stretching modes in the ν(C–H) region, the ν(C–C) modes are sensitive to true *trans* and *gauche* conformers and not to methylene rotations or bond deformations. The *trans*/*gauche* ratio (defined as I_{1086}/I_{1128}) of PDBVT sample as

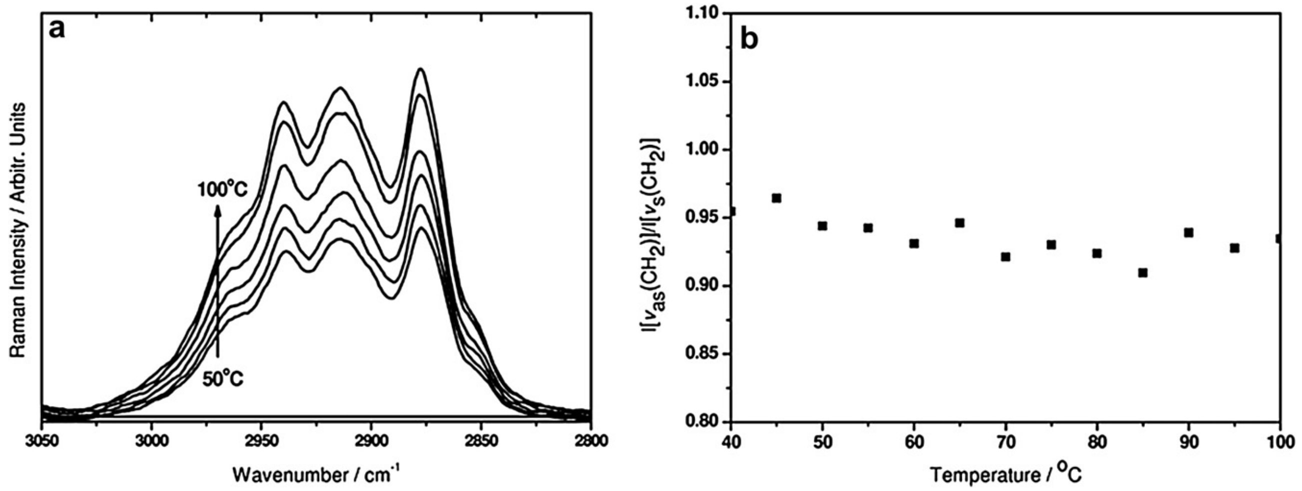


Fig. 2. a) Differential spectra of PDBVT sample in the 3050–2800 cm^{-1} region obtained in the temperature region of 40–100 °C (the spectrum recorded at 40 °C was used as the reference); b) Temperature dependence of ratio η (I_{2913}/I_{2878}).

a function of temperature is shown in Fig. 3 b. In the amorphous state, the ratio increased from 0.78 at 40 °C to 0.84 at 90 °C whereas eventually reached 1.13 at 160 °C, indicating that there is a substantial change in the *trans*/*gauche* ratio upon the phase transition. As temperature increased, chain disorder and mobility increased, and more *gauche* conformation was formed in the alkyl chain which is favourable for the ordered mesophase formation.

The relative *trans*/*gauche* content was defined as an equilibrium constant $K_{t/g}$, and the thermodynamic behaviour of phase transition could be studied according to the van't Hoff relation:

$$\ln K_{t/g} = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R}$$

It is assumed that the enthalpy and entropy change is not a function of temperature over the individual temperature range (40–90, 90–160 °C), which coincides with the main temperature range of the phase transition. The natural logarithm of K was plotted against the reciprocal of absolute temperature and the plot was analyzed by linear fitting to obtain the enthalpy over the transition temperature range (Fig. 4 a). The value of ΔH in the phase transition was determined to be 5.52 kJ mol^{-1}, and the value of ΔS was calculated to be 14.02 J mol^{-1} K^{-1}, which is much smaller than the value obtained by van't Hoff analysis in typical first-order phase transition (*e.g.* polymorph–liquid phase transition). Additionally, the weak phase transition temperature is figured out to be at *ca.* 85 °C, which is comparable to the result of wide-angle X-ray diffraction and 2D infrared correlation analysis [5].

It is especially noteworthy that it is the first time that the thermodynamic parameters of PDBVT sample were estimated. During the DSC heating experiments no obvious mesophase transition has been observed except for the glass transition (Fig. 4 b), indicating the potential entropy-driven nature of the mesophase transition. The entropy-driven isotropic–nematic transition in a liquid crystal system was first described in a classic paper of Onsager [31]. Though the aliphatic chains in the mesophase are translationally disordered, the molecules undergo a transition from the amorphous phase to the nematic phase upon heating and the orientations of the polymer chains are normally aligned. It may seem strange that the system increased its entropy by going from a disordered phase to an orientationally ordered phase. Actually, the entropy loss was offset by the increment in the translational entropy of the system, that is, the free-volume available increases as the molecules become more aligned [32].

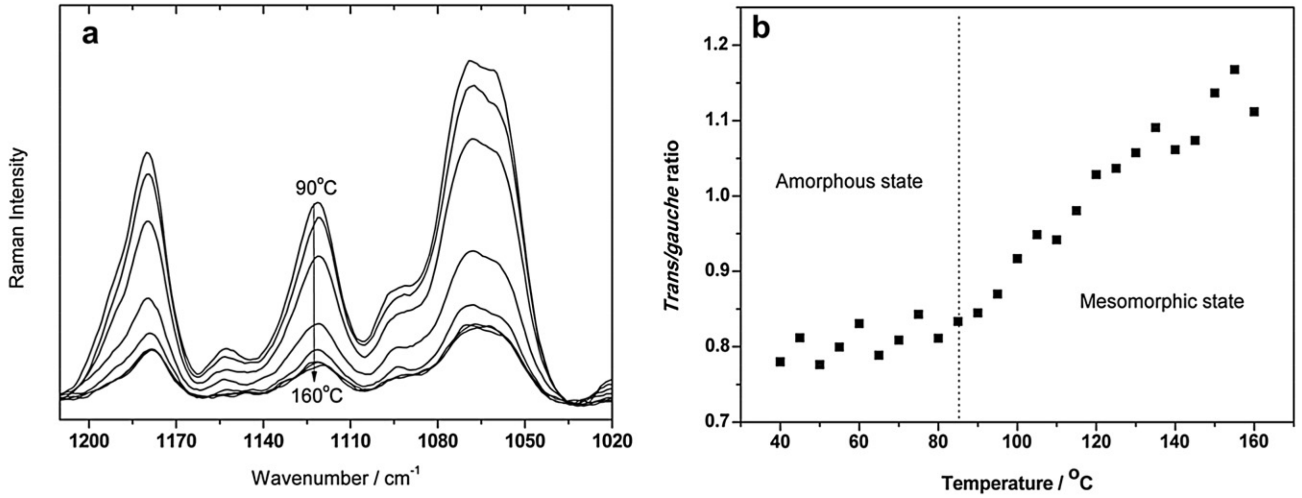


Fig. 3. a) Raman spectra of PDBVT sample in the 1220–1020 cm^{-1} region obtained in the temperature region of 90–160 °C; b) The *trans*/*gauche* content of PDBVT sample as a function of temperature.

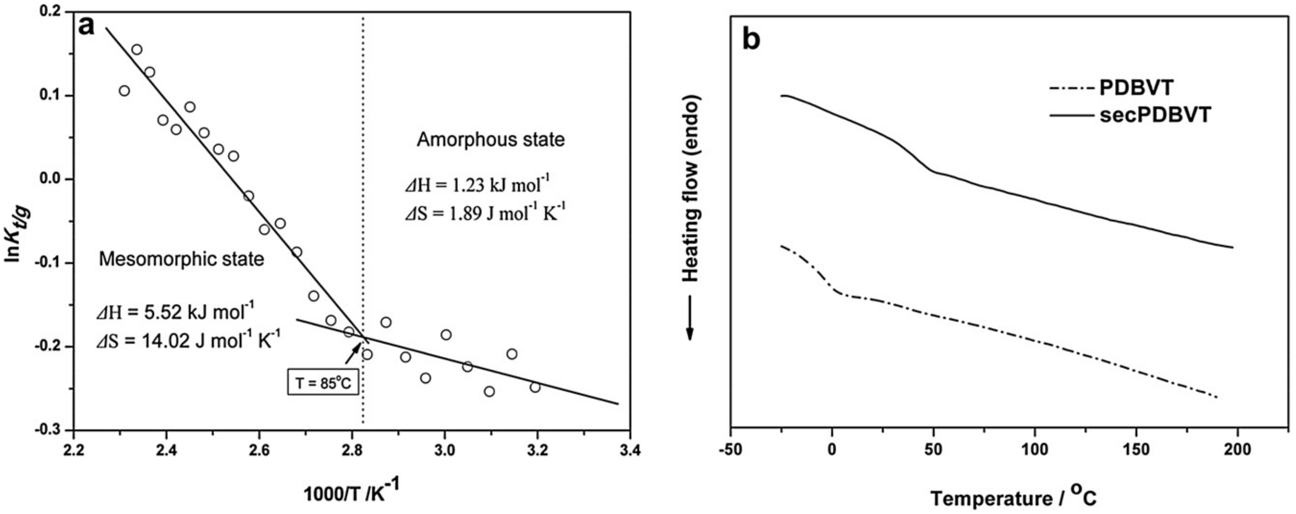


Fig. 4. a) A van't Hoff plot for PDBVT sample and the corresponding thermodynamic parameters in the phase transition; b) Differential scanning calorimetry curves of PDBVT and secPDBVT sample during the second heating process at a heating rate of 10 °C min^{-1} after cooling at 2 °C min^{-1}.

Marked change related to the *trans*/*gauche* ratio is also observed in the region around 990–720 cm^{-1} (Fig. 5 a). The band at 886 cm^{-1} is assigned to a C–H rocking mode of a *gauche* conformation of the aliphatic residue [11]. According to the Raman spectra of poly (*m*-methylene terephthalate)s, bands at 910, 950, and 965 cm^{-1} are assigned to the C–H rocking mode of a all *trans* sequence of crystalline glycol residue in the polymer with intensity increment on annealing. Band intensity ratio at 886 and 965 cm^{-1} as a function of temperature is shown in Fig. 5 b. It is to be noted that the ratio increased from 0.87 at 40 °C to 1.10 at 100 °C whereas eventually tended towards a plateau of 1.00 at 160 °C, indicating the increased number of *gauche* defects in the mesomorphic state.

3.3. Specific interaction among phenyl-ring groups

Two-dimensional (2D) correlation spectroscopy, proposed by Noda in 1986, has been widely used to monitor spectral intensity fluctuations of chemical species as an arbitrary function of external perturbations (*e.g.* time, temperature, pressure, concentration) [33–37]. By plotting spectral signals along the second dimension, 2D correlation spectrum emphasizes the spectral features not readily observable in conventional one-dimensional spectra and helps to probe the specific order of spectral changes under certain physical variables [38]. It has been shown that 2D correlation spectroscopy could provide more detailed information on the mechanism of thermodynamic liquid crystalline phase development than conventional one-dimensional spectroscopy [5,39,40]. As a supplementary of one-dimensional spectra analysis, 2D Raman correlation spectroscopy is applied in this work to discern information about the molecular motion and conformational change occurring under temperature variation.

The bands between 1660 and 1210 cm^{-1} region can be assigned to the stretching vibrations of phenyl-ring and C–H deformation vibrations. Generalized 2D Raman correlation analysis was carried out in the above Raman band region to explore the self-assembly nature of PDBVT sample upon heating. In the synchronous plot of 2D correlation spectra, the appearance of autopeaks which refer to the diagonal peaks represent that the intensity at this spectral region changes to a large extent [33]. Particularly, in 2D synchronous correlation spectrum from 40 to 110 °C (Fig. 6 a), a prominent

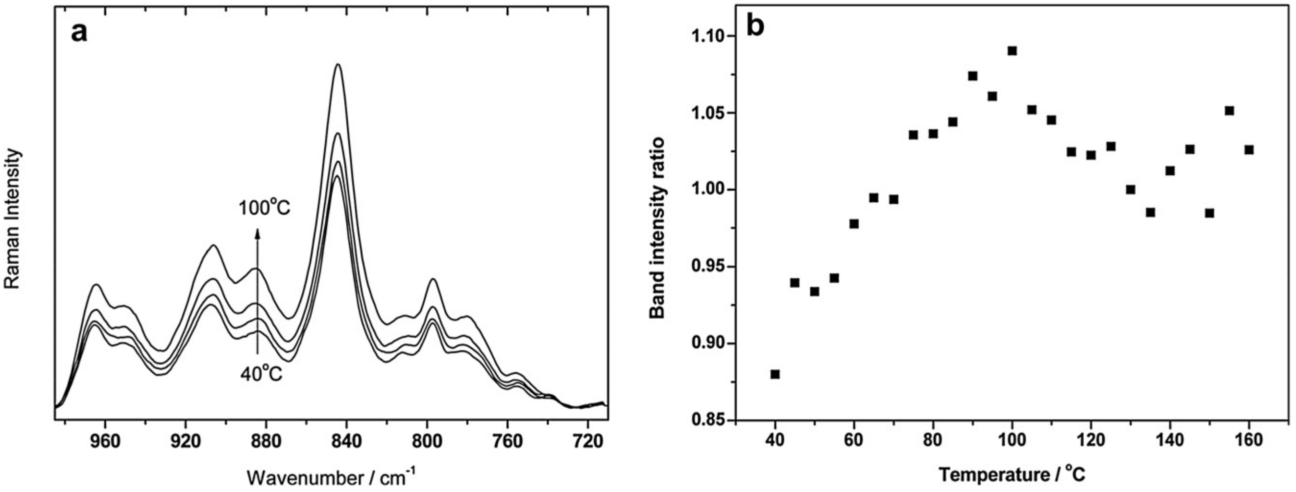


Fig. 5. a) Raman spectra of PDBVT sample in the 990–720 cm^{-1} region obtained at 40, 60, 80 and 100 °C; b) Temperature dependence of PDBVT band intensity ratio I_{886}/I_{965} from 40 to 160 °C.

autopeak at 1611 cm^{-1} was observed, which indicates significant temperature-dependent intensity variation in the above band region. The bands at 1611 and 1570 cm^{-1} are assigned to the C—C stretching mode of trisubstituted phenyl-ring. Apart from the temperature-dependant, the intensive correlation at above bands is indicative of specific interaction involved in the mesophase developing process. The appearance of crosspeaks in the synchronous spectrum indicates that the simultaneous intensity variations occurred at two different bands. Noticeably, a band located at 1450 cm^{-1} with moderate intensity in the 1D spectra shows crosspeaks with above bands due to the phenyl-ring stretching mode. The band at 1450 cm^{-1} is assigned to the CH_2 deformation mode of PDBVT sample. The white-colored (positive) crosspeak means the same trends of two bands upon temperature variation. According to the rule described above, crosspeaks around 1611/1303 cm^{-1}, 1611/1264 cm^{-1}, 1450/1303 cm^{-1}, and 1450/1264 cm^{-1} indicated that the band intensity changed in the same direction in the thermally induced process.

The corresponding asynchronous correlation spectrum is shown in Fig. 6 b. Asynchronicity is found between bands due to phenyl-ring and C—H deformation modes. According to Noda's rule, the off-diagonal crosspeaks in the asynchronous plot indicate that the intensity responses of corresponding bands occur at different rates [33]. From the sign of asynchronous crosspeak, it is possible to sort out the specific sequence of events responding to certain perturbation. The intensity change of the band at 1303 cm^{-1} due to the CH_2 twist mode occurs predominantly in comparison with that of the bands at 1615, 1606, and 1450 cm^{-1}. The bands at 1615 and 1606 cm^{-1} arise from the phenyl-ring stretching mode and the asynchronous correlation was attributed to a peak shift combined with the intensity changes or band splitting of 1611 cm^{-1} band. The intensity change of these phenyl-ring stretching bands reveals the specific interaction among the phenyl-ring side groups. Since the phenyl-rings stretching vibrations are influenced only by strong interactions, the specific interaction should be considerably favorable in the mesophase developing process [24].

With 2D correlation infrared spectroscopy, we studied the motion sequence of PDBVT sample in the heating process and an "extension—distortion—slight extension" consecutive motion of backbone has been elucidated. It is speculated that the mesophase formation contributes from the cooperative movements of responding groups, and the carbonyl groups play a key role as the starting point of group motion upon heating [5]. However, in the present study, specific interaction of phenyl-ring in the mesophase formation and the influence of conformational change of alkyl chain residues were emphasized. It explicated the fact that only if the alkyl group was in an appropriate range (from propyl to hexyl) could PDAVTs develop into two-dimensional hexagonal columnar liquid crystalline phase [4].

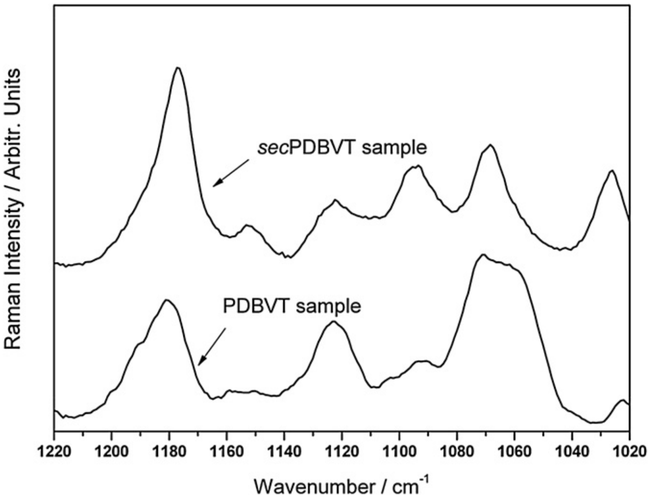


Fig. 7. Raman spectra of PDBVT and *sec*PDBVT samples in the 1220–1020 cm^{-1} region at 40 °C.

The bands in 1220–1020 cm^{-1} region are clearly complicated by overlapped bands, but it is reasonable to assign these to underlying phenyl-ring vibrations and C—H bending modes of the aliphatic residues. Fig. 7 shows the representative Raman spectra of PDBVT and *sec*PDBVT samples in the spectral region 1220–1020 cm^{-1} at 40 °C. Most strikingly, Raman spectrum of *sec*PDBVT sample shows an obvious increment in 1097 cm^{-1}. In poly(ethylene terephthalate) (PET) system, the band at 1097 cm^{-1} is to be associated with the planar terephthalate residue and assigned to C—O stretching mode [22]. During the crystallization process of PET, the reduction in intensity of above band is observed, indicating unfavourable planar form in the crystalline region. For the thermotropic LC polymers investigated in the present study, the phase transition temperature

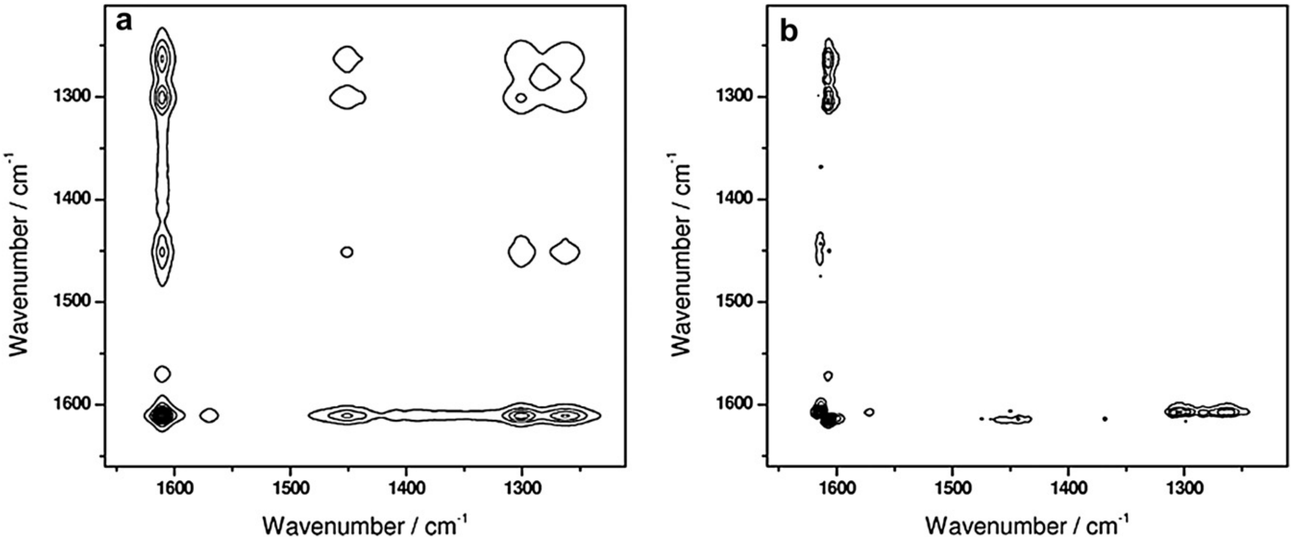


Fig. 6. Synchronous a) and asynchronous b) 2D Raman correlation spectrum of PDBVT sample obtained from 40 to 110 °C in the 1660–1210 cm^{-1} region.

of *sec*PDBVT is figured out to be about 70 °C, which is much lower than that of PDBVT. This result is consistent with the view that the terephthalate residue is in somewhat planar form and rotation of the carbonyl groups from the plane of the benzene ring is restrained due to the favourable specific interaction of aromatic residues in the amorphous-mesomorphic state transition.

3.4. Carbonyl groups in the liquid crystalline polymers

In our previous work, infrared spectroscopy is employed to elucidate the self-assembly nature and motional sequence of groups in PDBVT sample upon heating *via* correlation analysis. It indicated that carbonyl groups acted as the starting point of the molecular motions in the phase transition process, and had a significant influence on the mesophase formation. In support of this hypothesis, the thermal response of carbonyl groups during the phase transition is investigated *via* Raman spectroscopy.

Generally, the Raman spectrum in the region of 1780–1680 cm^{-1} contains the geometry information of the ester groups. Here, only one strong band at 1725 cm^{-1} corresponding to C–O stretching vibration was observed (Fig. 8 a). With temperature increasing, the band shifted to higher frequency with intensity decreasing. Differential spectra analysis in this region disclosed two splitting bands located at 1734 and 1716 cm^{-1}, respectively. As the temperature-induced hypochromic effect on the band at 1716 cm^{-1} was more intense than the hyperchromic effect on the band at 1734 cm^{-1}, the band intensity at 1725 cm^{-1} decreased. However, spectual decomposition is not a practical way to achieve individual components of bands due to the absence of any obvious peak components. It indicates that the ester carbonyl groups may be distributed in many local micro-environments in the amorphous state as well as in the mesomorphic state [41].

Temperature dependence of band intensity ratio I_{1725}/I_{1612} is shown in Fig. 8 b, which provides a measure of thermal sensitivity of different functional groups in the mesophase transition. The ratio increases from 0.78 at 40 °C to 0.86 at 100 °C, indicating that the carbonyl groups is sensitive to increased thermal energy than the phenyl-ring groups. However, the value changes significantly from 0.86 to 0.75 over the amorphous–mesomorphic phase transition boundary, indicates that the specific interaction among the phenyl-ring should be favorable in the mesophase developing process. Similar increment in the I_{1725}/I_{1612} value is observed in the successive heating process (120–160 °C).

It is worth noting that though splitting bands located at 1734 and 1716 cm^{-1} were disclosed *via* differential spectra analysis in the region corresponding to C–O stretching vibration, detailed discussion about the conformational change of carbonyl groups could not be carried out with the Raman spectroscopic analysis. Recently, a combination method of infrared spectral analysis and molecular simulation is employed to interpret the carbonyl band splitting phenomenon of PDBVT sample in the phase transition process. Based on the carbonyl rotation in pi-electron resonance system, four PDBVT conformers were put forward. It revealed that the rotation of carbonyls at 2-position (close to backbone) made a material contribution to the eventual formation of columnar phase [5].

4. Discussion

Now, we paid attention to the conformational influence of alkyl side chains in terephthalate residues on the liquid crystalline behaviour of liquid crystalline samples. Conformational properties of molecules are of increasing importance since they are correlated closely to the physical and chemical properties of the system. In many substances, the alkoxyl groups are found to play a significant role in the emergence of their functions. Experimental and theoretical studies have shown that the OC–CC bond prefers *gauche* conformation, whereas *trans* conformation is more stable than the *gauche* conformation for the CC–CC bond [42].

Jonas investigated the Raman noncoincidence effect and conformation of alkyl side chain in alkyl benzoate by applying high pressure [28]. Due to the conformational change in favour of a folded form of the alkyl side chain shielding the carbonyl groups (with the alkyl chain coiled towards the aromatic ring), possible close contact between methyl end and carbonyl groups which results in strong repulsion could be avoided by relatively long alkyl chain. It is notable that the energy difference between the folded and extended conformations is small.

According to Jonas's analysis results, the lowest energy conformation for alkyl benzoate residue is fully extended conformation with carbonyl groups exposed to the neighbouring molecules. With temperature rising, the molecular movement increased and the interaction between carbonyl groups on neighbouring molecules could be reduced due to the steric shielding effect of the folded alkyl chain. It is consistent with the above fact that there is a substantial change in the *trans*/*gauche* ratio upon the phase

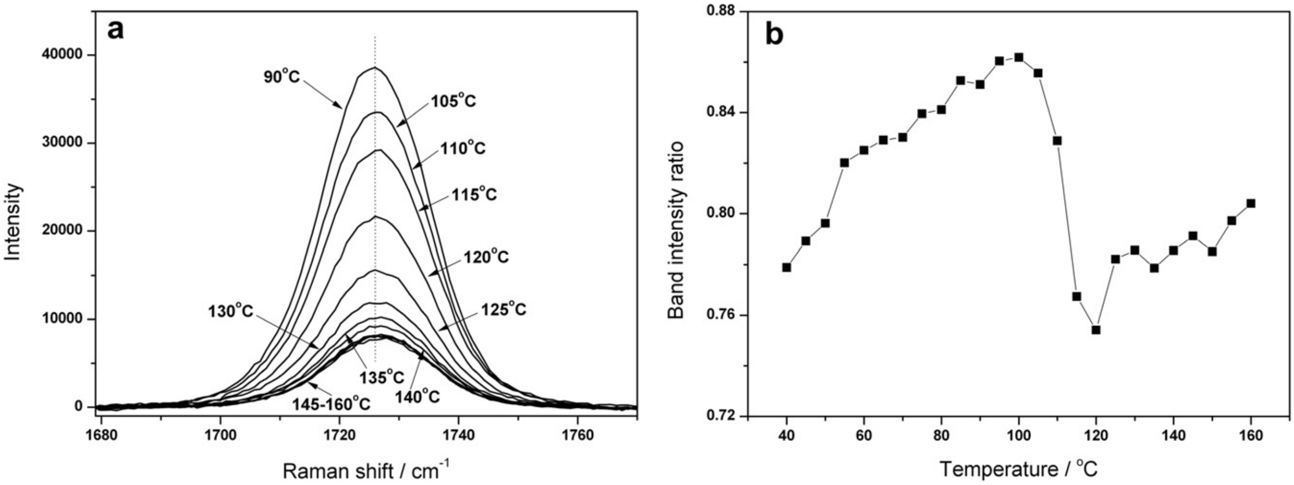


Fig. 8. a) Raman spectra of PDBVT sample in the 1780–1680 cm^{-1} region obtained in the temperature region of 90–160 °C; b) Temperature dependence of PDBVT band intensity ratio I_{1725}/I_{1612} from 40 to 160 °C.

transition. Since the volume of methylene units in hydrocarbon chains is smaller in the *gauche* conformation than in the *trans* conformation, the mesomorphic form in which more *gauche* conformation was formed in the alkyl chains should be of larger density than amorphous form. However, the discrepancy in density at amorphous and mesomorphic state of PDBVT has not been observed due to the limits of experimental sensitivity.

The thermotropic liquid crystalline nature of PDAVTs could be explained in the following way. At the first stage (amorphous state), small molecular segment movement is present in the polymer and the *trans*/*gauche* ratio remain essentially unchanged over the temperature range studied. As the molecular segment movement increased, the repulsive forces compel the molecules to change conformation. Thus, more *gauche* conformation was formed in the alkyl chain which is favourable for the mesophase formation, which may be helpful to provide some information for the entropy-driven nature of mesophase formation. In addition, specific interaction among the phenyl-ring was elucidated, which takes a majority role in the mesophase developing.

Besides, the effects of side group size on the mesophase formation of PDAVTs may also be illuminated. As mentioned above, two-dimensional hexagonal columnar liquid crystalline phase could only be developed if the linear alkyl group was in an appropriate range [4]. When the alkyl side group was too short (methyl and ethyl), little leeway was left for the conformation rearrangement and the energy barrier between folded and extended conformation is too large. As the alkyl chains are too long, the molecular mobility of side groups upon heating was substantially decreased which also resulted in the disruption of liquid crystallinity.

5. Conclusion

The present study demonstrates the conformational change in novel thermotropic liquid crystalline polymer without conventional mesogens *via* temperature-dependant Raman spectroscopy. Correlation of Raman spectral indicators for the determination of alkyl chain interactions and conformational change is presented. The aliphatic chains were sufficiently decoupled to allow *gauche* conformers to be formed both in the amorphous state and in the mesomorphic phase. Upon temperature increase, intermolecular interactions decrease and the terminal methyl groups experience increased rotational and vibrational freedom and more *gauche* conformation is formed in the alkyl chains. Raman spectra analysis of ester groups stretching vibration shows that the carbonyl groups may have many local micro-environments wherever in the amorphous and in the mesomorphic state.

Based on the van't Hoff relation, the thermodynamic parameters of PDBVT sample in the phase transition were estimated. Both the experimental results and the conformational analysis suggested that aliphatic side groups do have a significant influence on the formation of stable liquid crystalline phase, which is closely related to its conformation change in the heating process.

According to the generalized 2D Raman correlation analysis of stretching vibrations of phenyl-ring and C—H deformation vibrations, specific interaction between the phenyl-ring side groups was elucidated, which should be considerably favourable in the mesophase developing process. It is consistent with the view that the terephthalate residue is somewhat planar form and rotation of the carbonyl groups from the plane of the benzene ring is restrained during the mesophase formation process.

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