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# Photoluminescence and Raman spectra study of para-phenylenevinylene at low temperatures

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## Abstract

The photoluminescence and Raman spectra of poly (para-phenylenevinylene) (PPV) have been investigated at low temperatures down to 83 K. With decreasing temperature the photoluminescence spectra peaks are shifted to the lower energy side while the peak intensities are enhanced. The fitted Huang–Rhys parameter for the conjugated length has indicated that the conjugated length is elongated by 2.2 repeat units from 294 to 83 K. Though a distinct shift for the Raman band frequencies was not found, the Raman band intensities are, however, intensified at low temperatures. The Raman band intensity ratio  $I_{1548}/I_{1626}$  is enhanced with decreasing temperature, indicating that the disorder is reduced and the conjugated length is increased at low temperatures.

## 1. Introduction

Conjugated polymers, especially poly (para-phenylenevinylene) (PPV) and its derivatives have attracted tremendous interest due to their ease of synthesis via a soluble precursor route, from which high quality thin film can be obtained [1, 2]. Furthermore, PPV and its derivatives are among the most promising organic materials for exploitation in novel efficient optical and electro-optical devices; this is exemplified by the large number of studies devoted to the use of these polymers as emission layers in light emitting diodes [3–5], lasers [6, 7] and photovoltaic cells [8, 9]. It is therefore interesting to study the optical properties of PPV. At room temperature, spectroscopic experiments have been carried out to investigate in detail the structure—electronic properties of PPV, which depend not only on the synthetic methods used but also on the mechanical processes applied. For studying its optical properties, absorption and photoluminescence (PL) methods have been applied [10, 11]. Infrared, Raman and resonant Raman spectroscopy were used to analyse the ground state vibrational mode [12, 13]. The detailed structural information, such as conjugated length, defects and disorder of the chain, has been obtained by comparing with theoretical calculations for oligomers [14, 15].

The optical properties of a conjugated polymer are strongly related to the conformational defect and disorder of the chains [10]. It has been shown that the absorption and PL spectra of the oligo{2,5-bis[2-(S)-methylbutoxy]p-phenylenevinylene}s (OPV<sub>ns</sub> with *n* the number phenyl rings) shift to longer wavelengths with increasing conjugated length [16]. The variation in pressure [17], synthesis method [10] and temperature [16] can vary the conjugated length of the polymer. This work aims to study the PL and Raman spectra at low temperatures down to 83 K for a better understanding of the physical properties of PPV. We have found a PL red shift with decreasing temperature, but the Raman band frequencies have not been obviously changed. From the ratios between the vibronic intensities of the 0–0 and 0–1 transition, the dependence of the Huang–Rhys parameter on temperature has been obtained, by which the relative conjugated length of PPV is estimated to be elongated by 2.2 repeat units from 291 to 83 K. The Raman intensity ratio  $I_{1548}/I_{1626}$  is enhanced with decreasing temperature, which can also be reasonably attributed to the increase in conjugated length at low temperatures.

## 2. Experimental details

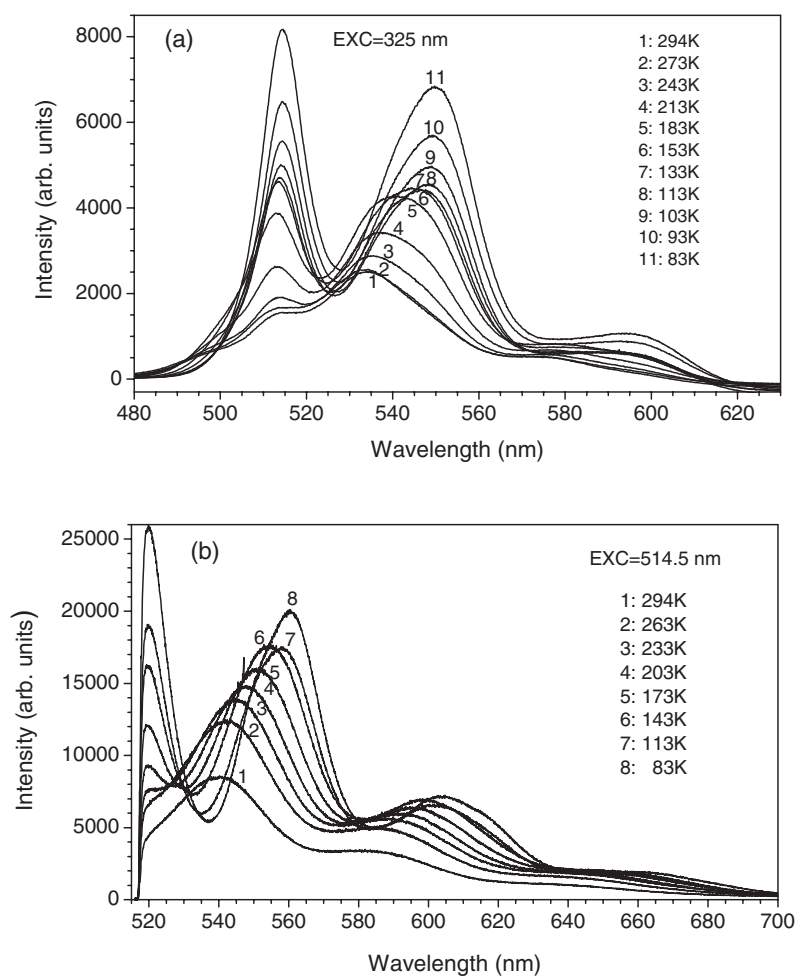
The precursor polymer to PPV is prepared following the standard polyelectrolyte Wessling routes [18], using  $\alpha$ ,  $\alpha$ -dichloro-*p*-xylene and tetrahydrothionphene as the starting reactants. Polymerization is carried out in methanol, with tetrabutylammonium hydroxide as a base catalyst. At the end of the polymerization, the reaction is quenched by neutralizing the basic reaction mixture with dilute HCl(aq) (0.5 M) to a pH of  $\sim$ 4–6. The PPV precursor was cast onto a glass substrate for preparing a free-standing film, and then heat-treated at 200 °C for 2 h in vacuum ( $\sim$ 10<sup>-5</sup> MPa). The PPV film is obtained by peeling off the substrate.

A confocal laser micro-Raman spectrometer (LABRM-HR) is used for obtaining the low temperature PL and Raman spectra in the reflect mode, with the PPV sample mounted in a nitrogen-flow cryostat at temperature down to 83 K. The focused 514 nm-line of an Ar<sup>+</sup> laser and an He–Cd laser of 325 nm wavelength, with a spot size 5  $\mu$ m in diameter and intensity less than 0.1 mW to avoid sample damage, were used for PL experiments, and a semiconductor laser of 785 nm wavelength for Raman measurements.

## 3. Results

Figure 1(a) shows the low temperature PL spectra of PPV for the excitation wavelength of 325 nm. Because the intensity of the second order diffraction of the grating in monochromator is very strong, the PL spectra cannot be exactly measured at about 650 nm with such an excitation wavelength. We then used another excitation wavelength of 514.5 nm for the measurement of the PL spectra in the higher wavelength range, as shown by figure 1(b). These two spectra provide complementary information about the full PL spectra. By comparing these two PL spectra with different excitation wavelengths, about 8 nm red shift is distinctly observed.

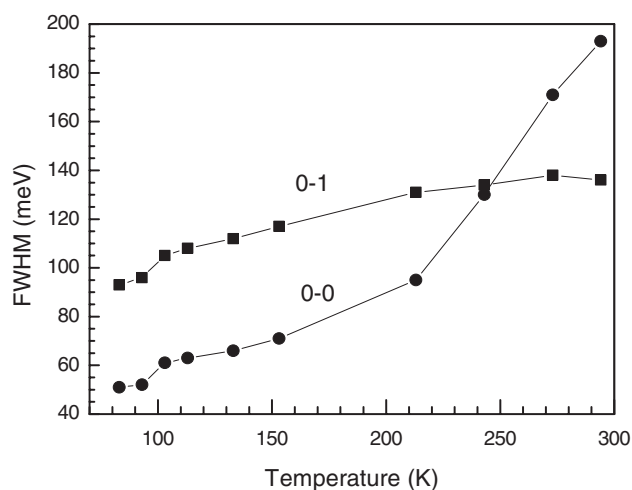
Generally, PPV emits fluorescence in yellow–green range. The yellow peak at 540 nm is attributed to the 0–1 transition, while the green peak at 515 nm is the 0–0 transition. The 0–2 and 0–3 transition peaks at, respectively, 584 and 630 nm, are relatively weak at room temperature. The four transitions all belong to the S<sub>1</sub>  $\rightarrow$  S<sub>0</sub> transition [16]. The low-temperature PL spectra (83 K) clearly show the four vibronic features (see figure 1). With decreasing temperature, the PL spectra peaks of 0–1, 0–2 and 0–3 are red shifted, with the peak intensities being increased. For the 0–0 peak, the intensity other than position shift is more obvious. By decomposing the full spectrum with Gaussian functions representing each vibronic component, we have obtained the full width at half maximum (FWHM) of each peak. For the 0–0 and 0–1 transitions, they decrease monotonically as a result of the decrease of the conformation defect, owing to the



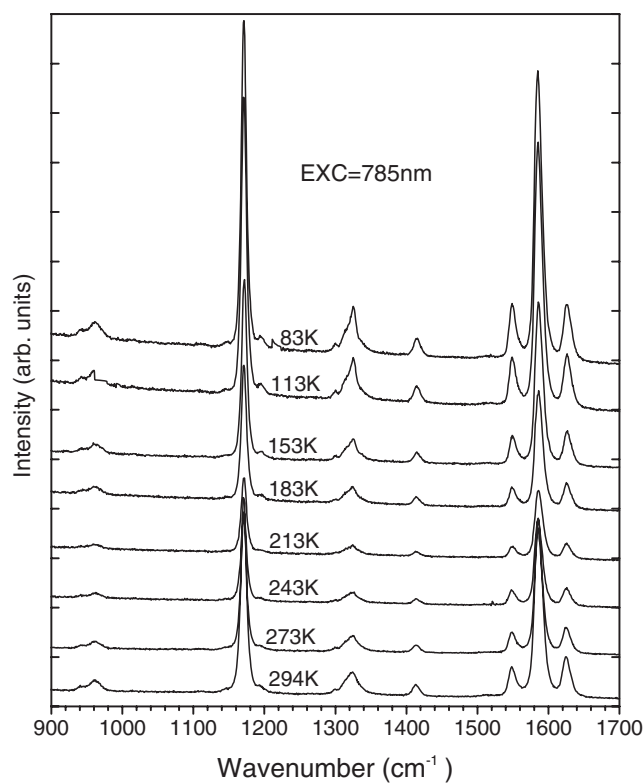
**Figure 1.** Photoluminescence spectra of PPV at various temperatures: (a) excitation wavelength at 325 nm; (b) excitation wavelength at 514.5 nm.

suppression of thermal disorder at low temperatures [19]. In figure 2 the low-temperature PL spectra (83 K) show that the FWHMs of the 0–0 and 0–1 transition vibrational bands have been narrowed by 140 and 44 meV, respectively, when compared with the high-temperature spectra (294 K). But for poly (2,5-bis(2-ethyl-hexyl)-1,4-phenylenevinylene), when cooled to the same temperature, the FWHM is only narrowed by about 45 meV for the 0–0 transition [19]. In addition, it is observed that for the 0–0 and 0–1 transitions, the behaviour of the temperature dependence of the FWHM is somewhat different for temperatures above and below 213 K.

Figure 3 shows the Raman spectra of PPV measured at various temperatures. In comparison with the PL spectra, the Raman band frequencies have not been distinctly shifted at low temperatures but the band widths have been reduced. This can be explained as follows: when the temperature is decreased, the PPV chains tend to become planar and the conformational defects of the PPV are diminished. Therefore, the ordering of the PPV chain is increased. In addition, it is interesting, however, to note that the Raman band intensities decreased initially with decreasing temperature from room temperature to 213 K, and increased from 213 to 83 K.

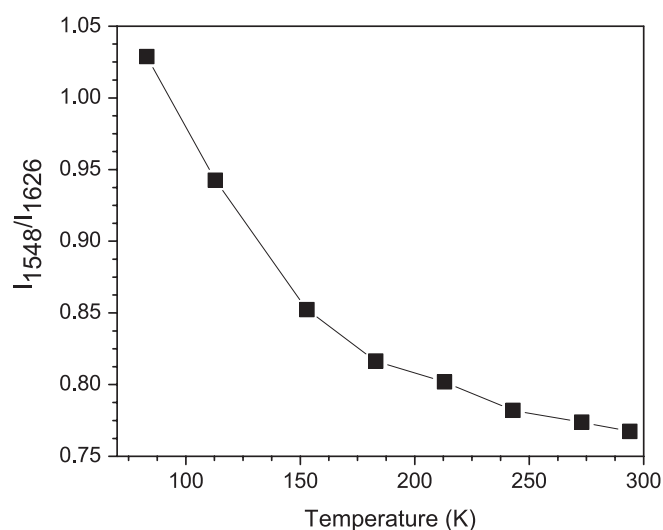


**Figure 2.** Temperature dependence of the FWHM of the PL peaks for 0-0 and 0-1 transitions.



**Figure 3.** Raman spectra of PPV at different temperatures.

In figure 4, the intensity ratio of the Raman bands between 1548 and 1626  $\text{cm}^{-1}$  ( $I_{1548}/I_{1626}$ ) versus temperature is plotted. It can be seen that this ratio, which is related to the chain planarity and conjugated length [20, 21], is enhanced with the decrease in temperature. The reason for such a variation may be due to the inducing of conjugation extension by the changes in the intercycle electronic distribution at low temperatures [22]. As a result, the degree of PPV chain conformation order is enhanced and the conjugation length is increased with decreasing temperature.



**Figure 4.** The Raman band intensity ratio  $I_{1548}/I_{1626}$  at different temperatures.

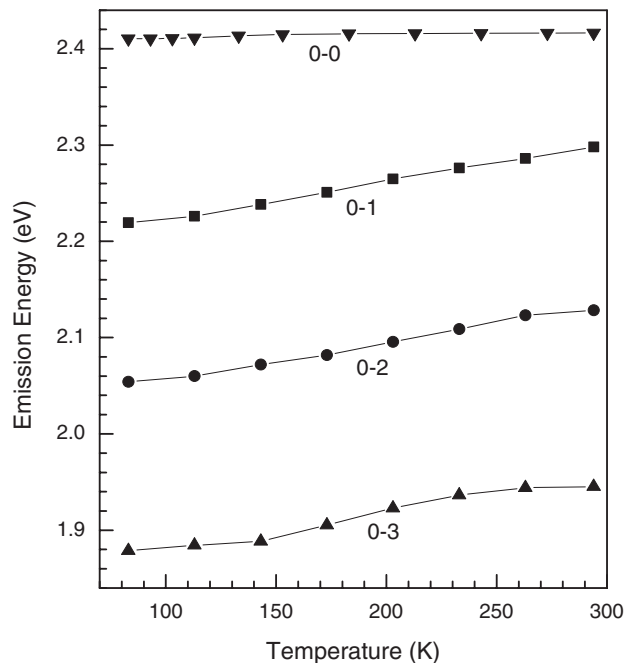
#### 4. Discussion

It is well known that the optical properties of a conjugated polymer depend on the chain's conformation, such as defects, disorder and twist, etc [10, 23]. The concept of conjugated length has played an important role in the study of the PL and Raman spectra of PPV. The conjugated length determines the energies of the electronic ground and excited states and also the extent of the electronic wavefunctions. Reports in the literature have indicated that the conjugated length has a strong effect on the PL spectra of  $OPV_{ns}$ , and that this varies with temperature [16]. With decreasing temperature, the coplanarity of the phenylene rings along the chain is enhanced and the  $\pi$  and  $\pi^*$  bandwidths are reduced, by freezing out of the torsion and loss of the conformational freedom. That means an increase of the conjugated length. Besides, another explanation suggested by Bassler *et al* is that exciton migration within the density of states occurs only energetically downhill to longer conjugated segments, and transfer to less conjugated segments is prevented [24]. As a result, the PL spectra are red shifted by cooling PPV. The four emission energies versus temperature are plotted in figure 5. With decreasing temperature, the emission energies for the four transitions are all shifted to lower energies. But the emission energy shift for the 0–0 transition is only 6 meV from 293 to 83 K, whereas for the other three transitions the emission energy shift is about 70 meV. Thus the temperature dependence of the 0–1, 0–2, 0–3 transitions are analogous, but different from 0–0 transition. From figure 2, it can be observed that the temperature dependence of the FWHM for the 0–0 transition is larger than for the 0–1 transition, which also shows that the two transitions are probably not analogous. More study is needed to fully understand this interesting phenomenon.

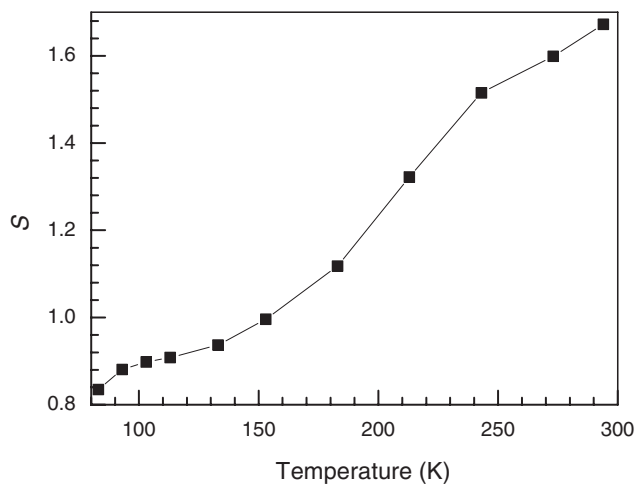
The probable reasons for the increased PL intensity at low temperatures are the results of reducing the main chain twists and the thermal disorder. This also implies that the chain structure of PPV has become rigid [25]. Therefore, the nonradiation recombination probability of the exciton is reduced.

The intensity of the consecutive vibronic bands in the emission is governed by the Franck–Condon factor. The intensities of the transitions between the vibrational ground state 0 in the electronic excited state and the vibronic level  $n$  in the electronic ground state are given by [16]

$$I_n = \frac{e^{-S} S^n}{n!}. \quad (1)$$

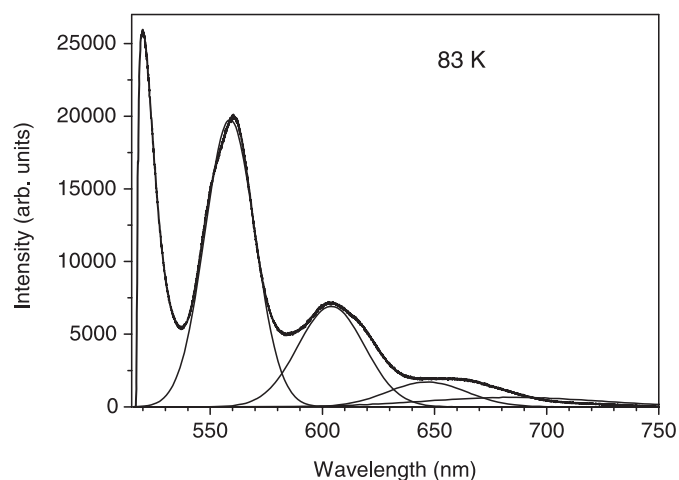


**Figure 5.** Variation of the emission energy with temperature for the 0-0, 0-1, 0-2, 0-3 transitions.

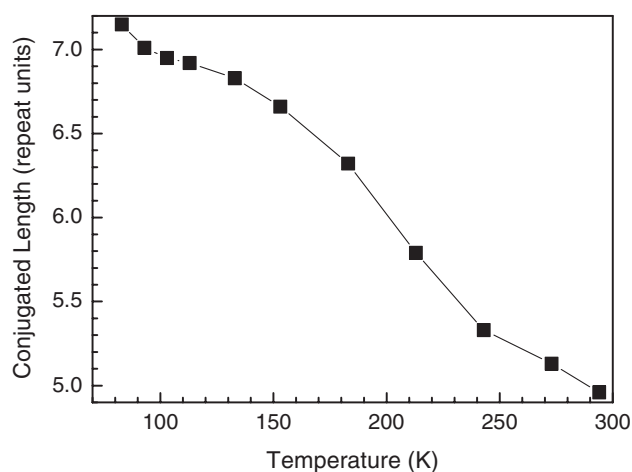


**Figure 6.** The Huang-Rhys parameter  $S$  as a function of temperature.

The Huang-Rhys parameter,  $S = I_1/I_0$ , where  $I_1$  and  $I_0$  are respectively the PL intensities for the 0-1 and 0-0 transitions, describes the extent of the geometry deformation in the excited state ( $S$  is proportional to the square of the displacement). From the plot of parameter  $S$  as a function of temperature in figure 6, it is obvious that the  $S$ -value is diminished with decreasing temperature. We know that the Huang-Rhys parameter is correlated with the disorder, i.e. the higher the disorder of the system, the larger the parameter  $S$  [16]. The dependence of the Huang-Rhys parameter on the conjugated length was also demonstrated theoretically by Shuai *et al* [26]. Therefore, a decrease in the value of the parameter  $S$  implies that the conjugated length is increased and the disorder is reduced at low temperatures. In addition,  $S$  can also be obtained from the 0-2 and 0-3 transition intensities. In figure 7 the PL



**Figure 7.** The PL spectrum decomposed into Gaussian functions at 83 K with an excitation wavelength of 514.5 nm.



**Figure 8.** The conjugated length obtained from the Huang–Rhys parameter  $S$  versus the temperature.

spectrum at 83 K has been decomposed into Gaussian functions. The  $S$ -values obtained from the intensity ratio between other transitions are  $S = 2I_2/I_1 = 0.837$  and  $S = 3I_3/I_2 = 0.840$ , which are also close to  $S = I_1/I_0 = 0.835$ .

For a quantitative understanding of the extent of the elongation of the conjugated length, we used an empirical formula to obtain the values of conjugated length at different temperatures:

$$S = a \exp\left(-\frac{N^2}{b}\right) \quad (2)$$

where  $a$ ,  $b$  are empirically chosen to be 3.2 and 38 [27], respectively, and  $N$  is the conjugated length with the unit of repeat unit. The calculated conjugated length at every temperature is plotted in figure 8. It can be seen that the conjugated length is increased by 2.2 repeat units from 293 to 83 K. At room temperature, the conjugated length is about 5 repeat units, which is lower than the obtained maximum value (8 repeat units) for coated PPV [23].

Compared with the PL spectra, the Raman bands have not demonstrated an obvious shift at low temperatures, indicating that the vibration frequencies are essentially unaffected by elongation of conjugated length. But the intensity ratio of the Raman band between 1548 and 1626  $\text{cm}^{-1}$  ( $I_{1548}/I_{1626}$ ) does increase with decreasing temperature (see figure 4). This



tendency agrees with the other reported observations for doped PPV [20, 21] that the conjugated length is enhanced with the increasing intensity ratio  $I_{1548}/I_{1626}$ .

## 5. Conclusion

At low temperatures, the PPV chain becomes rigid as well as the disorder and defects being reduced. Therefore, the conjugated length is increased by about 2.2 repeat units from 293 to 83 K. The PL spectra red shift and the intensities are intensified with the decrease in temperature. For the Raman bands, the vibrational frequencies have not been found to show any obvious changes. The intensity ratio of the Raman band between 1548 and 1626  $\text{cm}^{-1}$  ( $I_{1548}/I_{1626}$ ) increases with decreasing temperature, which also shows that the conjugated length is increased at lower temperatures.

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