

The Photoluminescence of Ph-LPPP Polymer Under Hydrostatic Pressure

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Abstract

The photoluminescence (PL) spectra of blue light emitted ladder type organic conjugated polymer (ladder-type poly para-phenylene) with trace concentrations of metallic impurities both in the form of thin film and powder at various pressures are measured. We find that the peak 00 in the PL spectrum of Ph-LPPP in the powder form is weaker than that of in film. A red shift and broadening of PL spectra with increasing of pressure in both forms are also observed. However, the shift rates in thin film and in powder are slightly different, which indicates the effect of aggregation on the PL of polymers. The effective conjugated length change of polymer under the pressure is discussed. By this investigation, we conclude that the structure, therefore, the interaction between chains of the polymer plays an important role in its PL spectrum.

Key Words: Polymer, Photoluminescence, Hydrostatic Pressure, Red Shift

1. Introduction

Ladder-type poly (p-phenylene) is an interesting class of materials due to their high potential for optoelectronic applications like polymer light-emitting diodes (PLEDs) [1–4], light-emitting electrochemical cells [5,6] (LECs) and organic lasers [7,8]. The process of charge transport across bandgap of organic conjugated polymer materials is important for these optimum device [9]. The main characteristic of these materials is the alternating single- and double-bonds in the backbone of a conjugated polymer make the π -electrons easier moved from one bond to the other. Thus, the π -electrons on the structure are delocalized. In other words, the level of the conductivity depends on the π conjugation of molecule. The ladder-type poly *para*-phenylene (LPPP), called Ph-LPPP (Figure 1) due to the phenyl group [10] in the X position in Figure 1, does not form crystallites and makes no torsional degree of freedom between the neighboring phenyl rings due to the bulky side groups. Thus, Ph-LPPP ex-

hibits an increase in conjugation, reduction of defects coupled with high intrachain order due to planarization of phenyl rings, and excellent solubility owing to the large side groups. Different to common PPP, LPPP has adjacent phenylrings planarized by methine bridges,

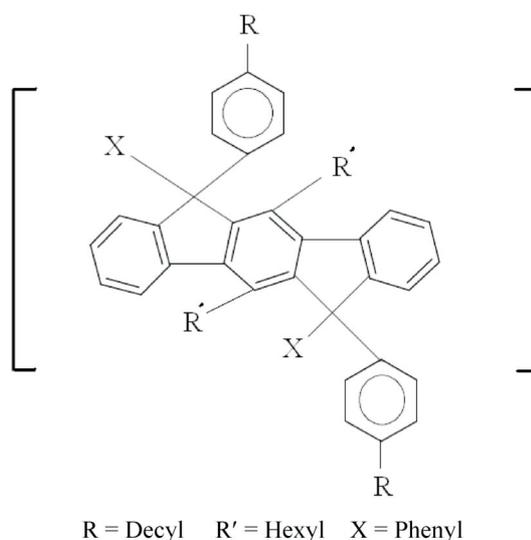


Figure 1. Chemical structure of phenylated ladder-type poly para-phenylene (Ph-LPPP).

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which results in a red shift of the electronic spectra [11, 12]. The contributions of the intermolecular interactions to the optical properties strengthen with intermolecular separation reduce, demonstrating structural and electronic properties that make polymers more efficient for lasers and other devices.

In this paper, we use hydrostatic pressure to change the intermolecular distances of Ph-LPPP, and then to tune the structural and electronic properties of conjugated molecules without changing the chemical nature of the material [13]. We probe the affects of the intermolecular interactions from the changes of the chain of the given molecule.

2. Experimental

The diamond anvil cell (DAC) with preindented stainless steel gaskets was used to introduce the hydrostatic pressure. The thin film used for PL measurements was made by evaporating a dilute solution of Ph-LPPP in acetone on the bottom diamond surface of the diamond anvil cell. The Ph-LPPP film was then put in the vacuum box for 24 hours such that the film was totally dry before sealed into the diamond anvil cell. The pressure transmitting fluid in the DAC was the hybrid fluid of methanol and ethanol. The rate of methanol and ethanol was 1:3. We used the luminescence of a ruby chip located in the pressure chamber for pressure calibration [14]. The pressure range was between 0 and 80 kbar. The PL spectra of both powder- and film-forms of Ph-LPPP were measured.

PL spectra were measured by using the 351 nm line

of Ar⁺-ion laser for the excitation beam. The laser light was focused to a diameter of 0.18 mm and covered the sample. The PL spectra were taken by a high resolution single grating JOBIN YVON SPEX TRIAX-550 monochromator with a water cooled high-voltage photomultiplier tube (PMT) as the detector. The signal was picked up by a Stanford Research lock-in amplifier referenced to the frequency of 167 Hz of the chopper wheel.

3. Result and Discussion

The PL of a polymer is observed when the excited electrons in LUMO (lowest unoccupied molecular orbital) recombine with the holes in the HOMO (highest occupied molecular orbital) and emit energy in the form of photons. In general, the PL spectra of conjugated polymers depend on their conjugated lengths [15]. Due to more planar molecular conformation, Ph-LPPP has a red shift in its PL spectrum relative to common PPP polyfluorenes (PFs) [12]. It means that Ph-LPPP has a longer effective conjugated length than common polymer.

The PL spectra of Ph-LPPP powder and Ph-LPPP film at 1 bar at 300 K are shown in Figure 2. The spectrum of Ph-LPPP powder shows four main peaks centered at 465 nm, 495 nm, 530 nm, and 560 nm. The spectrum of Ph-LPPP film also shows four main peaks but slightly shift to 462 nm, 492 nm, 527 nm, and 557 nm. The emissive transition of Ph-LPPP film that is highest in energy (shortest in wavelength) is called the 0-0 transition, and takes place between the zeroth vibronic level in the excited state to the zeroth vibronic level in the ground state. The 0-1 transition involves the creation of

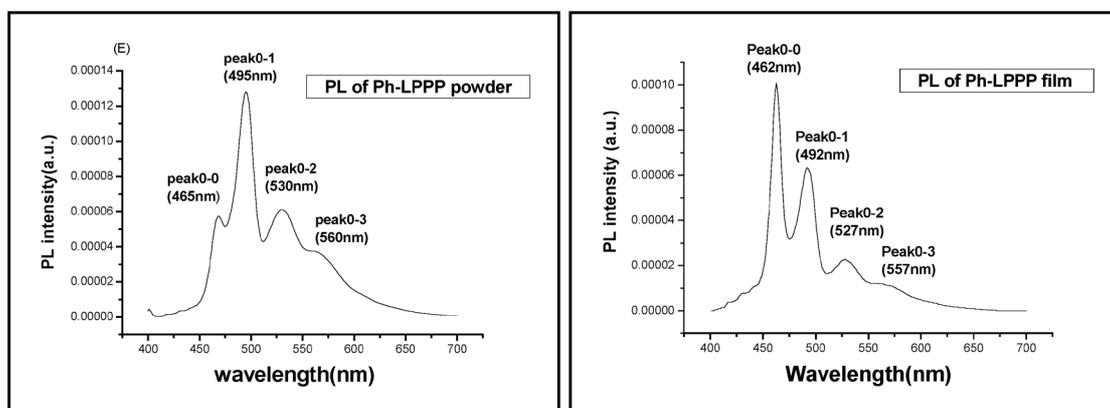


Figure 2. PL spectra of Ph-LPPP powder and Ph-LPPP film at 1 bar at 300 K.

one phonon. The strongest PL peak of Ph-LPPP powder is the 0-1 transition at 495 nm, Because of high optical density, the short wavelength edge is strongly affected by self-absorption [16,17]. Thus, the 0-0 peak is quenched and the 0-1 transition is the dominant peak observed. For the thin film of Ph-LPPP, however, the effect of self-absorption is weaker than that in the powder and the 0-0 transition peak is quite strong.

The absorption and PL spectrum of Ph-LPPP with different film thickness are measured to clarify the thickness effect on the PL. The thickness of the thinnest film is taken for the standard comparison. From the absorption of Ph-LPPP films with different thickness and $I = I_0 \exp(-\alpha t)$, where I_0 is the incident irradiance, I is irradiance at depth t , α is the absorption coefficient and t is the thickness of the film, the relative thickness of Ph-LPPP films with different thickness could be obtained. Figure 3 shows that the intensity of peak 00 of Ph-LPPP films is strongly affected by the thickness of the films due to self-absorption, as the same in the powder. The thicker the film, the weaker the peak 00 of the PL.

The PL spectra of both the powder and the film of the Ph-LPPP at pressure up to 65 kbar are observed as shown in Figure 4. We find a red shift and broadening in the PL peaks with increasing pressures. The broadening effect makes all PL peaks of Ph-LPPP powder unapparently defined beyond 30 kbar, and the 0-1, 0-2 and 0-3 PL peaks of Ph-LPPP film is poorly defined up to 36 kbar.

The red shift under pressure is caused by the de-

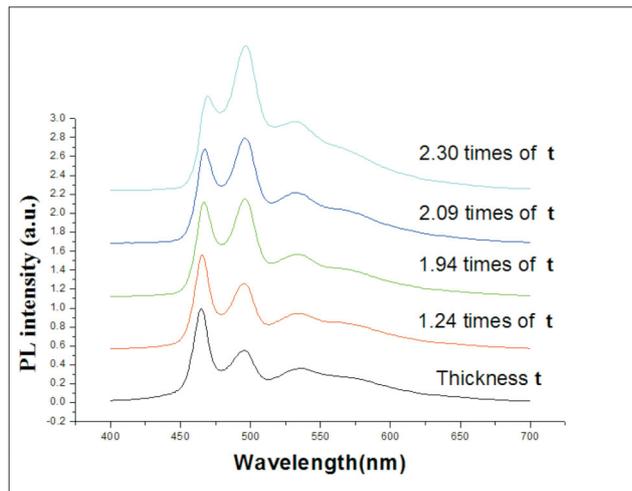


Figure 3. The PL spectra of Ph-LPPP films with different thickness.

creased distance between the bone and bond to make the energy gap smaller [18,19]. This is also characteristic of a $\pi-\pi^*$ transition. With increasing pressures the dipole moment of the excited state increases because of increasing charge separation which results in a decrease in the transition energies [20,10]. Using pressure as a tool for inferring effective conjugation length makes π electrons easily passing along the backbone and the conductive easier.

In order to quantify this behavior we use Gaussian fitting to find the peak positions and the FWHM of all PL peaks [21] at various pressures. The results are plotted in Figure 5 and the shift rates of these peaks are listed in Table 1. The broadening effect makes the PL peaks of

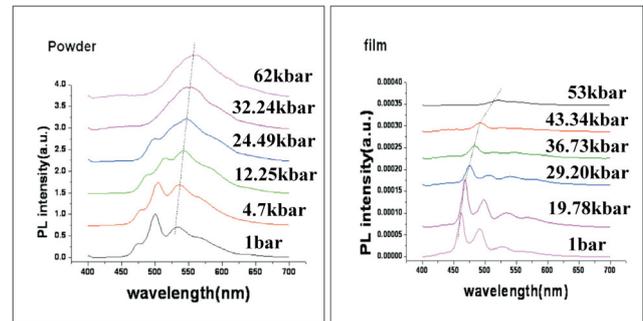


Figure 4. PL spectra of Ph-LPPP powder and film at various pressures at 300 K.

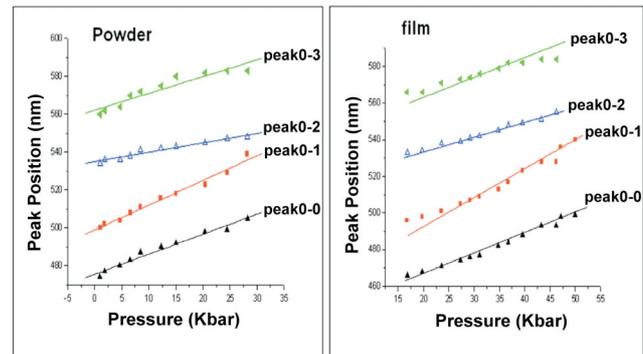


Figure 5. Pressure dependence of the PL peak position in Ph-LPPP powder and Ph-LPPP film at 300 K.

Table 1. The shift rates of PL peaks in powder and film under pressure at room temperature

	Shift rate (nm/kbar)	
	Powder	Film
Peak00	1.05 ± 0.06	1.04 ± 0.04
Peak01	1.31 ± 0.06	1.33 ± 0.07
Peak02	0.50 ± 0.04	0.74 ± 0.03

Ph-LPPP at high pressure hard to distinguish, especially in powder form. Therefore, this analysis is only up to pressure range of 50 kbar for film and 30 kbar for powder. We find that the behavior of these PL peaks is highly linear and the shift rates of all PL peaks are comparable. The strong broadening in the dominant peaks makes the determination of the positions difficult for increasing pressures. This may be the reason that the 0-0 and 0-1 PL peaks of both Ph-LPPP powder and film shift by a different rate. We also find that the PL peaks of both Ph-LPPP powder and Ph-LPPP film have similarly shift rates. Comparing our results to another branch of PPP with the methyl side chain substituent instead of phenyl, methylated ladder-type PPP (M-LPPP), which had the shift rates of -2.47 meV/kbar for the 0-0 peak and -2.08 meV/kbar for the 0-1 peak [22], the PL shift rates -1.43 meV/kbar for the 0-0 peak and -1.25 meV/kbar for the 0-1 peak of Ph-LPPP are smaller than that of M-LPPP. It means that the Ph-LPPP have more planar molecular conformation which leads to the π conjugation of molecule increasing. Because the emitting band gap of the polymer depends on the effective conjugated length [15], our observed results indicate that the pressure has the same effect on the effective conjugated length of both the Ph-LPPP powder and film.

With increasing pressures the peak strongly broaden that causes the difficulty of measuring the position. This may be reason that the peak 0-0 and peak 0-1 move a rate obviously different. In order to study the effect of the broadening, the full-width-half-maxima (FWHM) of the PL peaks are analyzed. Figure 6 shows that the FWHM of the peak 0-0 and peak 0-1 become bigger with increasing pressure for both Ph-LPPP powder and Ph-LPPP film. Broadening of the PL emission indicates stronger inter-chain coupling between two conjugated backbones. A change in the width of the vibronic peak with pressure implies that the compressibility of the ground and excited states are different. In Figure 6, we find that the change rate of FWHM of Ph-LPPP powder is bigger than that of Ph-LPPP film because of the weaker inter-chain coupling in Ph-LPPP film. In Ph-LPPP powder, molecules will form aggregation due to the thicker stacking. The aggregation is characterized by delocalization of the electronic wave function between chain and chain in both the ground and excited states [23,24]. It has shown

that the aggregation of conjugated polymers would cause a red shift in PL spectrum [23]. The positions of peak 0-0 in Ph-LPPP powder and film are 465 nm and 462 nm, respectively, which means that there are more aggregation in the powder than that in the film. This is the reason that the broadening is less in the film sample than in the powder sample. The electronic cloud layers affect together, so that the inter-chain coupling in Ph-LPPP powder is stronger that makes the electron larger probability jumping to another chain close by and the broadening of the PL peaks [25,26].

In Figure 7 we show the relative intensities of Peak 0-0/Peak 0-1 and Peak 0-2/Peak 0-1 of Ph-LPPP powder and Ph-LPPP film. In both powder and film, both ratios of Peak 0-0/Peak 0-1 and Peak 0-2/Peak 0-1 become larger with increasing pressure. It means that intensity of Peak 0-0 increases or Peak 0-0 decreases with increasing pressure. Because PL spectra shift to lower energy with increasing pressure, the influence of self-absorption diminishes that makes the less suppression on peak 0-0 and the increase of the ratio of peak 0-0/peak 0-1.

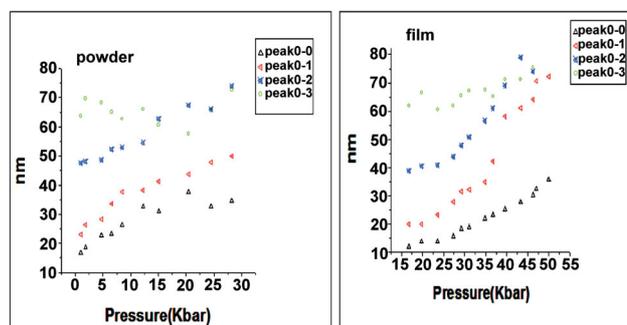


Figure 6. FWHM of the PL peaks of Ph-LPPP powder and film.

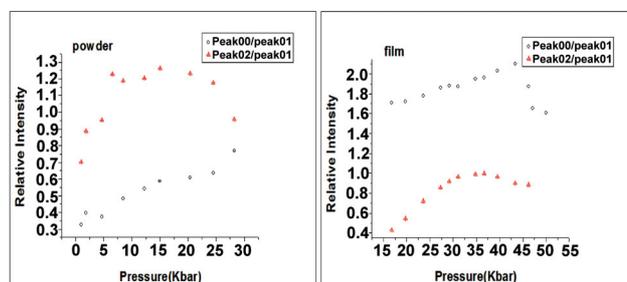


Figure 7. Relative intensities of PL peaks of Ph-LPPP powder and film.

4. Conclusions

We have presented PL spectra of both Ph-LPPP

powder and Ph-LPPP film at various pressures. The observed PL peaks show linear red shifts and broadening effect with increasing pressure. The different change rates of the FWHM of the PL peaks of Ph-LPPP powder and film indicate the different inter-chain interaction of this polymer in different forms due to the different aggregation. The smaller shift rates under pressure means that Ph-LPPP has stronger planarity and therefore longer effective conjugated length. Mbarek, etc. calculated the Stokes shift of absorption and PL of PPV [27] and concluded that the smaller the Stokes shift, the longer the conjugated length. From our observation, the Stokes shift in Ph-LPPP is 3 nm [28], which is much smaller than that of PPV [27]. This means the increase the planarity of the polymer could reduce the loss of energy in phonon.

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