Journal of Applied Science and Engineering, Vol. 18, No. 2, pp. 153–158 (2015) *DOI: 10.6180/jase.2015.18.2.07*

Pressure Effect to the Molecular Structure of Ladder-type Poly(*Para*-phenylene) Revealed by Raman Spectroscopy

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Abstract

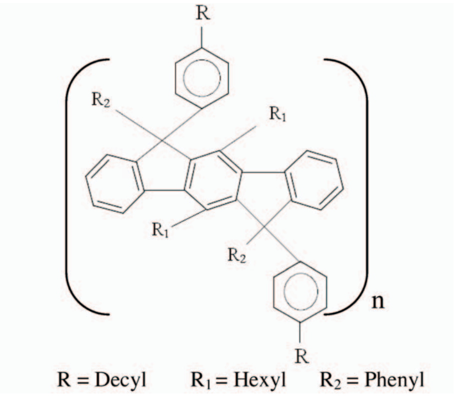
Raman scattering spectra of blue light-emitted organic conjugated polymer, ladder-type poly para-phenylene with a phenyl ring in the side chain (Ph-LPPP), in the form of powder with trace-concentrations of metallic impurities under various pressures are measured. We find that Raman spectra shift to higher frequency with the increase of pressure, indicating a strong electron-phonon interaction. We also find that the shift rates of Raman peaks from the backbone of Ph-LPPP are different comparing to our early observations of Raman spectra of methyl substituted ladder-type poly (Me-LPPP). Planarization under pressure, therefore, electronic delocalization is observed, which is also discovered from the optical properties of Ph-LPPP.

Key Words: Raman Scattering Spectrum, Hydrostatic Pressure, Conjugated Polymer, Electron-phonon Interaction

1. Introduction

Ladder-type poly(p-phenylene) (LPPP) are an important material of conjugated polymers due to their significant potential and their intense blue emission for optoelectronic applications such as polymer-light-emitting diodes (PLEDS) [1–3] and solar cells [4]. Early poly(p-phenylene) (PPP) was developed because of the higher energy bandgap in accordance with blue emission [5]. The structure of PPP consists of a rigid aromatic backbone of linearly arranged para-phenylene moieties, but it is insoluble. The attachment of alkyl side-chain substituents on the main PPP backbone forces a distortion of neighboring phenylene rings out of planarity, thereby reducing the degree of conjugation of inter-phenylene, and is soluble to common organic solvents [6].

Different to common PPP, LPPP has adjacent phenyl-rings planarized by methyl bridges, which results in a red shift of the electronic spectra [7,8]. The ladder-type poly para-phenylene, named Ph-LPPP (Scheme 1) due to the phenyl group [9] in the R_2 position, does not form crystallites and the bulky side groups make no torsional degree of freedom between the neighboring phenyl rings. Thus, Ph-LPPP has higher degree of conjugation and lower defects coupled with high intra-chain order due to planarization of phenyl rings and excellent solubility owing to the large side groups.



Scheme 1. Molecular structure of ladder-type poly para-phenylene (Ph-LPPP) [9].

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Raman spectra of some LPPPs with different attached side chains were quite different [10–14]. In this paper, we study Raman spectra of Ph-LPPP with pressure up to 50 kbar, and compare to that of Me-LPPP. Hydrostatic pressure is used to enhance intermolecular interaction [15,16] and to tune the structural and electronic properties of conjugated molecules systematically without changing the chemical nature of the material [17]. We try to investigate the relationship of inter-molecule interactions and the optical properties of Ph-LPPP polymer.

2. Experimental Setup

Raman scattering spectra were measured at pressure range from 1 bar to 50 kbar, at 300 K. In order to produce pressures on Ph-LPPP, the diamond anvil cells (DAC) with preindented stainless steel gaskets were used. Liquid mixture of methanol and ethanol were used as pressure transferring fluid in the DAC. Both Ph-LPPP powder and a tiny piece of ruby were put into the 180 μm-diameter hole in the gasket on the bottom diamond surface of the DAC at the same time. The ruby luminescence was used for pressure calibration [18]. Raman spectra were measured by using the 514 nm line of an Ar^{+}-ion laser focused to a diameter of 0.18 mm to cover the whole region of the hole in the gasket. Raman scattering spectra were detected by a JOBIN YVON SPEX TRIAX550 monochrometer with a grating of 1200 grooves/mm and a charge-coupled device (CCD) array detector. The typical resolution of this setup was 1 cm^{-1}.

3. Results and Discussions

Raman spectrum of Ph-LPPP powder at atmospheric pressure at 300 K is shown in Figure 1. The three strongest peaks observed arising from the vibration from the backbone, which includes two aromatic C-C stretching modes [19,20] (double peaks at 1600 and 1564 cm^{-1}), and the interring C-C stretching mode at 1311 cm^{-1}. In Raman spectrum of LPPP without side chains, the interring C-C mode is dominant at 1289 cm^{-1} [21]. Owing to additional side chain R_1 in Ph-LPPP, this mode weakly shifted frequency to 1311 cm^{-1}.

A shoulder at about 1548 cm^{-1} originated from the methyl bridge at the side chain induced aromatic C-C stretching is also discovered when using Lorentz curves to fit this spectrum. The asymmetric C-C stretching and compressing vibration is at 1368 cm^{-1} due to the additional strong part of C-C rocking localized in the connection of R_1 to the backbone. A weak mode at 1321 cm^{-1} should be increasing in intensity when LPPP is connected R and R_2 side chains [21], which shifts to 1329 cm^{-1} owing to additional side chain R_1 in Ph-LPPP.

Other vibration modes are also observed in Raman spectrum of Ph-LPPP. The peaks at 1169 cm^{-1}and 1259 cm^{-1} are identified as intermix of C-C stretching vibrations with vibrations of the side chains with the backbone (C-R stretching and C-R_2 bending/stretching of the central carbon atom at the methine bridge vibrating out of the backbone plane) [21]. The peak at 1046 cm^{-1} is an aromatic deformation vibration, and the peak at 1113 cm^{-1} is the phenylrings with side chain R_1 vibrating as breathing mode including an aromatic-R_1 stretching vibration [14].

By comparing to our early work on Me-LPPP [21], another LPPP with methyl substituent on side chain, we find that Raman spectra of both Ph-LPPP and Me-LPPP show the same vibration modes. Table 1 lists the peak positions of three main Raman peaks in the backbones of Me-LPPP and Ph-LPPP. We find that these three peaks of both Ph-LPPP and Me-LPPP shift to higher frequencies comparing to LPPP, but these of Ph-LPPP all shift less than these of Me-LPPP.

The phenyl rings within each molecule of LPPP are on the average coplanar. With different substituents of side chains, the torsions between phenyl ring and phenyl

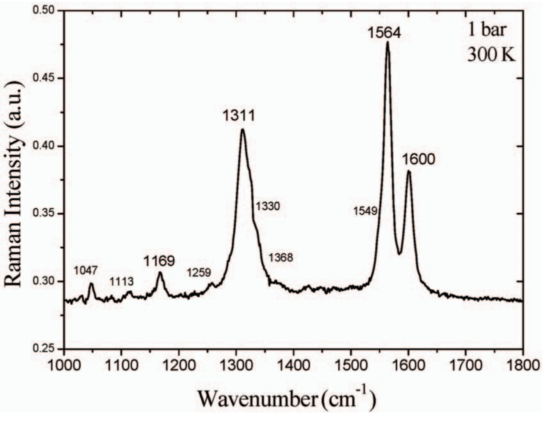

Figure 1. Raman spectrum of Ph-LPPP at atmospheric pressure and 300 K.

Table 1. The peak positions of three main vibration peaks in backbones of Me-LPPP [21] and Ph-LPPP

Bond	Peak position (Me-LPPP)	Peak position (Ph-LPPP)
Aromatic C-C stretching vibration	1605 cm^{-1} 1567 cm^{-1}	1600 cm^{-1} 1564 cm^{-1}
Aromatic interring C-C stretching vibration	1326 cm^{-1}	1311 cm^{-1}

ring are different [22]. The nature of the torsional motion of the neighboring phenyl rings is determined by two opposing influences: the intra-molecular repulsion and the degree of planarization. The first impact is from the increase of the dihedral angle between two neighboring phenylene rings due to the repulsive interaction of the ortho-hydrogens. The second impact is from the tendency towards planarization in a π-electronic system due to the resonance interaction [23]. Different to several known conjugated materials [24,25], both Ph-LPPP and Me-LPPP make no torsional degree of freedom between the neighboring phenyl rings due to the phenyl or methyl group in the R_2 position and the other bulky side groups. Besides, the molecular weight of the side chain of Ph-LPPP is higher than Me-LPPP which makes Ph-LPPP a better planarity. Because of the better planarity, Ph-LPPP has higher degree of conjugation and lower defects coupled with high intra-chain order due to planarization of phenyl rings, which results in the smaller Raman shift to regular LPPP comparing to Me-LPPP.

In order to understand more about the relationship of inter-molecule interactions and optical properties of Ph-LPPP polymer, we use hydrostatic pressure as the parameter to change the interatomic distances and, therefore, to tune the structural and electronic properties of ploy chains in a unique manner without changing the chemical nature of the material. Figure 2 demonstrate Raman scattering spectra of Ph-LPPP at various pressures. The three major peaks from the backbone vibrations could be clearly observed up to 51 kbar. Besides, the peak due to the C-R stretching at 1169 cm^{-1} is also observed up to 20 kbar. We could find that the three major peaks from the backbone vibrations in Raman spectra all shift to higher frequencies with the increase of pressure. The shift rates of backbone aromatic C-C stretching vibration (1600 cm^{-1} and 1564 cm^{-1}) are both about 0.8 cm^{-1}/kbar, whereas that of backbone aromatic interring C-C stretching vibration (1311 cm^{-1}) is 0.75 cm^{-1}/kbar as listed in Table 2. Table 2 also lists the shift rates of these three Raman peaks of Me-LPPP under pressure from our early work [21]. Because of the better planarity in Ph-LPPP, t would be easier to reduce the distance between two neighboring polymer chains with increasing the pressure. Thus, we could find that the shift rates of the peaks at 1600 cm^{-1}, 1564 cm^{-1} and 1311 cm^{-1} with pressures were all lower than those of Me-LPPP.

Except shifting to higher frequency under pressure, broadening effect on Raman scattering are also observed. Especially, the two peaks due to the backbone aromatic C-C stretching vibration (1600 cm^{-1} and 1564 cm^{-1}) merges

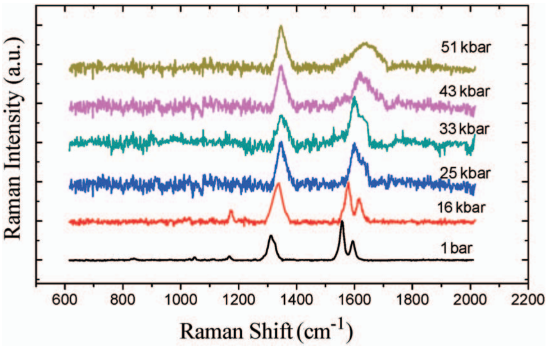

Figure 2. Raman spectra of Ph-LPPP at various pressures at 300 K.

Table 2. The shift rates of the peaks at 1600, 1564 cm^{-1} and 1311 cm^{-1} with pressures

	Me-LPPP	Ph-LPPP
	Shift rates (cm^{-1}/kbar)	Shift rates (cm^{-1}/kbar)
Aromatic C-C stretching vibration	1.0 1.1	0.8 (1600 cm^{-1}) 0.8 (1564 cm^{-1})
Aromatic interring C-C stretching vibration	1.0	0.7 (1311 cm^{-1})

when pressure is higher than 40 kbar. Due to the kinetic energy of the participating electrons increases with pressure increasing, the electronic density function would change [26]. The intramolecular bonds tend to be destabilized with compression by the pressure, which affect the molecular stability. Thus, the broadening of the C-C stretching modes is observed, which will cause these modes hard to distinguish at high pressure and look like only one peak.

The intensities of intermix of C-R stretching vibration mode at 1169 cm^{-1} to backbone aromatic interring C-C stretching vibration mode at 1311 cm^{-1} on the Raman spectra at various pressures are compared, as shown in Figure 3, to investigate the difference of pressure effect on the side chain and the backbone. Raman scattering from such unoriented material is usually weak and hard to observe. As indicated in the experimental setup, the powder of Ph-LPPP was loaded into a 180-μm drilled hole in the gasket used in the diamond anvil cell. It is even harder to study the Raman scattering from such tiny amount of Ph-LPPP. Therefore, the fluctuation of the curve in Figure 3 arose from the very weak signal from the side chain vibration under the pressure. We find that the ratio of I_{1169}/I_{1311} is increasing with increasing pressure. This matches the observation on Raman spectra of poly (para-phenylene vinylene) (PPV) [27]. It is an indication of better planarization of the Ph-LPPP molecule under compression. The stacking of molecules would be easier if the planarization of polymer is better, such that the vibration in the backbone harder than the side chain, therefore, the increase in the ratio of the side chain to backbone vibrational signals.

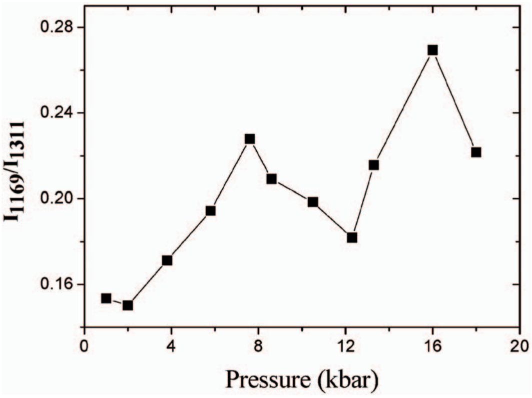

Figure 3. The rate of I_{1169}/I_{1311} of Ph-LPPP with pressure up to 20 kbar.

We also investigate the other optical properties, such as photoluminescence as well as modulated spectrum of Ph-LPPP under pressure. Except the observed red shift in both spectra [28,29], the observed triplet-triplet transition from modulated spectrum also has a sudden huge shift when pressure increases from 36 to 38 kbar [29]. Mulazzi et al. [30,31] used to calculate the Raman spectra of the different conjugated length under pressure, which indicated that the longer conjugated-length segments had stronger electronic interaction than the side chain, which would cause the electron delocalization. The better planarity of Ph-LPPP under pressure such that electrons are easier to transit along the backbone and to produce electronic delocalization, which makes the increase of the effective conjugated length, therefore, the sudden shift in the triplet-triplet transition.

4. Conclusions

We have presented Raman scattering of amorphous powder samples of ladder-type poly para-phenylene, Ph-LPPP, at hydrostatic pressures up to 50 kbar. All the peaks of Raman modes shift to higher frequency with increasing pressure due to the better planarity, therefore, longer effective conjugated length caused by pressure. The relative intensity of the intermix of C-C stretching vibration with vibration of the side chains with the backbone Raman mode at 1169 cm^{-1} to the Aromatic interring C-C stretching vibration Raman mode at 1311 cm^{-1} (I_{1169}/I_{1311}) provides insight into the electronic properties between backbone and side chain. Planarization under pressure is observed, which indicates the stronger electronic interaction.

Acknowledgements

The authors acknowledge Prof. U. Scherf in Bergische Universität Wuppertal, German for providing the sample and are also thankful to Ministry of Science and Technology and Tamkang University, Taiwan, R.O.C. for the financial support.

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Manuscript Received: Mar. 20, 2015
Accepted: Jun. 2, 2015