Pressure Dependence of Raman Scattering in Poly-methyl Stilbenemethacrylate

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Abstract

The Raman scattering spectra of fluorescent pendent polymer, poly-methyl stilbenemethacrylate (PMMS) with two different molecular weights under hydrostatic pressure up to 100 kbar are observed. We find that the Raman spectra shift to higher frequency with increasing pressure on both polymers. The shift rate is independent to their molecular weights. No phase change is observed in this pressure range.

***Key Words*: Raman Scattering, Conjugated Corrducting Polymer, Pressure**

1. Introduction

Conjugated conducting polymers have become highly interesting for basic research after the first successful doping of polyacetylene [1]. Although some electro-active organic materials are already used in industrial products [2] in last decades, there are still some shortages in these materials. Except the short lifetime, the low carrier transport mobility in organic conducting polymers is the most severe problem in application.

Indium-tin-oxide (ITO) is the most frequently used electrode in organic light-emitting diodes (LEDs). The most popular fluorescent pendent polymer (*poly*(n-vinyl carbazole), PVK) [3-7] has the highest occupied molecular orbital (HOMO) of -5.8 eV to -6.1 eV [8, 9], which is closer to the work function of ITO (-4.6 eV) than the other polymers. This property makes it a good hole-transport layer in a LED. However, the high drive voltage (15 V) of PVK is a drawback of this material.

The *trans*-4-Stilbenemethanol (SM) has the similar photoluminescence to PVK. According to the UV-VIS and CV measurements and calculations, the HOMO and lowest unoccupied molecular orbital (LUMO) of SM are -5.7 eV and -2.1 eV, respectively [10]. The HOMO of

SM is closer to the work function of ITO than that of PVK, which makes it a potential replacement of PVK to be a more effective hole transport layer in LEDs. In order to precisely control the chain length of polymers, a novel method called atom transfer radical polymerization (ATRP) is used to produce fluorescent pendent polymer, poly-methyl stilbenemethacrylate (PMMS) (Scheme 1) [11]. According to Lee's studies, the photoluminescence (PL) of this polymer is similar to the PL of SM, therefore the similar HOMO and LUMO to SM. Besides, the functional group in PMMS makes it much easier to be processed into a device. Under two different synthetic procedures, PMMS polymers of molecular weights (Mn) as

Scheme 1. The chemical structure of PMMS
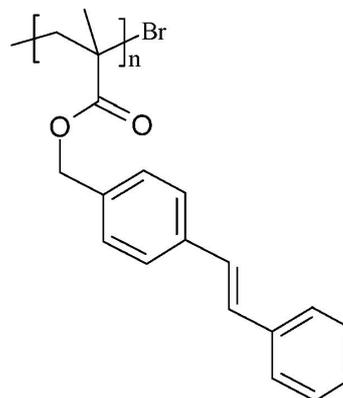
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9022 and 2395 were prepared.

The optical properties of conducting polymers are mainly determined by their structures. Chang et. al. reported that the chain length of polymers would affect their optical properties [12]. In this work, hydrostatic pressure is introduced to PMMS. The Raman scattering spectra of PMMS polymers of two different molecular weights under hydrostatic pressure up to 100 kbar are studied. Using this method, we could systematically tune the structure of PMMS without changing its chemical structure. Through this work, we could investigate the effect of chain length of a polymer on its structure change under pressure, and hopefully to understand the relationship between the molecular structure and the intermolecular interaction in the further studies.

2. Experimental

Pressure studies were conducted in a piston cylinder type diamond anvil cell (DAC) with a 4/1 mixture of methanol-ethanol as the pressure medium and ruby luminescence as the pressure calibration. The 514.1 nm line of an argon-ion laser was used to excite the PMMS. The Raman scattering spectra of PMMS powders under pressure up to 100 kbar were recorded by a Dilor XY type micro-Raman spectrometer with a charge-coupled device (CCD) detector.

3. Results and Discussion

Figure 1 shows the Raman spectra of PMMS powders of molecular weights as 9022 and 2395 at temperature 300 K at ambient pressure. On both samples, the major observable vibrational modes are the in-plane breathing mode at 997 cm^{-1}, the δ(C-H) mode at 1182 cm^{-1}, the ν(C-phenyl) mode at 1192 cm^{-1}, the in-plane ring δ(C-H) mode at 1595 cm^{-1}, and the vinylene ν(C=C) mode at 1633 cm^{-1}, which are similar to the observation in trans-stilbene [13]. Unlike the weak intra C-C stretch mode at 1608 cm^{-1} in trans-stilbene and polyfluorene [14], this peak is more in-
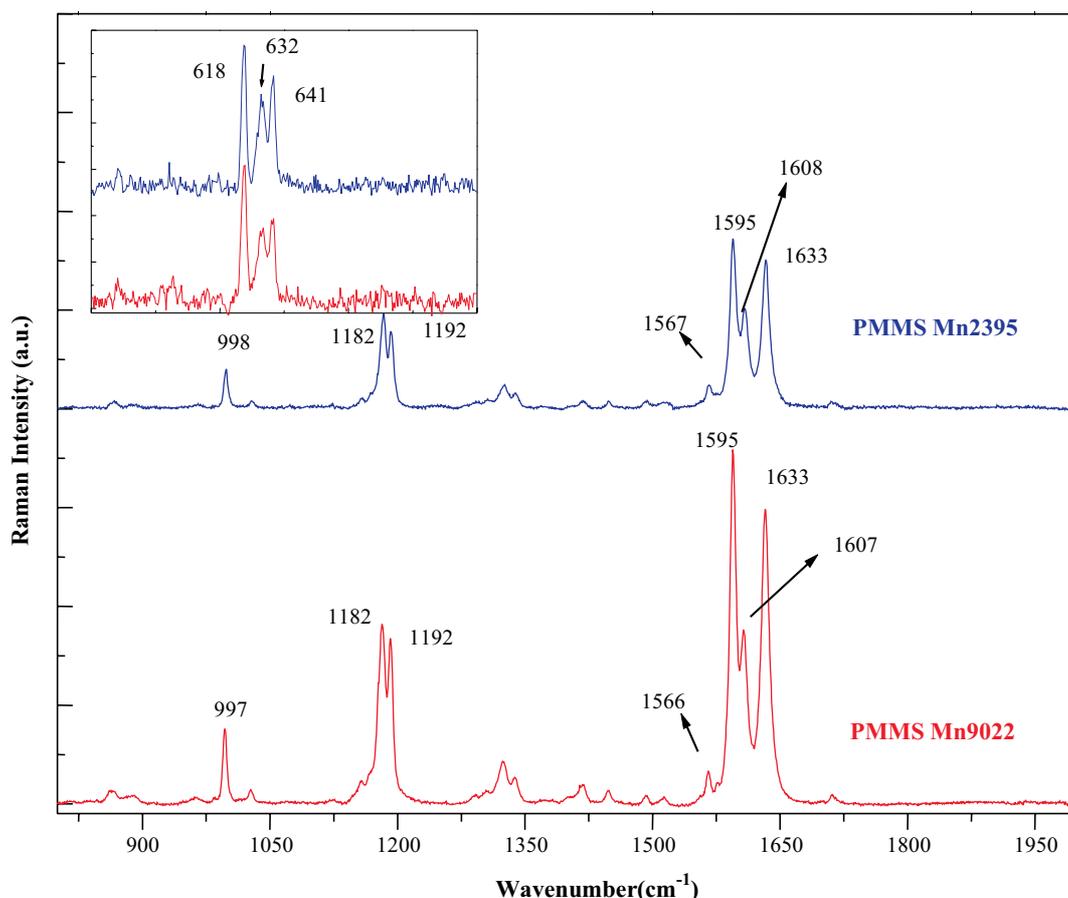

Figure 1. The Raman scattering spectra of PMMS powders with molecular weights (Mn) being 2395 and 9022 at temperature as 300 K at ambient pressure. The inset is the weaker Raman spectra of the same PMMS powders at the range 500 to 700 cm^{-1}.

tense in PMMS. We think that is due to the higher freedom of benzene at the side chain of PMMS, therefore the stronger intensity on the Raman peak. The Raman peaks arising from backbone stretch mode at 1300 to 1500 cm^{-1} and the in plane v_s(C-O-C) mode at 800 to 970 cm^{-1} [15] are also observed in the same scale.

According to the activity of Raman scattering, the Raman peaks arising from the v(C-Br) mode at the range 500 to 700 cm^{-1} are weaker than the other peaks [15]. In PMMS, the C-Br bindings only appear at the two ends of the backbone. Thus, we expected to observe very weak v(C-Br) mode. However, with longer observation time three Raman peaks at 618, 632, and 641 cm^{-1} are also observable, as indicated in Inset of Figure 1.

Although the energy of the laser line used for Raman measurements is below the PL energy, it still excites the low-energy tail of the PL spectrum. The PL tail at the frequency range at 1400 to 1800 cm^{-1} obscures the Raman signal in this region, as shown in Figure 2. The PL backgrounds are subtracted from all recorded Raman data in order to clarify the Raman peaks.

The Raman spectra of PMMS powders with molecular weights being 9022 and 2395 at various pressures are presented in Figures 3 and 4, respectively. The break at 1300 cm^{-1} denotes to the region where the Raman peak from diamond has been removed. Only the strong Raman peaks are observed because the sample in the DAC only has tiny amount. The Raman peaks in the range 1400 to 1800 cm^{-1} are clearly distinguished up to 100 kbar, while peaks in the range 800 to 1250 cm^{-1} can only be observed up to 70 kbar. From our observations, we find that all Raman peaks tend to increase in frequency and decrease in intensity with increasing pressure. The relative intensity of Raman peaks at 1182 cm^{-1} to 1192 cm^{-1} changes with increasing pressure. We find that the intensity of the Raman peak of the δ(C-H) mode at 1182 cm^{-1} is stronger than that of the v(C-phenyl) mode at 1192 cm^{-1} at pressure up to 10 kbar. The v(C-phenyl) mode shows higher Raman intensity than the δ(C-H) mode at pressure around 20 kbar on both samples.
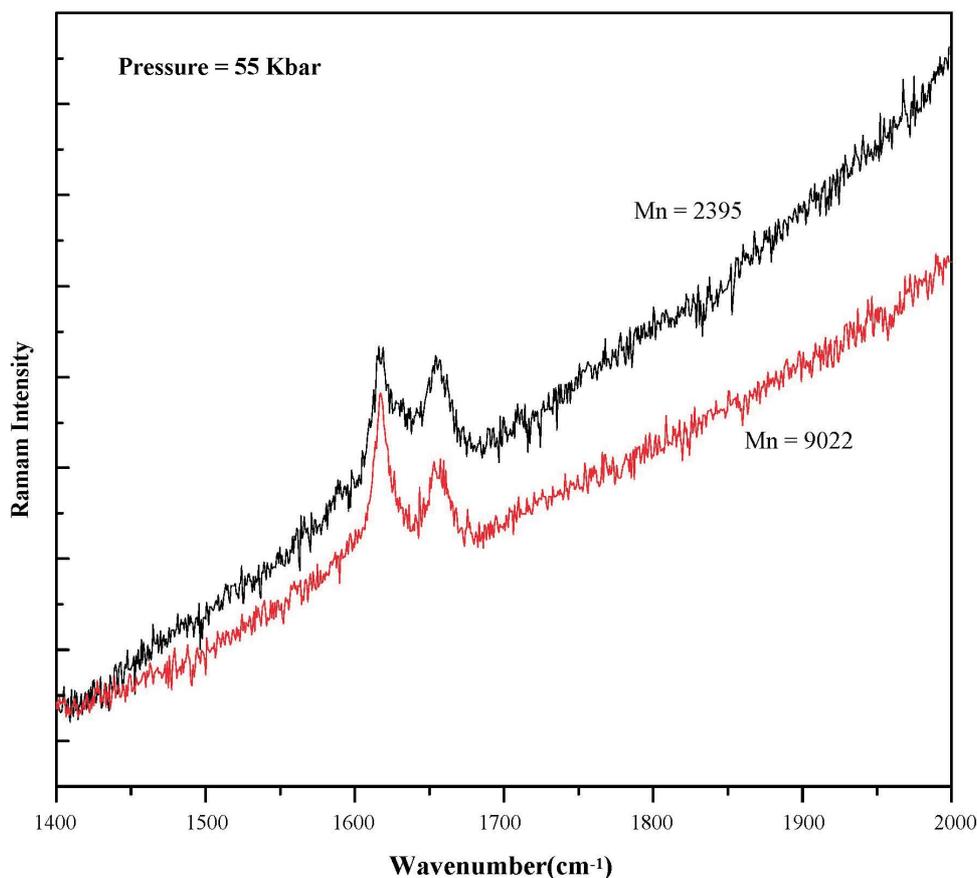

Figure 2. The Raman scattering spectra of PMMS at pressure as 55 Kbar at room temperature before subtracted the PL background.

The Raman peaks have been fitted with Lorentzian line shapes to determine the frequency positions of individual peaks. The Raman peak positions of two PMMS

as a function of pressure are plotted in Figures 5 and 6. According to the analysis, we find that all peaks shift linearly to higher frequency with increasing pressure. The
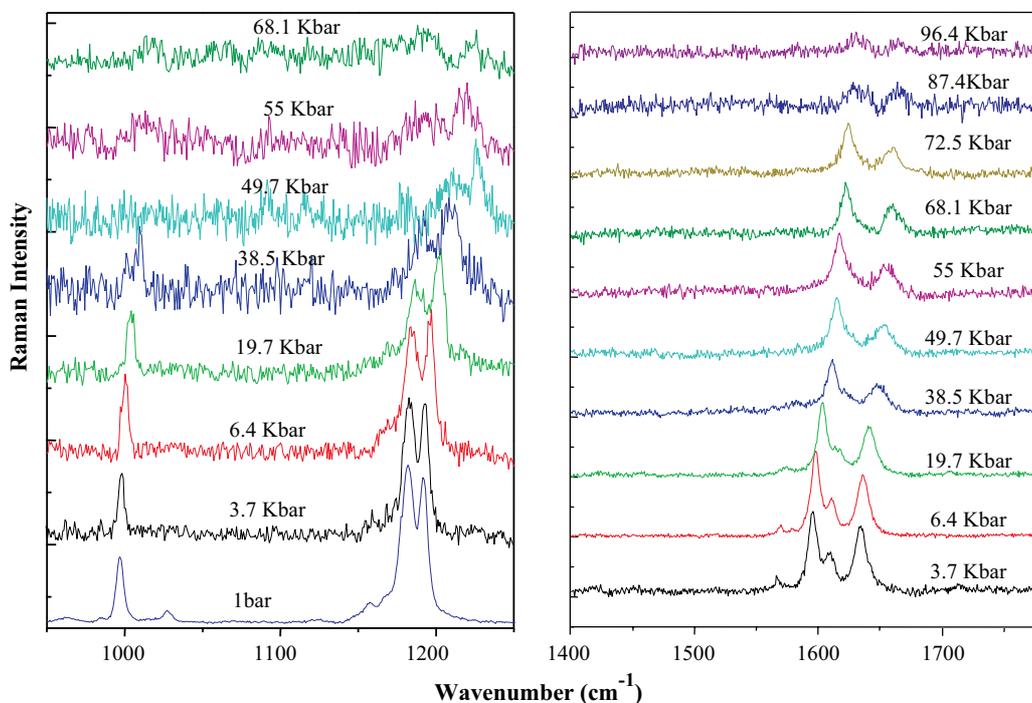

Figure 3. Raman spectra of PMMS powder with molecular weight being 9022 at various pressures at 300 K.
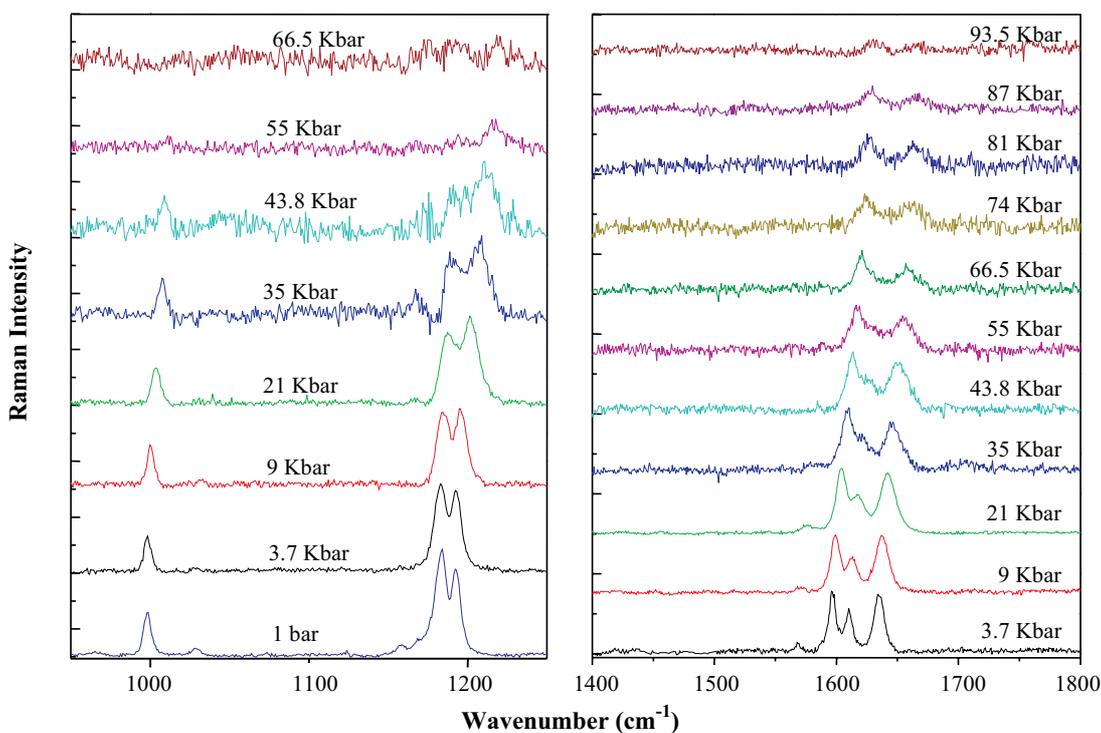

Figure 4. Raman spectra of PMMS powder with molecular weight being 2395 at various pressures at 300 K.

shift rates are independent to the polymer's molecular weights. All peaks shift with fairly similar coefficients, except the peak at 1182 cm^{-1} arising from the C-H bend-ing mode at the ethyl side group. No new peaks appear with either increasing or decreasing the pressure, which indicates no phase change in the observed pressure range.
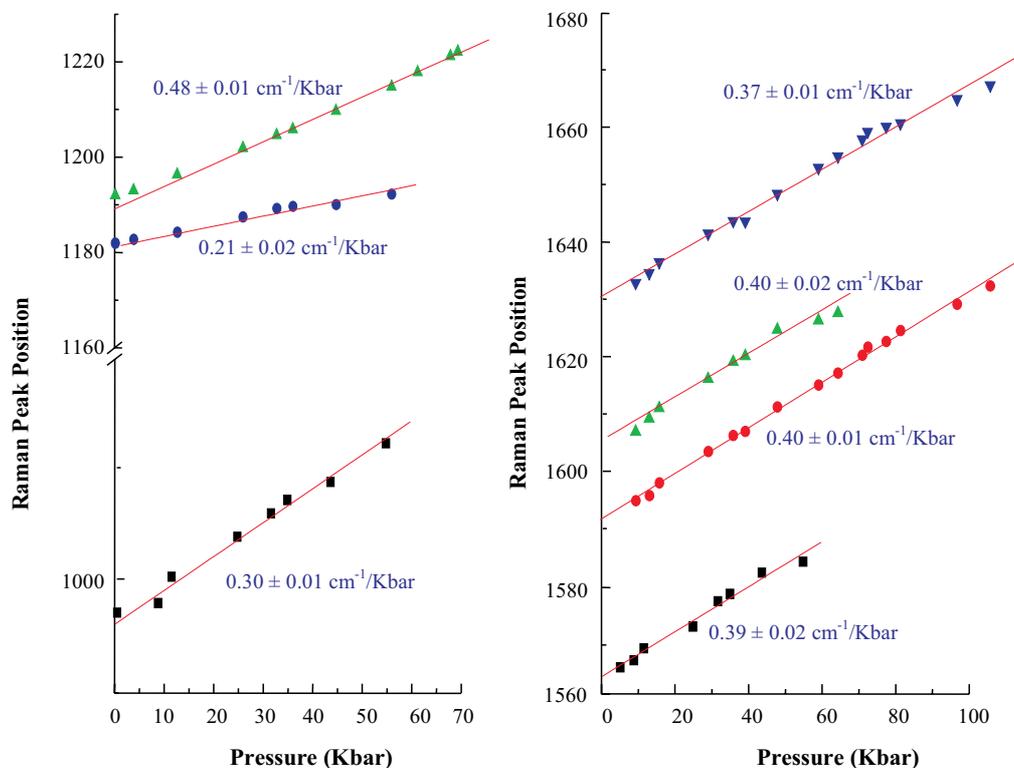

Figure 5. Raman peak positions of PMMS (Mn = 9022) as a function of pressure. The pressure coefficient of each individual peak is indicated.
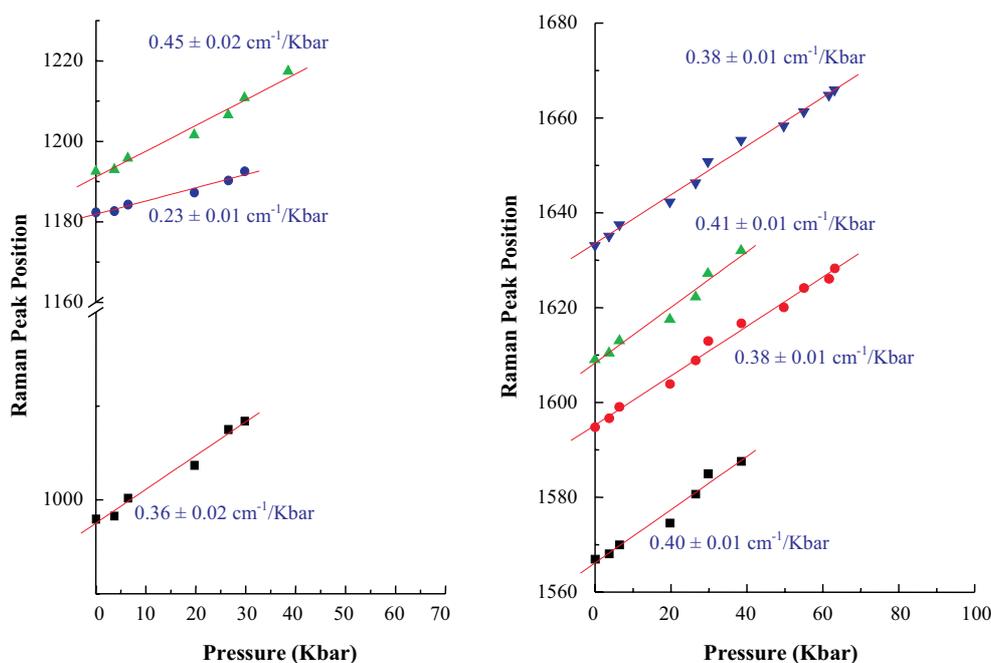

Figure 6. Raman peak positions of PMMS (Mn =2395) as a function of pressure. The pressure coefficient of each individual peak is indicated.

It has been reported that the planarization of para Hexaphenyl would cause the ratio of two Raman peaks' intensities change[16]. We think this could be the explanation of the particular behavior of the δ(C-H) mode at 1182 cm^{-1}. The lower pressure coefficient of the Raman peak at 1182 cm^{-1} indicates that the C-H bond at the ethyl side group of PMMS is harder to be pressed. We think that this bond is not at the same plane as the benzene at ambient pressure. At low pressure, the C-H bending mode would compress the vibration of the C-phenyl. When introducing the pressure, the δ(C-H) bond is gradually pressed to the same plane as the benzene. Thus, the ν(C-phenyl) mode at 1192 cm^{-1} shows stronger intensity compared to the δ(C-H) mode at 1182 cm^{-1} when the pressure is higher.

4. Conclusions

In this paper, we present the Raman scattering spectra of PMMS polymers with two different molecular weights. Based on our observation, we find that the behavior of Raman peaks of PMMS powders with different molecular weights under pressure has no difference. This indicates that the structure change of PMMS under pressure is independent to the chain length.

Acknowledgment

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