The effect of pressure on the fluorescence of a new type of light-emitting material

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Abstract
The fluorescence properties of two nitrogen-containing poly-(phenylene vinylene)-related copolymers were investigated under high pressure. Because of the large difference in interchain interaction between these two copolymers, the emission states are different from each other. Under the perturbation introduced by compression, the emission intensity exhibits different trends of change.

1. Introduction

The photophysics of conjugated copolymer has been of interest in recent years. The preliminary picture of photophysical processes of conjugated copolymers, particularly ladder-type poly(phenylene)s, is one in which excitons are produced by photoexcitation and then rapidly form excimers, due to the generally planar geometry and very strong intermolecular interactions [1].

Although much theoretical and experimental work has been carried out to study the nature of the excited states, the origin of the luminescence, and the nature of the charge photogeneration [2–5], the photophysical processes in conjugated polymer remain poorly understood and controversial, especially for copolymers with less stiff chains.

There is a new type of nitrogen-containing poly-(phenylene vinylene) (PPV)-related copolymer; copolymers of this type generally have more flexible chains than the ladder-type poly(phenylene)s. The structures of two typical copolymers studied in this work are given in

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the following diagram.

TPA-PAV   TPA-DMPPV
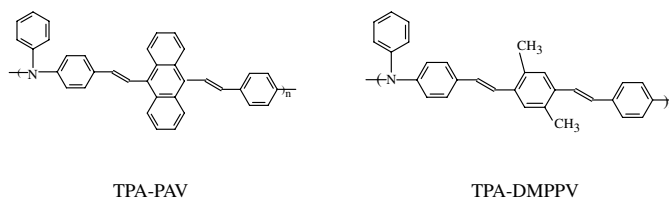
These two polymers have less stiff chains; these do not lead to shared-face chain packing in the solid, as is proved by means of x-ray diffraction. However, it has been reported that 9, 10-anthrylene has a stronger capability to accept electrons than 2, 5-dimethyl-1, 4-phenylene and thus charge-transfer complexes can be easily formed in TPA-PAV; so TPA and 9, 10-anthrylene are already configured into sandwich-type structures in the ground state in the neat polymer [6]. In this paper, we describe how pressure was introduced to change the distance between the polymer chains or the conformation of the molecular chain, and fluorescence measurements at high pressure were carried out.

2. Experimental details

The polymer TPA-PAV and TPA-DMPPV were synthesized in our laboratory [6, 7]. Poly(methyl methyacrylate) (PMMA) was purchased from Aldrich and was reprecipitated before use. Spectral grade chloroform was used for solution preparation.

The polymer TPA-PAV (or TPA-DMPPV) was dissolved in chloroform with PMMA and the solution was poured into a glass dish. After the chloroform evaporated, the blend film was then put into a vacuum oven and left there for a few days at 45 °C. Transparent and lightly coloured films of blends were obtained with concentrations of 0.02% for TPA-PAV in PMMA and 0.03% for TPA-DMPPV in PMMA. For absorption and fluorescence measurements a Merrill–Bassett diamond anvil cell (DAC) was used to generate high pressure. The hole diameter of the gasket used to hold the sample was about 300 μm with thickness of about 90 μm. A small chip of ruby was put in the hole to allow calibration of the pressure by measurement of its fluorescence red shift. Light mineral oil served as a pressure medium. For the emission measurement two CW He–Cd lasers (Omnichrom) at 325 and 441 nm were used as the excitation source. The fluorescence spectra were dispersed with a 0.3 nm spectrometer and a photomultiplier (PMT) coupled to a 32-bit microprocessor-based data acquisition and spectrometer-controller module (NCL Electronics Interface, Acton-Research Corporation) and computer. For the absorption measurement a Xe lamp was used as the light source and the light was dispersed with a 0.3 nm spectrometer. Two optical fibres were connected to the DAC and the other ends were connected to a monochromator and PMT, respectively. An NCL electronics interface and computer were used to record the spectra and control the system.

3. Results and discussion

In figures 1 and 2 we present the spectra at a number of pressures for the two neat copolymers, TPA-PAV and TPA-DMPPV. The emission intensity is normalized to the value at 1 atm. The changes in emission intensity differ under the perturbation introduced by compression.

A more explicit illustration is shown in figure 3, which exhibits the change of the emission area with pressure. The neat TPA-PAV shows a large drop with pressure, and when pressure increases to about 2.5 GPa, the total emission is very close to 0. For the neat copolymer
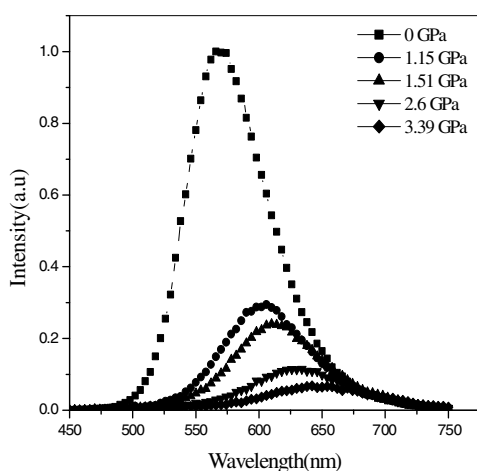
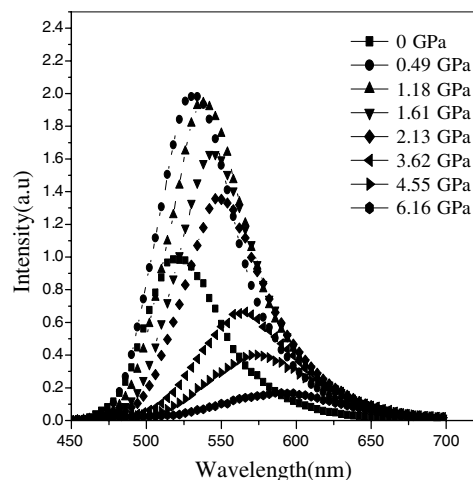**Figure 1.** Emission spectra of the neat TPA-PAV.

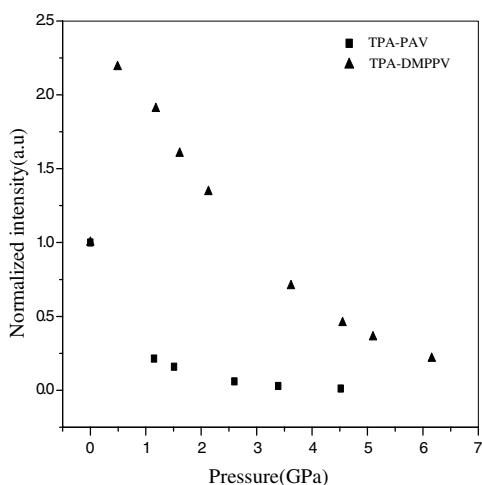**Figure 2.** Emission spectra of the neat TPA-DMPPV.

Figure 3. Total emission area versus pressure for the neat TPA-PAV and the neat TPA-DMPPV.
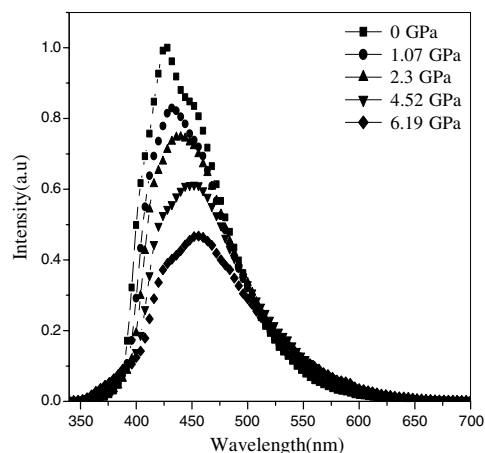

Figure 4. Emission spectra of the TPA-PAV/PMMA blend.

TPA-DMPPV, there is an increase evident at 0.5 GPa which is 2.2 times that at 1 atm, and then a continuing decrease with pressure increase.

Figure 4 shows emission spectra of the TPA-PAV in PMMA blend at a number of pressures. The emission spectra of TPA-PAV in PMMA peak at 425 nm with a shoulder at 451 nm at 1 atm, while the maximum emission wavelength for the neat TPA-PAV is 570 nm, which is red-shifted by about 145 nm compared with that for TPA-PAV in PMMA.

It has been reported that both intrachain and interchain charge-transfer complexes exist in the concentrated solution of TPA-PAV [6, 7]. The absorption maximum of the neat TPA-PAV is at 360 nm, with a broader absorption at 550 nm as compared with the absorption spectrum of the TPA-PAV/PMMA blend (see figure 5). This absorption of the neat TPA-PAV indicates that the interchain charge-transfer complex is formed in the ground state. This means that there are very strong interactions between TPA and 9, 10-anthrylene groups in different chains in the ground state.
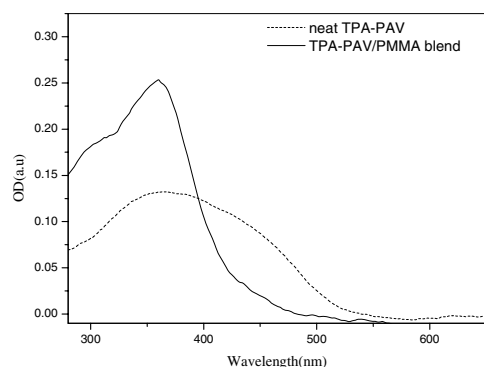
Figure 5. Absorption spectra of the neat TPA-PAV and the TPA-PAV/PMMA blend.
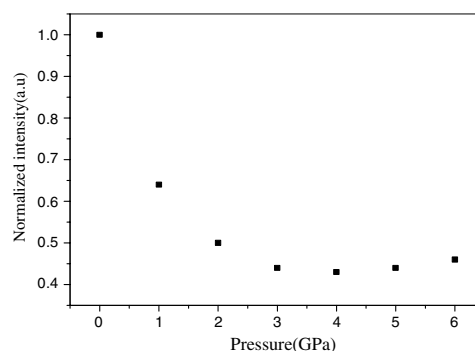
Figure 6. Total emission area versus pressure for TPA-DMPPV in PMMA.

However, these do not occur in the blend of TPA-PAV with PMMA. Although the interchain interaction between the groups is precluded in the blend of TPA-PAV with PMMA, whether the charge-transfer intrachain complex is formed in the blend or not is still in doubt. For the diluted solution of TPA-PAV, absorption and emission spectra show the formation of intrachain charge-transfer complexes, even in nonpolar solvents such as benzene [6]. However, the absorption and emission bands of the charge-transfer intrachain complex cannot be found in the absorption or emission spectra of the blend of TPA-PAV in PMMA. It can be reasonably assumed that the conformation of TPA-PAV in PMMA does not allow formation of a face shared between TPA and 9, 10 anthrylene, which is disadvantageous for the formation of the intrachain charge-transfer complex. So the emission of TPA-PAV in PMMA is mostly related to the excited state of segmental conjugated structures and this emission is not observed in neat polymer; thus the observed emission of the neat TPA-PAV is considered as mostly originating from interchain charge-transfer complexes, where TPA is the donor and 9, 10-anthrylene is the acceptor. Compression changes the distance between the polymer chains and increases the interchain interactions. Under pressure, most of the excited interchain charge-transfer complexes deactivate through radiationless processes, which may induce the great drop of the total emission for the neat TPA-PAV under pressure.

TPA-DMPPV was also dispersed into PMMA and its emission spectra at various pressures were measured. The emission maximum is at 484 and blue-shifted by about 37 nm compared with that of the neat TPA-DMPPV. The emission intensities are shown against pressure in figure 6.

The trend of change with pressure is distinctly different from that for the neat TPA-DMPPV, so the emission of the neat TPA-DMPPV is also affected severely by interactions between different chains and conformational change, especially under pressure. There are more complicated factors influencing the fluorescence for the neat TPA-DMPPV than for the neat TPA-PAV. For the neat TPA-DMPPV, the 2, 5-dimethyl-1, 4-phenylene has a much weaker ability to accept electrons than the 9, 10-anthrylene in TPA-PAV, which may cause the weaker interaction between the molecular chains. The two methyl groups may increase the distance between TPA and 2, 5-dimethyl-1, 4-phenylene in different chains; this is also responsible for the weaker interactions between them. So the change of the total intensity of the fluorescence with pressure for the neat TPA-DMPPV is noticeably different from that for the neat TPA-PAV. In the first 0.5 GPa, the higher light-emitting efficiency may be due to the change in the interactions between chains or the conformational change of chains induced by pressure. With

pressure increasing, the interactions between molecular chains become much more important and larger quenching occurs.

4. Conclusions

The photophysical properties for the two neat polymers TPA-PAV and TPA-DMPPV are evidently different from each other under pressure. This is mainly because 9, 10-anthrylene has a stronger capability to accept electrons than 2, 5-dimethyl-1, 4-phenylene and thus TPA and 9, 10-anthrylene are already configured into charge-transfer structures in the ground state. Compression decreases the distance between polymer chains, which is advantageous for charge transfer between the molecular chains. 2, 5-dimethyl-1, 4-phenylene has a much weaker capability of accepting electrons and the two methyl groups may increase the distance between TPA and 2, 5-dimethyl-1, 4-phenylene in different chains, which leads to weaker interactions between different chains of the neat TPA-DMPPV, and compression may be advantageous to change in the morphology of the molecular chain or increase in interchain interactions. These results provide a basis for understanding and controlling the photophysics of conjugated polymers using supramolecular structure and morphology.

Acknowledgments

References

[1] Jenekhe S A and Osaneni J A 1994 *Science* **265** 765
[2] Rauscher U, Bässler H, Bradley D D C and Hennecke M 1990 *Phys. Rev.* B **42** 9830
[3] Soos Z G, Etemad S, Galvão D S and Ramasesha S 1992 *Chem. Phys. Lett.* **194** 341
[4] Wang Z, Yin S, Yang X, Sun Z, Xu X and Zhang X 1999 *Chem. Phys. Lett.* **307** 75
[5] Brédas J-L, Cornil J, Beljonne D, Santos D A D and Shuai Z 1999 *Acc. Chem. Res.* **32** 267
[6] Zheng M, Bai F and Zhu D 1999 *J. Appl. Polym. Sci.* **74** 3351
[7] Zheng M, Bai F, Li Y, Yu G and Zhu D 1999 *J. Polym. Sci.* **37** 2587