

# Synthesis, electrostructure and spectral property of oligo(phenylene vinylenes) with different chain lengths

SUN, Jing-Zhi(孙景志) WU, Fang(吴芳) TIAN, Wen-Jing(田文晶) MA, Yu-Guang(马於光)  
CHEN, Yu(陈聿) SHEN, Jia-Cong\*(沈家骥)

Key Laboratory for Supramolecular Structure and Spectroscopy, Department of Chemistry, Jilin University, Changchun, Jilin 130023, China

The syntheses of a series of oligo(phenylene vinylenes) (OPVs) were described. The extended  $\pi$ -chains were built up by sequences of Wittig reactions. Their electronic structures were systematically studied with absorption spectra, photoluminescent spectra. The influences of the effective conjugation length on the performance of the light emitting devices were investigated.

**Keywords** OPVs, electronic structure, effective conjugation

## Introduction

Poly(paraphenylene vinylene) (PPV) and its derivatives are the subjects of continuing experimental and theoretical efforts for their promising applications in electronic and optical fields.<sup>1-3</sup> The electronic and optical properties of a conjugated organic polymer are basically determined by its effective conjugation length.<sup>4</sup> The real conjugated polymer can be considered as an assembly of the segments with different conjugation lengths which are organized by the weak interactions between them. Based on this conception, the electronic structure of the polymer is dependent on the electronic structure of the segments. The condensed entity property is dependent on the Van der Waals' interaction between the segments. The existence of molecular weight distribution and the insolubility of pristine PPV in organic solvents along with occurring structural inhomogeneities have severely inhibited detailed studies of the intrinsic electronic and optical properties.

There are two approaches towards this strategy.

One is to incorporate OPV segments with well-defined structure into the polymer main chain or polymer side chain.<sup>5-9</sup> The other is to synthesize OPVs with well-defined chemical structure and different conjugation lengths.<sup>10-13</sup> In this paper, we synthesized a series of OPVs with different conjugation lengths through sequences of Wittig reaction. The relationship between the spectral property and the effective conjugation length is systematically studied. The single layered light emitting devices are fabricated with these OPVs, their I-V characteristics and electro-luminescent properties are investigated.

## Experimental

Fig. 1 illustrated the chemical structure of the OPVs. We have synthesized the OPVs of  $n = 1, 2, 3$  and 5 according to the synthetic route schemed in Fig. 2. The detailed procedure for the synthesis of  $n = 1$  sample was described by Gourley *et al.*<sup>14</sup> The odd members of the homologous series OPVs can be regarded as being built up from two benzaldehyde and a xylene chain. From the bis-phosphonium salt (A), the molecular

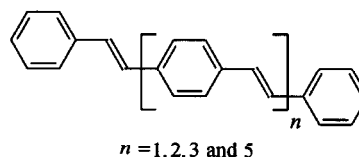


Fig. 1 Chemical structure of the oligo(phenylene vinylene).

\* Received February 21, 1999; accepted January 24, 2000.

Project (No. 59790050) supported by the National Natural Science Foundation of China

chain can be lengthened about two styryl unit, this process is similar to that of sample  $n = 1$  via a bis Wittig reaction with 4-methylbenzaldehyde. The following functionalization was done by bromination of the methyl groups with *N*-bromosuccinimide (NBS). The phosphonium salt was obtained by a subsequent reaction of C with triphenylphosphine in *para*-xylene. In principle,

the larger phosphonium salts were accessible in an analogous reaction sequence, but the insolubility of the lengthened bis-methyl-OPVs curbed their bromination, consequently, only the  $n = 5$  and  $n = 7$  can be obtained by this route in a very low yield (11% and 4%, respectively).

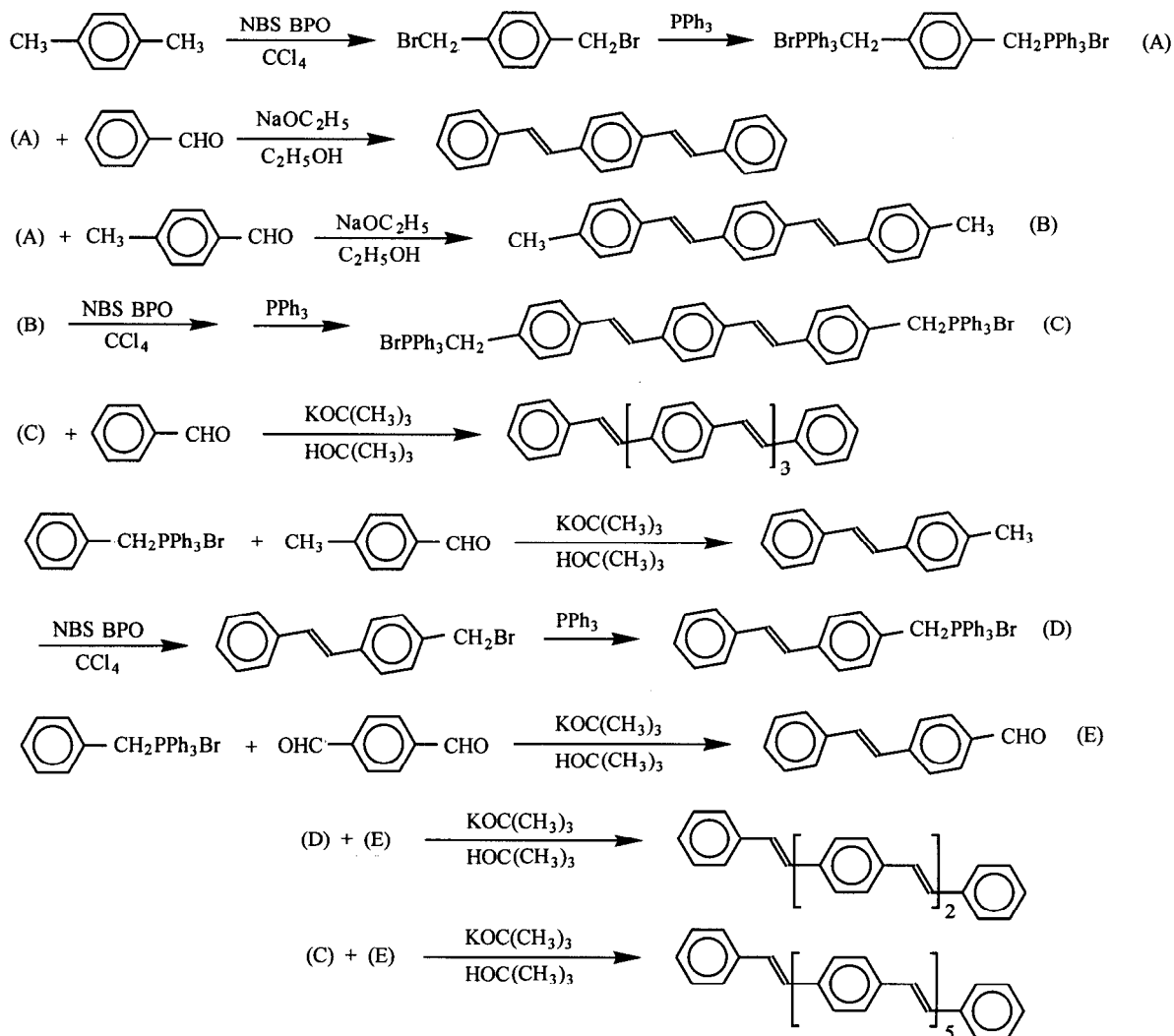


Fig. 2 Synthetic route of oligo(phenylene vinylene).

The even members of the homologous OPVs can be derived in another way, which is also shown in Fig. 2. The target molecule  $n = 2$  was obtained in a Wittig reaction of (E) and 4-styrylbenzaldehyde (D), which was synthesized by carefully controlled Wittig reaction of benzaldehyde triphenylphosphine and terephthalaldehyde. With (C) and (E),  $n = 5$  sample can be ob-

tained by a bis-Wittig reaction. The pure all-*trans* isomers of the OPVs were prepared by heating them with catalytic amount of iodine in toluene.<sup>15</sup> All the products were purified with a column chromatography on silica gel except  $n = 5$  sample, whose solubility was too low to be washed off the silica gel. This sample can be purified by recrystallization in *N,N*-dimethylformide (DMF). Fur-

ther characterization was carried out of the purified OPVs. The obtained physical/chemical characterization data were as follows:

$n = 1$  mp 273.8°C (DSC, 5°C/min).  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 7.54(2H, ArH), 7.49(2H, ArH), 7.43(2H, ArH), 7.37(1H, ArH), 7.14(1H, Vinyl H), 7.09(1H, Vinyl H).  $m/z$  (%): 282.2 ( $\text{M}^+ 100$ ). Anal.  $\text{C}_{22}\text{H}_{18}$ . Calcd: C, 93.57; H, 6.43. Found: C, 93.44; H, 6.50.

$n = 2$  mp > 400°C (DSC, 5°C/min).  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 7.51—7.43(m, 8H, ArH), 7.37(1H, ArH), 7.10—7.06(3H, Vinyl H).  $m/z$  (%): 384.2 ( $\text{M}^+, 100$ ). Anal.  $\text{C}_{30}\text{H}_{24}$ . Calcd: C, 93.70; H, 6.30. Found: C, 93.56; H, 6.42.

$n = 3$  and  $n = 5$ : These two samples are too insoluble in available organic solvents to be characterized with  $^1\text{H}$  NMR and common MS technique. The element analyses gave the following data:  $n = 3$ , Anal.  $\text{C}_{38}\text{H}_{30}$ . Calcd: C, 93.78; H, 6.22. Found: C, 92.92, H, 6.82.  $n = 5$ , Anal.  $\text{C}_{46}\text{H}_{36}$ . Calcd: C, 93.83; H, 6.17. Found: C, 93.29; H, 6.24. Their melting points are both higher than 400°C. Their melting endothermic have not been recorded up to 400°C on DSC experiments.

The UV-visible spectra and photo-luminescent spectra were measured on the UV-3100 spectrophotometer and RF5301 PC spectrafluorophotometer respectively. The configuration of the light emitting device was single layered structure, with Al and ITO as top and bottom electrodes, OPV as emitting material respectively. The I-V characteristics and electro-luminescent properties of the devices were measured on LM-15 digital multimeter and RF5301 PC spectrafluorophotometer, respectively.

## Results and discussion

Figs. 3 and 4 show the room temperature optical absorption spectra and photoluminescence (PL) spectra for all four OPVs in their dilute  $\text{CHCl}_3$  solution, respectively. The lowest energy peaks can be assigned to the zero-zero (phonon)  $\pi$ - $\pi^*$  transition.<sup>19</sup> For  $n = 1$ , this peak is at 3.20 eV, which agrees very well with the value reported by Tian *et al.*<sup>19</sup> In all of the absorption spectra, the phonon structure is evident on the absorption edges though the bands are broad. The highest energy emission peak for  $n = 1$  is at 2.77 eV. We as-

signed this emission to the radiative recombination of a singlet exciton from the lowest vibrational level of the first excited singlet state to the lowest vibrational level of the singlet ground state. The vibronic shoulders are a common feature to most fluorescent conjugated systems.<sup>16-18</sup> We consider the lower energy peaks to be induced by the excitation of vibrational quanta due to modes coupling excited and ground state geometries. The energy spacing between peaks of about 0.16 eV is consistent with this assignment.

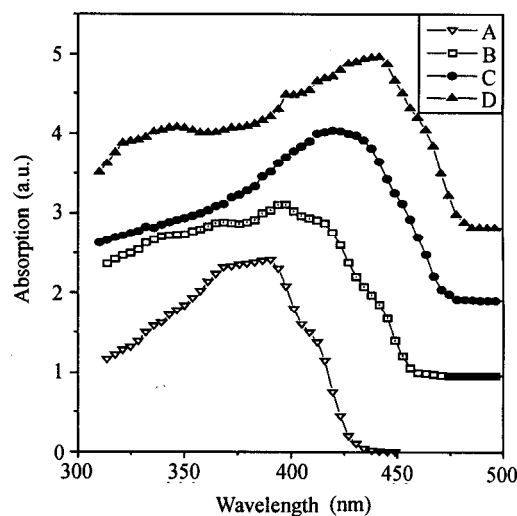


Fig. 3 Absorption spectra of the OPVs with different conjugation lengths, the curve A, B, C and D stand for the spectrum of  $n = 1, 2, 3$  and 5, respectively.

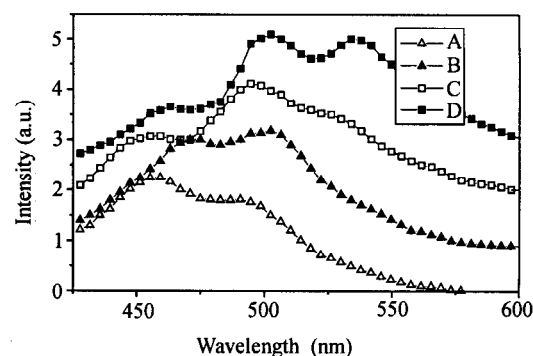


Fig. 4 Emission spectra of the OPVs with different conjugation lengths, the curve A, B, C and D stand for the spectrum of  $n = 1, 2, 3$  and 5, respectively.

The spectra from absorption and photo-luminescent spectra described above show a monotonic red-shift with the increase of chain lengths. To further study this ef-

fective conjugation length dependence, we have correlated the wavelength of the lowest energy peaks with the number of C = C bonds between two ends of the molecular chain. We extrapolated that the effective conjugation length in the polymer is between about 30 and 50 C = C bonds or 8 and 14 phenylene vinylene units. This value does not agree well with those reported by Tian *et al.*<sup>19</sup> and Schenk *et al.*<sup>20</sup> whose values were 10 to 17 phenyl rings and 10 to 11 phenyl rings, respectively. The effective conjugation length estimated by our experimental data may come from the weaker solvation effect due to the poor solubility of our OPV samples in CHCl<sub>3</sub>. According to the results of Woo, *et al.*,<sup>21</sup> the better solubility implied stronger solvation effect, and the solvation effect provided the necessary energy to overcome the potential barrier and the phenyl rings torsion would be a favorable conformation.

The single layered light emitting devices were fabricated with Al and ITO as top and bottom electrodes respectively. The emitting layer was made of the OPVs described in Figs. 1 and 2, which are sandwiched between top and bottom electrodes. For samples  $n = 1, 2,$  and 3 the emitting layer was vapor deposited onto the ITO substrates in high vacuum (about  $1 \times 10^{-4}$  Pa); but for  $n = 5$  sample, this layer was a casting film from its hot solution in DMF, because its sublime temperature is too high to be suitable for vapor deposition. DSC measurement presented that the decomposition temperature of sample  $n = 6$  was about 470°C, but it cannot sublime at 450°C in our experimental condition. Fig. 5 shows the I-V characteristics of these devices at forward bias. From Fig. 5, it can be seen that the turn-on voltages of the LEDs decreased with the increasing of the oligomer chain lengths, though this trend is not very evident in comparison with the results reported by Yu *et al.*<sup>22</sup> On the other hand, however, the increment of the inject current with the oligomer's chain length is more evident. The fundamental principle for this phenomenon is the narrowing of the energy gap between the HOMO and LUMO energy levels in the conjugated oligomers. The elongation of the conjugation length in a  $\pi$ -conjugated system leads to the elevation of the HOMO level, thereby results in the ease of the injection of holes from the ITO electrode. There are still an energy space between the optical energy gap and the turn-on voltage. This discrepancy may result from the device structure and the fabrication technique. But it is important to emphasize

that the I-V characteristics of these LEDs have confirmed the influence of the effective conjugation length on the electronic structure of OPVs.

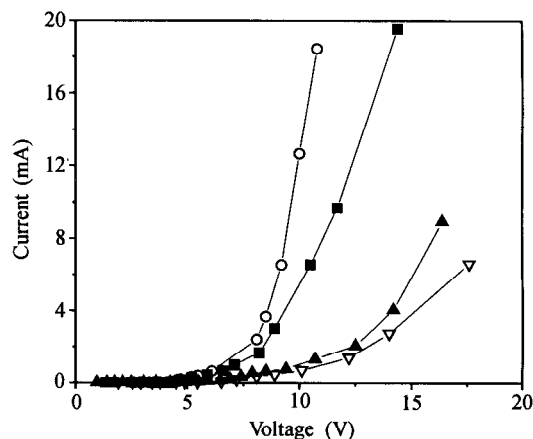


Fig. 5 I-V characteristics of LEDs fabricated with different OPVs' films, the lines from the left to the right stand for the samples of  $n = 5, 3, 2$  and 1, respectively.

The corresponding electro-luminescent spectra of the LEDs described above are shown in Fig. 6. The feature of these spectra is very similar to that of PL spectra, and a red-shift trend of the maxima with the conjugation length of the OPVs evidently demonstrated in the electro-luminescent spectra. These similarity lies

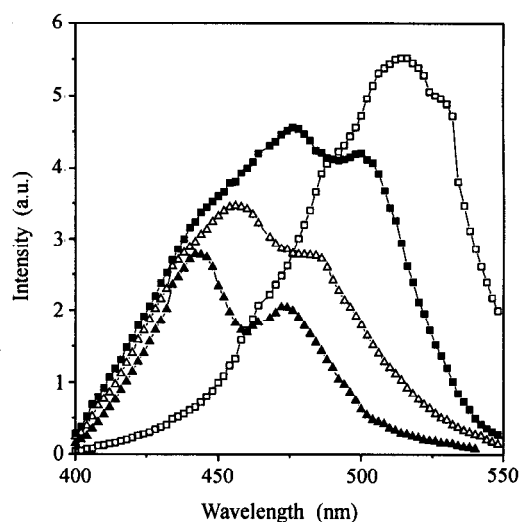


Fig. 6 Electroluminescent spectra of the LEDs fabricated with different OPVs' films, the spectrum from bottom to top corresponds to the emission of sample  $n = 1, 2, 3$  and 5, respectively.

in the fact that the excitons generated in the electro-luminescent process are the same as those in the photo-excitation process.<sup>23</sup> We noted that the emission color varied from blue to yellow-green, it implies that the display color can be adjusted by changing the effective conjugation length. The high PL efficiency (81%) and the pure blue emission of the sample  $n = 1$  indicate the promising application in blue LEDs if the device structure can be optimized and the reasonable chemical modification can be introduced into this sample. Those are our ongoing research work.

## Conclusion

We have synthesized a series of OPVs containing from two to six phenylene vinylene units with standard Wittig reaction. The experimental data of the optical absorption and photo-luminescent spectra for these OPVs have been presented. The absorption shows a well-defined zero-zero phonon feature in the low energy side and the maxima of the absorption and emission spectra show evident red-shift trend. This tendency leads us to estimate the effective conjugation length in PPV as 8 to 14 phenylene vinylene units. The single layered light emitting devices based on these OPVs as emission materials were fabricated. Their I-V characteristics demonstrated the influences of the effective conjugation length on the turn-on voltage and carrier injection ability. The electro-luminescent spectra suggested that the display color of the devices can be modulated by adjusting the effective conjugation length of OPVs.

## References

1. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B., *Nature*, **347**, 539(1990).
2. Braun, D.; Heeger, A. J., *Appl. Phys. Lett.*, **58**, 1982(1991).
3. Son, S.; Dodabalapur, A.; Lovinger, A. J.; Calvin, M. E., *Science*, **269**, 376(1995).
4. Hay, M.; Klavetter, F. L., *J. Am. Chem. Soc.*, **117**, 7112(1995).
5. Yang, Z.; Sokolik, I.; Karasz, F. E., *Macromolecules*, **27**, 145(1995).
6. Zyung, T.; Hwang, D. H.; Kang, I. N., *Chem. Mater.*, **7**, 1499(1995).
7. Bazan, G. C.; Miao, Y. J.; Renak, M. L.; Sun, B. J., *J. Am. Chem. Soc.*, **118**, 2618(1996).
8. Hesemann, P.; Vestweber, H.; Pommerhne, J.; Mahrt R. F.; Greiner, A., *Adv. Mater.*, **7**, 388(1995).
9. Aguiar, M.; Hu, B.; Karasz, F. E.; Akcelrud, L., *Macromolecules*, **29**, 3161(1996).
10. Meghdadi, F.; Leising, G.; Fisher, W.; Stelzer, F., *Synth. Met.*, **76**, 113(1996).
11. Katz, H.; Bent, S.; Wilson, W.; Schilling, M.; Ungashe, S., *J. Am. Chem. Soc.*, **116**, 6631(1994).
12. Sakamoto, A.; Furukawa, Y.; Tasumi, M., *J. Phys. Chem. B*, **101**, 1726(1997).
13. Shirshendu, K. D.; Todd, M. M.; Yu, L. P., *J. Am. Chem. Soc.*, **119**, 9079(1997).
14. Gourley, K. D.; Lillya, C. P.; Reynolds, J. R.; James, C. W. Chien, *Macromolecules*, **17**, 1025(1984).
15. Manecke, G.; Lutke, S., *Chem. Ber.*, **103**, 700(1970).
16. Vardeny, Z.; Ehrenfreund, E.; Brafman, O.; Novak, M.; Schaffer, H.; Heeger, A. J.; Wudl, F., *Phys. Rev. Lett.*, **56**, 671(1986).
17. Friend, R. H.; Bradley, D. D. C.; Townsend, P. D., *J. Phys. D: Appl. Phys.*, **20**, 1367(1987).
18. Ruhe, J.; Colaneri, N. F.; Bradley, D. D. C.; Lawrence, R. A.; Friend, R. H.; Wegner, G., *J. Phys. Condens. Matter*, **2**, 5465(1990).
19. Tian, B.; Zerbi, G.; Schenk, R.; Mullen, K., *J. Chem. Phys.*, **95**, 3191(1991).
20. Schenk, R.; Gregorius, H.; Meerholz, K.; Heirze, J.; Mullen, K., *J. Am. Chem. Soc.*, **113**, 2634(1991).
21. Woo, H. S.; Graham, S. C.; Halliday, D. A.; Bradley, D. D. C.; Friend, R. H.; Burn, P. L.; Holmes, A. B., *Phys. Rev. B*, **46**, 7379(1992).
22. Goodson, T.; Li, W. J.; Gharavi, A.; Yu, L. P., *Adv. Mater.*, **8**, 639(1997).
23. Bradley, D. D. C.; Brown, A. R.; Burn, P. L.; Burroughes, J. H.; Friend, R. H.; Holmes, A. B.; Mackay, K. D.; Marks, R. N., *Synth. Met.*, **41-43**, 3135(1991).