Macromol. Symp. **2003**, *201,* 119—125

Optical Absorption and Photoluminescence Properties of the PPV Nanotubes and Nanowires

Kyungkon Kim,[1] *Sae Chae Jeoung,*[2] *Jinwoo Lee,*[3] *Taeghwan Hyeon,*[3]
*Jung-Il Jin**[1]

[1] Division of Chemistry and Molecular Engineering and Center for Electro- and Photo-Responsive Molecules, Korea University, Seoul 136-701, Korea
[2] Spectroscopy Laboratory, Korea Research Institute of Standards and Science, Taejon 305-600, Korea
[3] School of Chemical Engineering and Institute of Chemical Processes, Seoul National University, Seoul 151-742, Korea

Summary: We measured optical absorption and time resolved photoluminescence decay properties of the PPV nanotubes and nanowires which were prepared by CVD polymerization using templates. When compared with bulk PPV films, their nano objects showed different optical properties, long photoluminescence decay time and higher photoluminescence efficiencies.

Keywords: nanotubes; nanowires

Introduction

The present world-wide, explosive interests in nanotechnology is arousing renewed attention to organic conductors because of their potentials in a wide variety of applications, especially in nanodevices. Among many organic conductors, poly(*p*-phenylenevinylene) (PPV) [1, 2]is unique in that the polymer can be prepared by many synthetic routes and possesses many interesting electrical and optical properties including photo- and electroluminescence.[3] In general, nano sized materials show much different properties from those of macroscopic bulk state.[4] In order to find proper applications of nano structured materials in the nano devices, it is essential to understand structure-properties relationship of nano dimension materials. Recently[5, 6], we reported that PPV nanotubes and nanorods can be easily prepared by performing the chemical vapor deposition (CVD) polymerization of α, α'-dichloro-*p*-xylene inside of pores of organic or inorganic templates. We have extended our studies of PPV nano objects to examine their optical properties and time resolved photoluminescence decay behavior.

DOI: 10.1002/masy.200351114

Experimental

In the synthesis of PPV nanotubes and nanowires we used commercially available nano porous alumina membrane (nominal pore diameter: 200 nm; Whatman, England) and mesoporous silica[7] (3.2, and 10 nm pore diameter), respectively. The detailed CVD polymerization and PPV nano object preparation procedure can be found in our previous report.[5] For the preparation of PPV nanowires, we increased deposition zone temperature up to 100°C to facilitate penetration of activated monomer molecules into the small pores of the template. After CVD polymerization of PPV inside pores of mesoporous silica, the product was washed with THF several times to remove PPV formed outside of the pores. PPV films were prepared on the quartz substrate by CVD polymerization.

Measurement of UV-vis absorption and photoluminescence (PL) spectra of the PPV nanotubes was performed after the alumina membrane was dissolved by 3 M NaOH solution. Isolated PPV nanotubes were dispersed in $CHCl_3$ using ultrasonification. In the case of PPV nanowires, UV-vis absorption and PL spectra were obtained for the mesoporous silica template containing the nanowires. In order to reduce the scattering from the template, glycerol / propanol index matching solution was used.[8]

Absolute quantum yield of the dispersed PPV nano objects was obtained by using coumarin 307 as a reference material. Experimental setup for the time resolved PL decay can be found elsewhere.[9]

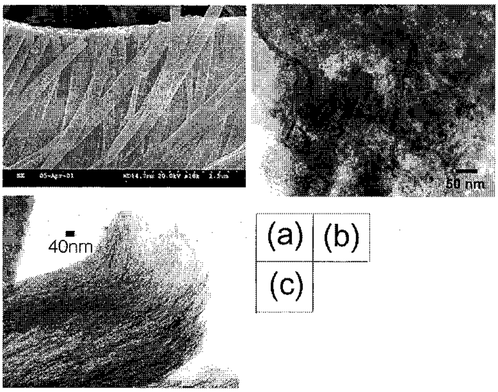

Fig. 1. SEM and TEM images of PPV nanotubes and nanowires: (a) PNT-200 (SEM) (b) PNW-10 (TEM) (c) PNW-4 (TEM).

Result and Discussion

Figure 1 shows SEM and TEM images of PPV nanotubes and nanowires prepared on the inner surface of the pores of alumina membrane and inside the pores of the mesoporous silica, respectively. The nominal pore diameter of the alumina membrane was 200 nm and the pore sizes of the mesoporous silicas were 10 and 3.2 nm. The shape of the prepared nano object was dependent on the size of the template used. When we used alumina membrane as a template, we obtained PPV nanotubes. In contrast, mesoporous silica produced PPV nanowires. The diameter and wall thickness of PPV nanotubes (PNT-200) obtained from the alumina membrane was 285 ± 25 nm and 28 ± 3 nm, respectively. Although it is difficult to determine the exact diameter of the PPV nanowires due to low resolution of TEM images, diameter of PPV nanowires obtained using 3.2 (PNW-4) and 10 nm (PNW-10) pore diameter mesoporous silica were about 4 and 10 nm, respectively.

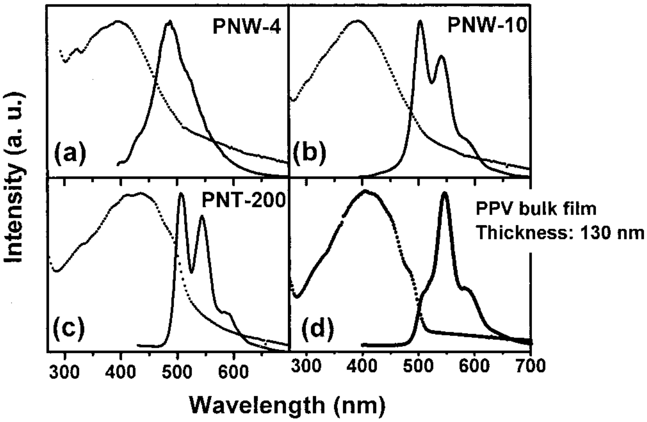

Fig. 2. Comparison of UV-vis absorption and photoluminescence spectra of PPV nanotubes and nanowires.

Figure 2 compares optical properties of the prepared nano objects. When compared with absorption spectrum of the bulk PPV film, overall shapes of other spectra are very similar to that of the bulk film with no significant shift in their absorption maxima positions. Since PPV molecules are in an inhomogeneous environment in the pores of alumina membrane and mesoporous silica, spectral broadening was observed. This phenomenon was also earlier observed in the UV-vis absorption spectrum of MEH-PPV prepared in an aligned mesoporous silica.[8, 10] On the other hand, there are observed significant differences among the PL spectra of the samples. The PL peak from the $S_1 \rightarrow S_0$ 0-0 transition, i. e., highest electronic energy transition, increases in energy as the pore size of template is reduced. Especially, in the case of PNW-4, the peak from the 0-0 transition was shifted to the shortest wavelength (higher energy) side. This is due to reduced reabsorption by neighboring chains of the emitted light originated from the 0-0 transition because of complete isolation of the nano particles suspended in the solvent medium that consist of much fewer polymer chains compared to bulk films and also due to much reduced interchain contacts between the polymer chains. We could observe an increased intensity of PL originated from the 0-0 transition when we decreased the thickness of the bulk PPV film, which can be explained from viewpoint of reabsorption.

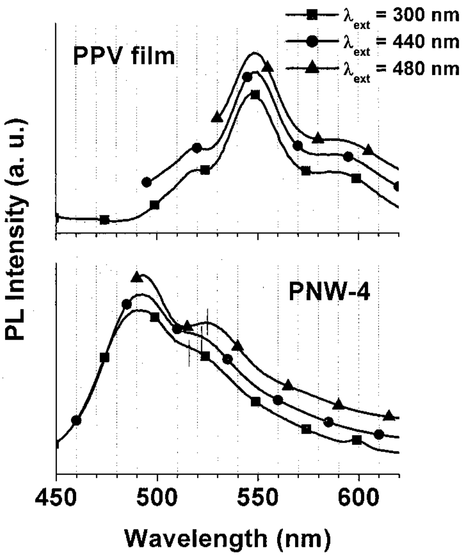

Fig. 3. Comparison of photoluminescence spectra of PPV films and nanowires at different excitation wavelengths.

Another observation made is that the PL from the PNW-4 red-shifted substantially as the excitation wavelength is increased from 300 nm to 480 nm (Figure 3). In contrast, as we can see from Figure 3, the position of the PL spectra of the PPV films, however, did not change when we changed the excitation wavelength, because the rate of intermolecular energy transfer (few ps) is more rapid than radiative recombination in the PPV chain. When PPV chains are in the pores of the mesoporous silica, they are separated by the walls of the mesoporous silica, which remarkably reduces the chances for energy transfer among the polymer chains. In other words, the rate of the intermolecular energy transfer is reduced. As a result, the higher energy excitation at 300 nm could not be transferred to the lower energy sites and PL from the $S_1 \rightarrow S_0$ 0-1 transition is observed at 517 nm which is shorter than 525 nm that is observed when the excitation wavelength was 480 nm.

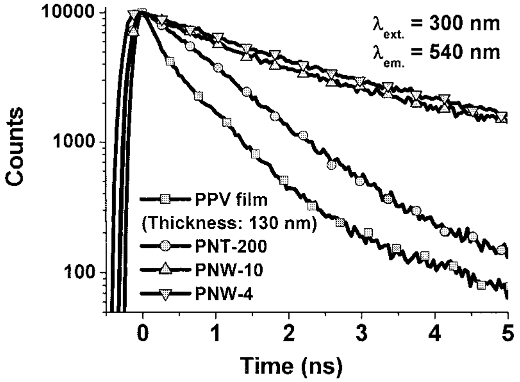

Fig. 4. Photoluminescence decay of PPV film, nanotubes and nanowires.

This also could be confirmed by the time resolved PL decay of the PPV nano objects and films (Figure 4). And the results of the spectral analysis are summarized in Table 1. As one can see from Figure 4, the PL decay for the PPV film was fastest and PNT-200 revealed the second fastest decay in PL. They both exhibit a fast initial decay followed by a slower decay. But decay rate of the PNT-200 (τ_1: 310 ps, τ_2: 880 ps) is much slower than that of the bulk film (τ_1: 87 ps, τ_2: 480 ps). Usually, impurity and structural defects of polymer chains are the non-radiative decay sites and most polymers have these kinds of sites. When polymer chains are contacted to each other, the probability of interchain energy transfer to the radiative sites or non-radiative decay increases, which causes a fast radiative decay for the bulk film. PNT-200, PNW-4 and

PNW-10 are different from true solutions of polymers. They, however, form nano domains in the dispersed solution and, thus, they are much closer to dilute solutions than bulk films. It means that they are far apart enough to prevent interchain energy transfer to non-radiative decay sites, which, in turn, would result in a long radiative decay when compared to that of bulk films. Especially, PNW-4 and PNW-10 show exceptionally long radiative decay rates (τ_3 in Table 1) and the decay time parameter values are 2.2 and 2.4 ns, respectively. It is quite likely that as soon as PNW-4 and PNW-10 are exposed to excitation beam, polymer chains outside of the pores are first excited and then generated excitons migrate to the lower energy sites along the chains which are isolated in solution-like environment by the walls of the mesoporous silica.[10] This appears to be the origin of the longest radiative decay time (τ_3 in Table 1). The τ_3 value is comparable to that of a diluted solution of MEH-PPV[11] and a diluted blend film of PPV oligomer and PMMA.[11] Therefore, this kind of isolation effect would result in a high PL quantum efficiency for the PPV nano objects.[12, 13] In fact, the value of PL quantum efficiency increases in reverse order of pore size of the template used as shown in Table 2. The maximum PL efficiency obtained was 22.7% (PNW-4) which is twice the value for the bulk PPV film.

Table 1. Photoluminescence decay times of PPV film, nanotube and nanowire.

	τ_1	τ_2	τ_3
	Decay time (ratio) (ns)	**Decay time (ratio) (ns)**	**Decay time (ratio) (ns)**
Bulk film (130 nm thick)	**0.087 (0.83)**	**0.48 (0.17)**	-
PNT-200	**0.31 (0.86)**	**0.88 (0.14)**	-
PNW-10	**0.17 (0.46)**	**0.75 (0.33)**	**2.4 (0.21)**
PNW-4	**0.27 (0.36)**	**0.92 (0.46)**	**2.2 (0.18)**

Table 2. Absolute PL quantum efficiencies of PPV film and PPV nano objects.

	Quantum efficiency (%)
PPV film	**12.0**[14]
PNT-200	**14.8**
PNW-10	**18.2**
PNW-4	**24.7**

Conclusion

In conclusion, we measured optical absorptions and time resolved PL properties of PPV nanofilms, nanotubes, and nanowires which were prepared by CVD polymerization method using various nano sized templates. In comparison with bulk PPV film, the PL peak from the $S_1 \rightarrow S_0$ 0-0 transition increased for the PPV nano objects. And in the case of PNW-4, a spectral shift to short wavelength was observed. Also their PL decay times increased as the pore size of the template was reduced. For the case of the PL decay of PNW-4 and PNW-10, exceptionally long radiative decay time was observed. The much slower radiative decay time is in accord with absolute PL quantum yield. All the results could be interpreted as a result of the prevention of interchain interactions throuth the isolation of the PPV chains in form of nanosized domanins.

Acknowledgment

This work was supported by the Korea Science and Engineering Foundation through the Center for Electro- and Photo- Responsive Molecules, Korea University. Kyungkon Kim is the recipients of Brain Korea 21 assistantship supported by the Ministry of Educations and Human Resources Development.

[1] C. Kvarnstrom, A. Ivaska, in *Habdbook of Conductive Molecules and Polymers, Vol.*, ed. (Ed.:H. S. Nalwa), John Wiley & Sons, New York, **1997**, Chapter 9.

[2] C. S. Moratti, in *Handbook of Conducting Polymers,* 2nd ed. (Eds.T. A. Skothtim, R. E. Elsenbaumer, J. R. Reynolds), Marcel Dekker, New York, **1998**, Chapter 13.

[3] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, *347*, 539.

[4] S. A. Empedocles, R. Neuhauser, K. Shimizu, M. G. Bawendi, *Adv. Mater.* **1999**, *11*, 1243.

[5] K. Kim, J.-I. Jin, *Nano Letters* **2001**, *1*, 631.

[6] K. Kim, G. Zhong, J.-I. Jin, J. H. Park, S. H. Lee, D. W. Kim, Y. W. Park, W. Yi, *ACS Symp. Series in press.*

[7] A. Stein, B. J. Melde, R. C. Schroden, *Adv. Mater.* **2000**, *12*, 1403.

[8] J. Wu, A. F. Gross, S. H. Tolbert, *J. Phys. Chem. B* **1999**, *103*, 2374.

[9] Y. H. Kim, S. C. Jeoung, D. Kim, S. J. Chung, J.-I. Jin, *Chem. Mater.* **2000**, *12*, 1067.

[10] T.-Q. Nguyen, J. Wu, V. Doan, B. J. Schwartz, S. H. Tolbert, *Science* **2000**, *288*, 652.

[11] C. M. Heller, I. H. Campbell, B. K. Laurich, D. L. Smith, D. D. C. Bradley, P. L. Burn, J. P. Ferraris, K. Mullen, *Phys. Rev. B: Condens. Matter* **1996**, *54*, 5516.

[12] R. C. Smith, W. M. Fisher, D. L. Gin, *J. Am. Chem. Soc.* **1997**, *119*, 4092.

[13] T. W. Lee, O. O. Park, J. H. Yoon, J. J. Kim, *Adv. Mater.* **2001**, *13*, 211.

[14] U. Lemmer, R. F. Mahrt, Y. Wada, A. Greiner, H. Bassler, E. O. Gobel, *Appl. Phys. Lett.* **1993**, *62*, 2827.